Continuum Thermodynamics

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A. *Units of pressure and stresses*

(p and partial pressures in mixtures, Piola-Kirchhoff $\mathbf{P}$ and Cauchy $\mathbf{T}$;
pressure in SI: 1Pascal=1kg/s^{2}m)

Pa=$\frac{\mathrm{N}}{\mathrm{m}^2}$	at=$\frac{\mathrm{kp}}{\mathrm{cm}^2}$	atm	bar	torr	mmWs=$\frac{\mathrm{kp}}{\mathrm{m}^2}$
1	$1.02 \cdot 10^{-5}$	$9.87 \cdot 10^{-6}$	10^{-5}	$75 \cdot 10^{-4}$	0.102
$9.81 \cdot 10^{4}$	1	0.968	0.981	736	10^{4}
$1.013 \cdot 10^{5}$	1.033	1	1.013	760	$1.033 \cdot 10^{4}$
10^{5}	1.02	0.987	1	750	$1.02 \cdot 10^{4}$
133	$1.36 \cdot 10^{-3}$	$1.32 \cdot 10^{-3}$	$1.33 \cdot 10^{-3}$	1	13.6
9.81	10^{-4}	$9.68 \cdot 10^{-5}$	$9.81 \cdot 10^{-5}$	$7.36 \cdot 10^{-2}$	1

B. *Units of the force*

(body forces $\rho\mathbf{b}$ have the SI unit: [Newton/m^3]; force in SI: 1Newton=1kg·m/s^2)

N	kp	Mp	p	dyna
1	0.102	$1.02 \cdot 10^{-4}$	102	10^{5}
9.81	1	10^{-3}	10^{3}	$9.81 \cdot 10^{5}$
$9.81 \cdot 10^{3}$	10^{3}	1	10^{6}	$9.81 \cdot 10^{8}$
$9.81 \cdot 10^{-3}$	10^{-3}	10^{-6}	1	981
10^{-5}	$1.02 \cdot 10^{-6}$	$1.02 \cdot 10^{-9}$	$1.02 \cdot 10^{-3}$	1

C. *Units of energy and work*

(energy density $\rho\varepsilon$ has the SI unit: [Joule/m^3]; energy in SI: 1 Joule=1kg·m^2/s^2)

J	kpm	kWh	kcal	erg	eV
1	0.102	$2.78 \cdot 10^{-7}$	$2.39 \cdot 10^{-4}$	10^{7}	$6.24 \cdot 10^{18}$
9.81	1	$2.72 \cdot 10^{-6}$	$2.34 \cdot 10^{-3}$	$9.81 \cdot 10^{7}$	$6.12 \cdot 10^{19}$
$3.6 \cdot 10^{6}$	$3.67 \cdot 10^{5}$	1	860	$3.6 \cdot 10^{13}$	$2.25 \cdot 10^{25}$
$4.19 \cdot 10^{3}$	427	$1.16 \cdot 10^{-3}$	1	$4.19 \cdot 10^{10}$	$2.61 \cdot 10^{22}$
10^{-7}	$1.02 \cdot 10^{-8}$	$2.78 \cdot 10^{-14}$	$2.39 \cdot 10^{-11}$	1	$6.24 \cdot 10^{11}$
$1.6 \cdot 10^{-19}$	$1.63 \cdot 10^{-20}$	$4.45 \cdot 10^{-26}$	$3.83 \cdot 10^{-23}$	$1.6 \cdot 10^{-12}$	1

D. *Units of power*

(working of body forces $\rho\mathbf{b} \cdot \mathbf{v}$, energy radiation ρr, working of stresses $\mathbf{P} \cdot \frac{\partial \mathbf{F}}{\partial t}$ and $\mathbf{T} \cdot \mathbf{L}$ have SI unit: [Watt/m^3]; power in SI: 1Watt=1kg·m^2/s^3)

W	kW	$\frac{\mathrm{kpm}}{\mathrm{s}}$	PS	$\frac{\mathrm{cal}}{\mathrm{s}}$	$\frac{\mathrm{kcal}}{\mathrm{h}}$
1	10^{-3}	0.102	$1.36 \cdot 10^{-3}$	0.239	0.86
10^{3}	1	102	1.36	239	860
9.81	$9.81 \cdot 10^{-3}$	1	$1.33 \cdot 10^{-2}$	2.34	8.43
736	0.736	75	1	176	632
4.19	$4.19 \cdot 10^{-3}$	0.427	$5.69 \cdot 10^{-3}$	1	3.6
1.16	$1.16 \cdot 10^{-3}$	0.119	$1.58 \cdot 10^{-3}$	0.278	1

Remark: Heat fluxes $\mathbf{Q}$ and $\mathbf{q}$ have SI unit: [Watt/m^2];
entropy has SI unit: [Joule/m$^3 \cdot$ K]; entropy fluxes $\mathbf{H}$ and $\mathbf{h}$ have SI unit: [Watt/m$^2 \cdot$ K];
entropy radiation ρs has the SI unit: [Watt/m$^3 \cdot$ K].

Lecture 1: Introduction to the theory of continua

Thermodynamics of continua is based on four fundamental principles

1. **Continuity,**
2. **Balance equations,**
3. **Local action,**
4. **Thermodynamical admissibility.**

The principle of continuity means that we consider functions on a three-dimensional manifold $\mathcal{B}_0$ called *a body* which satisfy certain mathematical assumptions on a continuity with respect to the volume measure defined on this manifold. These assumptions yield the existence of densities. For example, instead of mass of material points of the classical mechanics we deal with masses of *subbodies* which are certain three-dimensional subsets of $\mathcal{B}_0$. Such masses are given by integrals of mass densities over subbodies. In continua it does not make any sense talking about a mass of a material point. The material point $\mathbf{X} \in \mathcal{B}_0$ is only a geometrical notion and densities (fields) of a continuum are functions of these points and of the time. Values of these functions have no direct physical meaning known from the classical mechanics. We speak about mass density, momentum density, energy density, etc. but we measure in laboratories their integrals over finite volumes.

Continuity means that densities are continuous functions of the point $\mathbf{X}$ of the body and of time t except of sets of volume measure zero. This means that these functions may possess finite discontinuities on surfaces, lines and at separate points. This is, for example, the case when we consider the propagation of waves. We return to this point later.

The continuity assumption means as well that we consider a special form of changes of the shape of the body due to **motions**. The motion is defined by a differentiable global mapping (*diffeomorphism*) of the manifold $\mathcal{B}_0$ on the three-dimensional Euclidean space $\Re^3$. This space is called the *space of configurations.* For our purposes we can identify the body $\mathcal{B}_0$ with a domain in this space occupied by the body at a chosen *reference time*, say t_0[1]. Then the **function of motion**

$$\mathbf{f}\left(.,.\right) : \mathcal{B}_0 \times \mathcal{T} \rightarrow \Re^3, \tag{1}$$

defines for each instant of time $t \in \mathcal{T}$ a *current configuration* of the body. The derivative of this function with respect to $\mathbf{X}$ is called the *deformation gradient* $\mathbf{F}\left(\mathbf{X}, \mathbf{t}\right)$ (see: Fig.1) and the derivative with respect to time is the *velocity* $\mathbf{v}\left(\mathbf{X}, t\right)$ at the material point $\mathbf{X}$. We discuss these notions further in details. The deformation gradient is a linear mapping defined on the so-called *tangent space* to the material manifold and it defines *material vectors* essential for the description of deformations of the body.

We assume that the mapping $\mathbf{f}\left(., t\right)$ is *invertible* which means that each position $\mathbf{x}$ can be occupied only by one material point $\mathbf{X}$. This requires

$$\det \mathbf{F} \neq 0. \tag{2}$$

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[1] Certain models do no not admit such an identification. For example, there are continuous models of dislocations which require a more general structure of the manifold than this indicated by the Euclidean space.

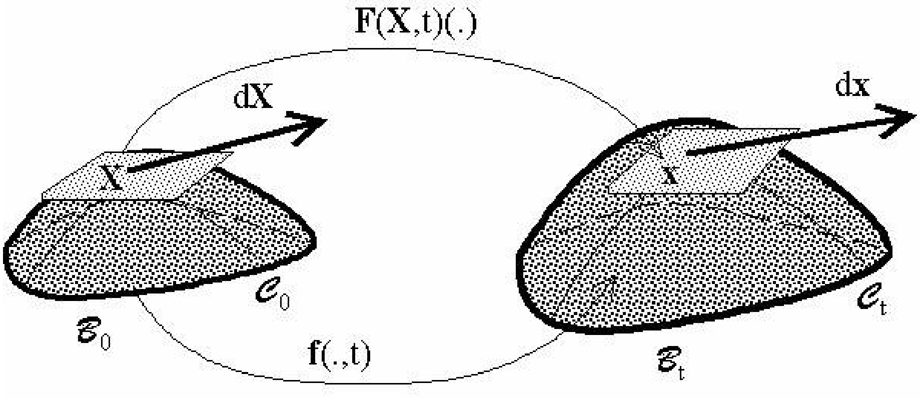

Fig. 1: *Local configuration of a continuum*

The existence of a continuous function of motion $\mathbf{f}$ imposes severe limitations on possible motions of the body. For instance, a creation of new surfaces (opening of a crack in solids, tearing or a creation of vortices) is forbidden by the topological continuity. Also the description of strong mixing (e.g. cigarette smoke in the air) is not possible.

The second principle – **balance equations** – means that some most fundamental quantities appearing in models of the continuum satisfy relations describing their time changes in terms of surface and volume supplies. In thermomechanical models which we consider in this course these quantities are: mass density, momentum density, angular momentum density, energy density and entropy density. In particular cases balance equations become **conservation laws** of mass, momentum, angular momentum and energy. We discuss further the detailed structure of these equations. Apart of balance equations a particular model may contain additional equations such as **evolution equations** of internal variables but we assume that the above listed conservation laws are unconditionally satisfied in any model. The violation of conservation laws of mass, momentum or energy leads to *perpetuum mobile,* i.e. the system may do a useful work without any time limit and without any supply from the surrounding. Even though it may not be excluded in a microscopic world described by a quantum theory the existence of perpetuum mobile contradicts our macroscopic observations.

The principle of **local action** requires that a reaction of the body on external actions is transmitted to material points by interactions of parts of the body through *surfaces of contacts*, i.e. a reaction of each material point is limited to an influence of its infinitesimal neighborhood. Direct interactions of two or more material points at finite distances are not possible. Consequently, such actions as gravitational forces between parts of the body or Coulomb electromagnetic interactions are not modelled by a continuum. Attempts to include these **nonlocal** interactions failed and only some approximations of such actions by the so-called higher gradient theories are possible without the violation of some basic mathematical assumptions of the continuum. We discuss this problem within the subject of constitutive (material) relations.

Finally the principle of thermodynamical admissibility reflects the requirement that the **second law of thermodynamics** and certain **thermodynamical stability conditions** are satisfied. These will be the main subject of this course.

We proceed to discuss the geometry of the body changing in time due to the motion. As already mentioned the current configuration of the body is defined by the function $\mathbf{f}$.

Let us choose an arbitrary smooth curve $\mathcal{C}_0$ in the initial configuration $\mathcal{B}_0$ and investigate its current image $\mathcal{C}_t := \mathbf{f}\left(\mathcal{C}_0, t\right)$. It is convenient to write the equation of $\mathcal{C}_0$ in the parametric form

$$\mathbf{X} = \mathbf{X}\left(S\right), \tag{3}$$

where S is the parameter defining the distance along the curve. Then the vector

$$\mathbf{T} = \frac{d\mathbf{X}}{dS}, \tag{4}$$

is a unit vector (i.e. $\mathbf{T} \cdot \mathbf{T} = 1$) tangent to the curve. The infinitesimal vector

$$d\mathbf{X} = \mathbf{T}dS \tag{5}$$

is then also tangent to the curve $\mathcal{C}_0$. According to the definition of the current image $\mathcal{C}_t$ its tangent infinitesimal vector $d\mathbf{x}$ is given by the relation

$$\forall \mathbf{X} \in \mathcal{C}_0 : \quad d\mathbf{x} = \left(\operatorname{Grad}\mathbf{f}\right) d\mathbf{X} \equiv \mathbf{t}dS, \quad \mathbf{t} := \mathbf{F}\mathbf{T}, \quad \mathbf{F} := \operatorname{Grad}\mathbf{f}, \tag{6}$$

where $\mathbf{F}$ is the deformation gradient at the point $\mathbf{X}$ and the instant of time t. Hence the infinitesimal vectors $d\mathbf{x}$ tangent to the curve $\mathcal{C}_t$ which deforms with the body are given by a *linear transformation* of the infinitesimal vector $d\mathbf{X}$. This transformation is defined by the quadratic matrix which is given by components of the deformation gradient $\mathbf{F}$. It is easy to be seen in the representation in Cartesian coordinates which are admissible due to the assumption that configuration spaces are Euclidean. If we choose the unit orthogonal base vectors $\left\{\mathbf{e}_K\right\}, K = 1, 2, 3$ for the initial configuration and $\left\{\mathbf{e}_k\right\}, k = 1, 2, 3$ for the current configuration then the above relations can be written in the form

$$\begin{aligned} d\mathbf{X} &= dX_K\mathbf{e}_K = T_K\mathbf{e}_K dS, \\ d\mathbf{x} &= dx_k\mathbf{e}_k = t_k\mathbf{e}_k dS, \quad t_k := F_{kK}T_K. \end{aligned} \tag{7}$$

The tangent vector $\mathbf{t}$ is the current image of the vector $\mathbf{T}$ and it is given by the rule defined by the relation (6). This rule of transformation defines the so-called *material* vectors. Not all vectors transform according to this rule and we see an example of a different rule of transformation in the sequel.

The most important property of the above transformation is that it is independent of the choice of curve going through a chosen point $\mathbf{X}$. The deformation gradient $\mathbf{F}$ depends only on $\mathbf{X}$ and t and defines the transformation of an arbitrary tangent vector $\mathbf{T}$ located at the point $\mathbf{X}$. We say that the gradient $\mathbf{F}$ considered as a mapping maps a tangent space at point $\mathbf{X}$ into the tangent space at the point $\mathbf{x} = \mathbf{f}\left(\mathbf{X}, t\right)$.

Let us consider the transformation of a vector which is perpendicular to a material surface $\mathcal{S}_0$. Such a surface is defined as a collection of material curves and, for simplicity, we assume that it is parametrized by two orthogonal families of such curves. At a chosen point $\mathbf{X}$ we consider two orthogonal parametric curves whose unit tangent vectors are $\mathbf{T}_1$ and $\mathbf{T}_2$, respectively. Then a unit vector perpendicular to the surface $\mathcal{S}_0$ is given by the vector product

$$\mathbf{N} = \mathbf{T}_1 \times \mathbf{T}_2. \tag{8}$$

This surface in the current configuration $\mathcal{S}_t$ has at the point $\mathbf{x} = \mathbf{f}(\mathbf{X},t)$ the following tangent and unit orthogonal vectors

$$\mathbf{t}_1 = \mathbf{F}\mathbf{T}_1, \quad \mathbf{t}_2 = \mathbf{F}\mathbf{T}_2, \quad \mathbf{n} = \frac{\mathbf{t}_1 \times \mathbf{t}_2}{|\mathbf{t}_1 \times \mathbf{t}_2|}. \tag{9}$$

Simultaneously we have

$$\begin{aligned} (\mathbf{t}_1 \times \mathbf{t}_2) \cdot \mathbf{e}_k &= \varepsilon_{kmn} t_{1m} t_{2n} = \varepsilon_{kmn} F_{mM} T_{1M} F_{nN} T_{2N} = \\ &= \varepsilon_{imn} F_{iP} F^{-1}_{Pk} F_{mM} F_{nN} T_{1M} T_{2N} = \varepsilon_{PMN} J F^{-1}_{Pk} T_{1M} T_{2M} = \\ &= J N_P F^{-1}_{Pk}, \quad J := \det \mathbf{F} > 0. \end{aligned}$$

Consequently

$$\mathbf{n} = \frac{\mathbf{F}^{-T}\mathbf{N}}{|\mathbf{F}^{-T}\mathbf{N}|}. \tag{10}$$

This is the rule of transformation for vectors perpendicular to material surfaces.

The Jacobian J, as we see further determines changes of infinitesimal volume elements caused by the transformation from the reference to current configuration. Its value for the identical mapping is equal to one. According to the condition (2) it cannot cross the line of zero values and consequently, due to continuity, it must be positive.

As already mentioned the transformation of vectors $d\mathbf{X}$ caused by the motion determines local deformations of the body. We need only changes of length of infinitesimal vectors in an arbitrary direction in order to find the local changes of the size and shape of material elements. These length changes follow from the relation

$$d\mathbf{x} \cdot d\mathbf{x} = (\mathbf{F} d\mathbf{X}) \cdot (\mathbf{F} d\mathbf{X}) = d\mathbf{X} \cdot \mathbf{C} d\mathbf{X}, \quad \mathbf{C} := \mathbf{F}^T\mathbf{F} = \mathbf{C}^T, \quad \det \mathbf{C} = J^2 > 0, \tag{11}$$

where the symmetric tensor $\mathbf{C}$ is called the *right Cauchy-Green deformation tensor.* There arises the question what happens to nine components of the deformation gradient $\mathbf{F}$ if six components of $\mathbf{C}$ are sufficient to describe the deformation. The answer is given by the polar decomposition theorem: under the assumption of nonsingularity of motion (2) there exists a unique decomposition of the deformation gradient of the following form[2]

$$\mathbf{F} = \mathbf{R}\mathbf{U}, \quad \mathbf{R}^{-1} = \mathbf{R}^T, \quad \mathbf{U}^T = \mathbf{U}, \tag{12}$$

i.e. there exist a unique orthogonal tensor $\mathbf{R}$ (it rotates vectors without changing their length) and a unique symmetric stretch tensor $\mathbf{U}$ whose product is equal to the deformation gradient.

The proof of the theorem is easy and, simultaneously, it shows the procedure of calculating these two tensors. Namely, for the right Cauchy-Green tensor we have the following eigenvalue problem

$$(\mathbf{C} - \boldsymbol{\lambda}_C \mathbf{1})\, \mathbf{K}_C = 0, \tag{13}$$

where the eigenvalues λ_C satisfy the characteristic equation

$$\lambda_C^3 - I\lambda_C^2 + II\lambda_C - III = 0, \quad I = \operatorname{tr}\mathbf{C}, \quad II = \frac{1}{2}\left(I^2 - \operatorname{tr}\mathbf{C}^2\right), \quad III = \det \mathbf{C}, \tag{14}$$

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[2] the dual form $\mathbf{F} = \mathbf{V}\mathbf{R}, \quad \mathbf{R}^{-1} = \mathbf{R}^T, \quad \mathbf{V}^T = \mathbf{V}$, holds true as well.

and I, II, III are the so-called principal invariants of $\mathbf{C}$. Hence, there exist three eigenvalues $\lambda_C^\alpha, \alpha = 1, 2, 3$, and due to the symmetry of $\mathbf{C}$ they are all real. They are called *principal stretches.* The corresponding three unit eigenvectors $\mathbf{K}_C^\alpha$ are linearly independent and this yields the following spectral representation of the deformation tensor $\mathbf{C}$

$$\mathbf{C} = \sum_{\alpha=1}^{3} \lambda_C^\alpha \mathbf{K}_C^\alpha \otimes \mathbf{K}_C^\alpha. \tag{15}$$

Simultaneously for the stretch tensor $\mathbf{U}$ we have the following eigenvalue problem

$$\left(\mathbf{U} - \boldsymbol{\lambda}_U \mathbf{1}\right) \mathbf{K}_U = 0. \tag{16}$$

If we multiply this relation by $\mathbf{U}$ from the left and use (13) we obtain

$$\left(\mathbf{C} - \boldsymbol{\lambda}_U^2 \mathbf{1}\right) \mathbf{K}_U = 0 \quad \Longrightarrow \quad \lambda_U = \sqrt{\lambda_C}, \quad \mathbf{K}_U = \mathbf{K}_C, \tag{17}$$

where we have used the relation

$$\mathbf{C} = \mathbf{U}^2. \tag{18}$$

This means that the spectral representation of the stretch tensor is as follows

$$\mathbf{U} = \sum_{\alpha=1}^{3} \sqrt{\lambda_C} \mathbf{K}_C \otimes \mathbf{K}_C. \tag{19}$$

As both the determination of $\mathbf{C}$ as the product of the deformation gradient $\mathbf{F}$ with itself and the solution of the eigenvalue problem for $\mathbf{C}$ are straightforward the above relation determines easily the stretch tensor $\mathbf{U} = \mathbf{C}^{1/2}$. It remains to find the inverse of $\mathbf{U}$ and we have

$$\mathbf{R} = \mathbf{F}\mathbf{U}^{-1} \quad \Longrightarrow \quad \mathbf{R}^T\mathbf{R} = \mathbf{U}^{-1}\mathbf{F}^T\mathbf{F}\mathbf{U} = \mathbf{U}^{-1}\mathbf{C}\mathbf{U}^{-1} = \mathbf{1}, \tag{20}$$

and, consequently, $\mathbf{R}$ is orthogonal.

The above considerations show that local changes of geometry are given only by the tensor $\mathbf{U}$ and, consequently, by the tensor $\mathbf{C}$. The orthogonal tensor $\mathbf{R}$ possesses, of course, 3 independent components (e.g. Euler angles) and it determines local rotations as an infinitesimal material element were a rigid body.

Depending on a particular application there are many possibilities to define deformation tensors. They are all equivalent. Some of them are quoted in the Table 1.

Table 1: *Measures of deformation*

Name		Definition	Eigenvalues	Eigenvectors	Author
right Cauchy -Green	$\mathbf{C}$	$\mathbf{F}^T\mathbf{F}$	$\lambda^2 \equiv \lambda_C^2$	$\mathbf{K} \equiv \mathbf{K}_C$	G. Green, 1841
left Cauchy -Green (Finger)	$\mathbf{B}$	$\mathbf{F}\mathbf{F}^T$	λ^2	$\mathbf{k} \equiv \mathbf{F}\mathbf{K}$	J. Finger, 1894
right stretch	$\mathbf{U}$	$\mathbf{C}^{1/2}$	λ	$\mathbf{K}$	Euler?
left stretch	$\mathbf{V}$	$\mathbf{B}^{1/2}$	λ	$\mathbf{k}$	Euler?
Cauchy	$\mathbf{c}$	$\mathbf{B}^{-1}$	$1/\lambda^2$	$\mathbf{k}$	L. A. Cauchy, 1827
Green-St.Venant (Lagrange)	$\mathbf{E}$	$0.5\,(\mathbf{C}-\mathbf{1})$	$0.5\,(\lambda^2-1)$	$\mathbf{K}$	A. de St.Venant, 1844
Almansi-Hamel (Euler)	$\mathbf{e}$	$0.5\,(\mathbf{1}-\mathbf{c})$	$0.5\,(1-1/\lambda^2)$	$\mathbf{k}$	E. Almansi, 1911
Piola	$\mathbf{C}^{-1}$		$1/\lambda^2$	$\mathbf{K}$	G. Piola, 1833

We proceed to discuss kinematics of the continuum. The main notions are the velocity field $\mathbf{v}\,(\mathbf{X},t)$ and the acceleration field $\mathbf{a}\,(\mathbf{X},t)$. They are defined by the following relations

$$\mathbf{v}\,(\mathbf{X},t) = \frac{\partial \mathbf{f}}{\partial t}\,(\mathbf{X},t)\,, \quad \mathbf{a}\,(\mathbf{X},t) = \frac{\partial \mathbf{v}}{\partial t}\,(\mathbf{X},t)\,. \tag{21}$$

Another quantity frequently appearing in the theory of continuous bodies is the gradient of velocity $\mathbf{L}$. It is defined by the time derivative of the deformation gradient $\mathbf{F}$

$$\mathbf{L} = \frac{\partial \mathbf{F}}{\partial t}\mathbf{F}^{-1}. \tag{22}$$

Later we discuss this notion in some details.

In relation to kinematics of the body it is useful to introduce a ceratin transformation group which has a great influence on the construction of constitutive relations. Namely, it is assumed that material properties of bodies cannot change by changing the reference frame in such a way that *distances* of material points in the configuration space remain unchanged. If we introduce two reference systems, say, with position vectors without and with star – in Figure 2 we demonstrate such systems without a rotation of the body – then we require that in both systems the distance between two arbitrary points of the body must be the same. Vectors $\mathbf{r}_2 - \mathbf{r}_1$ $\mathbf{r}_2^* - \mathbf{r}_1^*$ may not be the same due to the rigid rotation of the body but for both reference systems (*observers*) we have

$$|\mathbf{r}_2 - \mathbf{r}_1| = |\mathbf{r}_2^* - \mathbf{r}_1^*|\,. \tag{23}$$

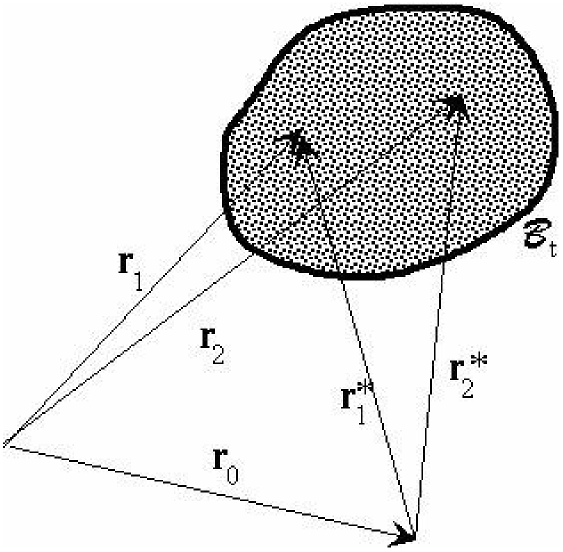

Fig. 2: *Change of a reference system in Euclidean spaces*

This is the property of the configuration space which we call *isometry.* The most general form of the transformation which leads to the relation (23) is as follows

$$\mathbf{x}^* = \mathbf{O}\left(t\right)\mathbf{x} + \mathbf{c}\left(t\right), \quad \mathbf{O}^T = \mathbf{O}^{-1}, \tag{24}$$

where $\mathbf{O}$ is an arbitrary time dependent orthogonal tensor and $\mathbf{c}$ an arbitrary time dependent vector. This class of transformations forms an *isometry group* and each member of this group is called an *Euclidean transformation.* We require that material properties are independent of the choice of two reference systems which differ on the isometry transformation. Incidentaly, the transformation in which $\mathbf{O}$ and $\mathbf{c}$ are constant is called *Galilean.* Classical equations of motion are invariant with respect to these transformations.

It is useful to check the transformation properties of objects which we were discussing in this lecture. After easy calculations we obtain

$$\begin{array}{rcl}
\mathbf{f}^*\left(\mathbf{X},t\right) & = & \mathbf{O}\left(t\right)\mathbf{f}\left(\mathbf{X},t\right) + \mathbf{c}\left(t\right), \\
\mathbf{v}^* & = & \mathbf{O}\mathbf{v} + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}}, \quad \dot{\mathbf{O}} := \dfrac{\partial \mathbf{O}}{\partial t}, \quad \dot{\mathbf{c}} := \dfrac{\partial \mathbf{c}}{\partial t}, \\
\mathbf{F}^* & = & \mathbf{O}\mathbf{F}, \\
\mathbf{C}^* & = & \mathbf{C}, \quad \mathbf{B}^* = \mathbf{O}\mathbf{B}\mathbf{O}^T, \\
\mathbf{a}^* & = & \mathbf{O}\mathbf{a} + \mathbf{2}\dot{\mathbf{O}}\mathbf{v} + \ddot{\mathbf{O}}\mathbf{x} + \ddot{\mathbf{c}}, \quad \ddot{\mathbf{O}} := \dfrac{\partial^2 \mathbf{O}}{\partial t^2}, \quad \ddot{\mathbf{c}} := \dfrac{\partial^2 \mathbf{c}}{\partial t^2}, \\
\mathbf{L}^* & = & \mathbf{O}\mathbf{L}\mathbf{O}^T + \mathbf{\Omega}, \quad \mathbf{\Omega} := \dot{\mathbf{O}}\mathbf{O}^T.
\end{array} \tag{25}$$

Scalars which do not change due to the transformation (24): $\varphi^* = \varphi$, vectors which change according to the rule: $\mathbf{b}^* = \mathbf{O}\mathbf{b}$, and tensors which transform according to the rule: $\mathbf{T}^* = \mathbf{O}\mathbf{T}\mathbf{O}^T$ are called *objective.* Hence in the above quoted examples $\mathbf{B}$ is objective, $\mathbf{F}$ behaves like a collection of three objective vectors (objects in parenthesis): $\mathbf{F} = (F_{kK}\mathbf{e}_k)\mathbf{e}_K$, $\mathbf{C}$ behaves like a collection of six scalars C_{KL}. The remaining objects are nonobjective. It is convenient to write them in the form in which the deviation from the objectivity is better exposed. For the velocity and acceleration we have

$$\begin{array}{rcl}
\mathbf{O}\mathbf{v} & = & \mathbf{v}^* - \mathbf{\Omega}\left(\mathbf{x}^* - \mathbf{c}\right) - \dot{\mathbf{c}}, \quad \mathbf{\Omega} := \dot{\mathbf{O}}\mathbf{O}^T, \quad \mathbf{\Omega}^T = -\mathbf{\Omega}, \\
\mathbf{O}\mathbf{a} & = & \mathbf{a}^* - 2\mathbf{\Omega}\left(\mathbf{v}^* - \dot{\mathbf{c}}\right) + \mathbf{\Omega}^2\left(\mathbf{x}^* - \mathbf{c}\right) - \dot{\mathbf{\Omega}}\left(\mathbf{x}^* - \mathbf{c}\right) - \ddot{\mathbf{c}},
\end{array} \tag{26}$$

where the antisymmetric tensor $\mathbf{\Omega}$ denotes the spin matrix (matrix of relative angular velocities of both reference systems). The contributions to the acceleration are called: $2\mathbf{\Omega}(\mathbf{v}^* - \dot{\mathbf{c}})$ – Coriolis, $-\mathbf{\Omega}^2(\mathbf{x}^* - \mathbf{c})$ – centrifugal, $\dot{\mathbf{\Omega}}(\mathbf{x}^* - \mathbf{c})$ – Euler and $\ddot{\mathbf{c}}$ – relative translational accelerations, respectively. They play an important role in the description of motion with respect to the so-called noninertial reference frames.

It is also convenient to separate objective and nonobjective contributions to the velocity gradient $\mathbf{L}$

$$\begin{aligned}
\mathbf{L} &= \mathbf{D} + \mathbf{W}, \\
\mathbf{D} &= \frac{1}{2}\left(\mathbf{L} + \mathbf{L}^T\right) = \mathbf{D}^T, \quad \mathbf{D}^* = \mathbf{ODO}^T, \\
\mathbf{W} &= \frac{1}{2}\left(\mathbf{L} - \mathbf{L}^T\right) = -\mathbf{W}^T, \quad \mathbf{W}^* = \mathbf{OWO}^T + \mathbf{\Omega}.
\end{aligned} \tag{27}$$

Hence the *stretching* tensor $\mathbf{D}$ is objective and the *spin* tensor $\mathbf{W}$ is nonobjective.

Finally, we consider the problem of the so-called *objective time derivatives.* This problem appears in constructions of constitutive laws.

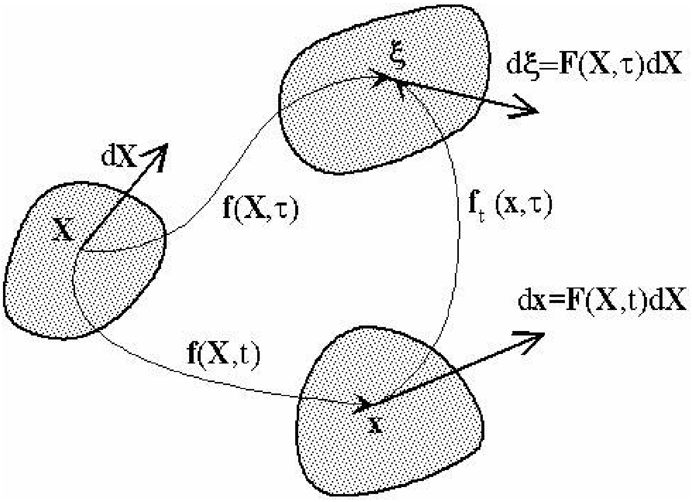

Fig.3: *Relative deformation gradient*

Let us begin with the analysis of a change of the reference configuration. This is demonstrated in Fig. 3. The purpose is to use the current configuration at the instant of time t as the reference configuration for the motion in the vicinity of the instant t. The function of motion defined on the current configuration will be denoted by $\mathbf{f}_t(.,.)$. For an arbitrary point $\boldsymbol{\xi}$ in the configuration at the instant of time τ it is given by the following relation

$$\boldsymbol{\xi} = \mathbf{f}\left[\mathbf{f}^{-1}(\mathbf{x}, t), \tau\right] = \mathbf{f}_t(\mathbf{x}, \tau). \tag{28}$$

Corresponding deformation gradients are as follows

$$\begin{aligned}
d\boldsymbol{\xi} &= \mathbf{F}(\mathbf{X}, \tau)\, d\mathbf{X} = \mathbf{F}\left(\mathbf{f}^{-1}(\mathbf{x}, t), \tau\right) \mathbf{F}^{-1}\left(\mathbf{f}^{-1}(\mathbf{x}, t), t\right) d\mathbf{x} = \\
&= \mathbf{F}_t(\mathbf{x}, \tau)\, d\mathbf{x} \quad \Longrightarrow \quad \mathbf{F}_t(\boldsymbol{\xi}, \tau) = \mathbf{F}_t\left(\mathbf{f}_t^{-1}(\boldsymbol{\xi}, \tau), \tau\right),
\end{aligned} \tag{29}$$

with an appropriate change of variables given by (28). The quantity $\mathbf{F}_t(\mathbf{x}, \tau)$ is called the *relative deformation gradient* with respect to the current configuration.

In order to see time changes at the current configuration we investigate a material vector $\mathbf{Q}(\mathbf{X})$. Its images in two instances of time t and τ are as follows

$$\begin{aligned} \mathbf{q}(\mathbf{x},t) &= \mathbf{F}\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right)\mathbf{Q}\left(\mathbf{f}^{-1}(\mathbf{x},t)\right), \\ \mathbf{q}(\boldsymbol{\xi},\tau) &= \mathbf{F}\left(\mathbf{f}^{-1}(\boldsymbol{\xi},\tau),t\right)\mathbf{Q}\left(\mathbf{f}^{-1}(\boldsymbol{\xi},\tau)\right) \quad \Longrightarrow \\ &\Longrightarrow \quad \mathbf{q}(\mathbf{x},t) = \mathbf{F}_t^{-1}(\boldsymbol{\xi},\tau)\,\mathbf{q}(\boldsymbol{\xi},t)\big|_{\boldsymbol{\xi}=\mathbf{f}_t^{-1}(\mathbf{x},\tau)}. \end{aligned} \tag{30}$$

We define the time derivative of $\mathbf{q}(\mathbf{x},t)$ as a limit $\tau \to t$ of the time derivative of $\mathbf{q}(\boldsymbol{\xi},\tau)$. In this way we account for time changes due to explicit dependence on time, due to the changes of position of the material point $\mathbf{X}$ as well as due to rotation of basis vectors along the trajectory. Such an operator is called *Lie derivative related to the field of velocity* $\mathbf{v}$. We have

$$\begin{aligned} \mathcal{L}_{\mathbf{v}}\mathbf{q}(\mathbf{x},t) &= \left.\frac{d\left[\mathbf{F}_t^{-1}(\boldsymbol{\xi},\tau)\,\mathbf{q}(\boldsymbol{\xi},t)\right]}{d\tau}\right|_{\tau=t} = \\ &= \frac{\partial\mathbf{q}(\mathbf{x},t)}{\partial t} + \mathbf{v}\cdot\operatorname{grad}\mathbf{q}(\mathbf{x},t) + \left.\frac{d\left[\mathbf{F}_t^{-1}(\boldsymbol{\xi},\tau)\right]}{d\tau}\right|_{\tau=t}\mathbf{q}(\mathbf{x},t). \end{aligned}$$

Bearing (29) in mind we get

$$\frac{d\mathbf{F}_t^{-1}\mathbf{F}_t}{d\tau} = 0 = \frac{d\mathbf{F}_t^{-1}}{d\tau}\mathbf{F}_t + \mathbf{F}_t^{-1}\frac{d\mathbf{F}_t}{d\tau} \quad \Longrightarrow \quad \frac{d\mathbf{F}_t^{-1}}{d\tau} = -\mathbf{F}_t^{-1}\frac{d\mathbf{F}_t}{d\tau}\mathbf{F}_t^{-1},$$

i.e.

$$\left.\frac{d\left[\mathbf{F}_t^{-1}(\boldsymbol{\xi},\tau)\right]}{d\tau}\right|_{\tau=t} = -\frac{d\mathbf{F}\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right)}{dt}\mathbf{F}^{-1}\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right) = -\mathbf{L}(\mathbf{x},t).$$

Hence

$$\begin{aligned} \mathcal{L}_{\mathbf{v}}\mathbf{q}(\mathbf{x},t) &= \frac{\partial\mathbf{q}(\mathbf{x},t)}{\partial t} + \mathbf{v}\cdot\operatorname{grad}\mathbf{q}(\mathbf{x},t) - \mathbf{L}(\mathbf{x},t)\,\mathbf{q}(\mathbf{x},t) \equiv \\ &\equiv \dot{\mathbf{q}} - \mathbf{L}\mathbf{q}. \end{aligned} \tag{31}$$

It is easy to check that this derivative is objective, i.e.

$$\mathcal{L}_{\mathbf{v}}\mathbf{q}^*(\mathbf{x}^*,t) = \mathbf{O}(t)\,\mathcal{L}_{\mathbf{v}}\mathbf{q}(\mathbf{x},t)\big|_{\mathbf{x}=\mathbf{O}^T\mathbf{x}^*}. \tag{32}$$

In the similar way we can define the time derivatives for material tensors of the second order. For example, one can introduce the following *Rivlin-Ericksen tensors* describing the rate of deformation

i/ as the time derivative of the right Cauchy-Green tensor $\dot{\mathbf{C}}$ is nonobjective one defines the Lie derivative of the relative Cauchy-Green tensor

$$\mathbf{C}_t(\tau) = \mathbf{F}_t^T(\tau)\,\mathbf{F}_t(\tau) \quad \Longrightarrow \quad \mathbf{A}_1(t) = \left.\frac{\partial C_t(\tau)}{\partial\tau}\right|_{\tau=t} = \mathbf{L}^T + \mathbf{L} = 2\mathbf{D}, \tag{33}$$

ii/ higher order Rivlin-Ericksen tensors

$$\mathbf{A}_n(t) = \mathbf{C}_t^{(n)}(t) = \left.\frac{\partial^n \mathbf{C}_t(\tau)}{\partial \tau^n}\right|_{\tau=t}, \quad n = 1, ..., \tag{34}$$

In the same way one can introduce objective time derivatives of nonmaterial vectors and tensors. For instance, the time derivative of a unit vector orthogonal to a material surface has the following form

$$\begin{aligned} \mathbf{n}(\mathbf{x},t) \quad &= \quad \mathbf{F}^{-T}(t)\,\mathbf{F}^{T}(\tau)\,\mathbf{n}(\boldsymbol{\xi},\tau)\big|_{\substack{\mathbf{X}=\mathbf{f}^{-1}(\mathbf{x},t)\\ \boldsymbol{\xi}=\mathbf{f}(\mathbf{X},\tau)}} \quad \Longrightarrow \\ &\Longrightarrow \quad \mathcal{L}_v\mathbf{n} = \dot{\mathbf{n}} + \mathbf{L}^T\mathbf{n}, \quad \dot{\mathbf{n}} := \frac{\partial \mathbf{n}}{\partial t} + \mathbf{v}\cdot \operatorname{grad}\mathbf{n}. \end{aligned} \tag{35}$$

Let us mention in passing that the time derivative $\dot{(...)}$ introduced above is the so-called *material time derivative.* It describes time changes along trajectories of material points and it is applied in the Eulerian description which we discuss in the next Lecture.

Lecture 2: Balance equations and field equations. Constitutive relations for thermomechanical processes

As we have already mentioned in the first Lecture fundamental quantities describing thermomechanical processes such as mass, momentum, angular momentum, energy and entropy satisfy balance equations. These notions are defined on a family of measurable subsets of the body $\mathcal{B}_0$. Let us choose a member of this family, say $\mathcal{P} \subset \mathcal{B}_0$. Then $\Phi(\mathcal{P}, t)$ denotes any of the above quantities prescribed to the subbody $\mathcal{P}$ at the instant of time t. It is the quantity which can be measured in laboratories. It is assumed that the set function $\Phi(., t)$ is *additive*, i.e. for two subbodies $\mathcal{P}_1$ and $\mathcal{P}_2$ which are separate $\mathcal{P}_1 \cap \mathcal{P}_2 = \emptyset$, $\Phi(\mathcal{P}_1 \cup \mathcal{P}_2, t) = \Phi(\mathcal{P}_1, t) + \Phi(\mathcal{P}_2, t)$. For instance, the energy of two subbodies which are not overlapping is the sum of energies of both subbodies. This assumption is usually a bit weaker in order to admit a concentration of energy on interfaces. We skip here these details. In addition, it is assumed that this set function is *continuous* with respect to the volume measure, i.e. there exist a constant α such that for any subbody $\mathcal{P}$

$$|\Phi(\mathcal{P}, t)| \leq \alpha \operatorname{vol} \mathcal{P}, \tag{36}$$

where $\operatorname{vol} \mathcal{P}$ is the volume of $\mathcal{P}$. According to the measure theory, these two assumptions, additivity and continuity, yield the existence of the *density* $\varphi(\mathbf{X}, t)$, $\mathbf{X} \in \mathcal{B}_0$ (the so-called *Radon-Nikodym derivative*) such that

$$\Phi(\mathcal{P}, t) = \int_{\mathcal{P}} \varphi(\mathbf{X}, t)\, dV, \tag{37}$$

where on the right hand side we have the so-called Lebegue integral. The above representation is the most fundamental feature of continuous models. It is obvious that the requirement of additivity eliminates long-range interactions from the model (compare remarks in Lecture 1). A contribution of such interactions would mean, for instance, that the energy of two separate subbodies would not be equal to the sum of energies of both subbodies but it would contain as well an energy of interaction.

The quantity Φ is assumed to satisfy the *balance equation*

$$\forall_{\mathcal{P}} \ \frac{d\Phi}{dt}(\mathcal{P}, t) = \Psi_{\mathcal{S}}(\partial\mathcal{P}, t) + \Psi_{\mathcal{P}}(\mathcal{P}, t), \tag{38}$$

where $\Psi_{\mathcal{S}}$ describes the *flux* of the quantity Φ through the surface $\partial\mathcal{P}$ of the subbody $\mathcal{P}$ and $\Psi_{\mathcal{P}}$ is the sum of the volume *supply* of the quantity Φ from the external world and of the *production* of Φ in the subbody $\mathcal{P}$. These two functions are assumed to satisfy axioms similar to (36) and, consequently, it can be proved that they possess the following representations

$$\Psi_{\mathcal{S}}(\partial\mathcal{P}, t) = \oint_{\partial\mathcal{P}} \psi_{\mathcal{S}}(\mathbf{X}, t)\, dS, \quad \Psi_{\mathcal{P}}(\mathcal{P}, t) = \int_{\mathcal{P}} \left[\psi_V(\mathbf{X}, t) + \hat{\varphi}(\mathbf{X}, t)\right] dV, \tag{39}$$

where $\psi_{\mathcal{S}}$ is the flux density per unit surface and unit time of the field density φ, ψ_V is the density of the volume supply of φ and $\hat{\varphi}$ is the *production* (*source*) per unit volume and time of the field φ[3].

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[3] The difference between the volume supply ψ_V and the production $\hat{\varphi}$ can be recognized only in relation to the constitutive definition of the material. Then the volume supply is a quantity which is controlled from the external world – it can be, for instance, switched off, and the production (source) is controlled by constitutive variables which characterize a particular material.

Additionally it is assumed that the surface $\partial\mathcal{P}$ is orientable and the dependence of the flux $\psi_{\mathcal{S}}(\mathbf{X},t)$ on the surface reduces only to the dependence on the unit vector $\mathbf{N}(\mathbf{X},t)$ orthogonal to the surface at the point $\mathbf{X}$ and oriented outwards, i.e. $\psi_{\mathcal{S}}(\mathbf{X},t) = \psi(\mathbf{N},\mathbf{X},t)$. Then one can show the following Cauchy Theorem: there exists a function $\boldsymbol{\psi}(\mathbf{X},t)$ such that

$$\psi_{\mathcal{S}}(\mathbf{X},t) = \boldsymbol{\psi}(\mathbf{X},t)\cdot\mathbf{N}(\mathbf{X},t). \tag{40}$$

It means that $\psi_{\mathcal{S}}$ is a *linear homogeneous* function of the unit vector $\mathbf{N}$. We prove this property.

We show first that $\psi_{\mathcal{S}}$ changes sign when the surface changes orientation: $\mathbf{N}\to-\mathbf{N}$. We divide a subbody $\mathcal{P}$ into two subbodies $\mathcal{P}_1$ and $\mathcal{P}_2$, $\mathcal{P}_1\cup\mathcal{P}_2$ such that they have a common part of the boundary $\mathcal{S}$. This surface has the outward orientation $\mathbf{N}$ for $\mathcal{P}_1$ and, consequently, it has the outward orientation $-\mathbf{N}$ for $\mathcal{P}_2$. Then the balance equation has the form

$$\frac{d}{dt}\int_{\mathcal{P}_1\cup\mathcal{P}_2}\varphi dV = \oint_{\partial\mathcal{P}}\psi_{\mathcal{S}}dS + \int_{\mathcal{P}_1\cup\mathcal{P}_2}\left[\psi_V+\hat{\varphi}\right]dV.$$

Using the balance equations for $\mathcal{P}_1$ and $\mathcal{P}_2$ separately we obtain

$$\int_{\mathcal{S}}\psi_{\mathcal{S}}dS = -\int_{\mathcal{S}}\psi_{-\mathcal{S}}dS,$$

where $-\mathcal{S}$ indicates the opposite orientation of the surface. Hence $\psi_{\mathcal{S}} = -\psi_{-\mathcal{S}}$ or, bearing the assumption on dependence on the normal vector in mind,

$$\psi(\mathbf{N},\mathbf{X},t) = -\psi(-\mathbf{N},\mathbf{X},t). \tag{41}$$

Now we are in the position to prove the linearity of the above function with respect to $\mathbf{N}$. As this function is defined only for unit vectors we define first the following extension on the space $\mathcal{V}^3$ of arbitrary vectors $\mathbf{W}$

$$\tilde{\psi}(\mathbf{W},\mathbf{X},t) = \begin{cases} |\mathbf{W}|\,\psi\left(\frac{\mathbf{W}}{|\mathbf{W}|},\mathbf{X},t\right) \text{ for } \mathbf{W}\neq 0, \\ \mathbf{0} \text{ for } \mathbf{W}=0. \end{cases} \tag{42}$$

We show that this extension is the linear function with respect to $\mathbf{W}$, i.e. for two arbitrary numbers a and b we have $\tilde{\psi}(a\mathbf{W}_1+b\mathbf{W}_2,\mathbf{X},t) = a\tilde{\psi}(\mathbf{W}_1,\mathbf{X},t)+b\tilde{\psi}(\mathbf{W}_2,\mathbf{X},t)$. This condition can be replaced by the following two conditions:

i/ for any real number a and any vector $\mathbf{W}$: $\tilde{\psi}(a\mathbf{W},\mathbf{X},t) = a\tilde{\psi}(\mathbf{W},\mathbf{X},t)$,
ii/ for any two vectors $\mathbf{W}_1,\mathbf{W}_2$: $\tilde{\psi}(\mathbf{W}_1+\mathbf{W}_2,\mathbf{X},t) = \tilde{\psi}(\mathbf{W}_1,\mathbf{X},t) + \tilde{\psi}(\mathbf{W}_2,\mathbf{X},t)$.

It is clear that the function (42) satisfies the above conditions for either $a=0$ or $\mathbf{W}=\mathbf{0}$ or $a>0,\mathbf{W}\neq\mathbf{0}$. Hence we confine our interest to the case $a<0$ and $\mathbf{W}\neq\mathbf{0}$. We have

$$\begin{aligned}\tilde{\psi}(a\mathbf{W},\mathbf{X},t) &= \tilde{\psi}(-|a|\,\mathbf{W},\mathbf{X},t) = |a|\,\tilde{\psi}(-\mathbf{W},\mathbf{X},t) = \\ &= -|a|\,\tilde{\psi}(\mathbf{W},\mathbf{X},t) = a\tilde{\psi}(\mathbf{W},\mathbf{X},t),\end{aligned}$$

which proves i/.

In the case of linearly dependent vectors $\mathbf{W}_1, \mathbf{W}_2$ the property ii/ reduces to i/. Therefore we assume that these vectors are linearly independent. Let

$$\mathbf{W}_3 = -\left(\mathbf{W}_1 + \mathbf{W}_2\right). \tag{43}$$

Let us consider a triangular block $\mathcal{P}_\delta$, containing $\mathbf{X}$, with the faces $\mathcal{S}_1, \mathcal{S}_2, \mathcal{S}_3$ normal to $\mathbf{W}_1, \mathbf{W}_2, \mathbf{W}_3$, respectively, and the two parallel end triangles $\mathcal{S}_4, \mathcal{S}_5$ apart by the distance δ (Fig. 4). Let ε be the height of the triangles $\mathcal{S}_4, \mathcal{S}_5$ and $A_i, i = 1, 2, 3$ be the areas of $\mathcal{S}_i$. From the construction of the block we have

$$\frac{A_1}{|\mathbf{W}_1|} = \frac{A_2}{|\mathbf{W}_2|} = \frac{A_3}{|\mathbf{W}_3|}. \tag{44}$$

The balance equation written for $\mathcal{P}_\delta$ yields

$$\frac{1}{\varepsilon}\int_{\mathcal{P}_\delta}\left(\frac{\partial \varphi}{\partial t} - \psi_V - \hat{\varphi}\right) dV - \frac{1}{\varepsilon}\int_{\mathcal{S}_4 \cup \mathcal{S}_5} \psi_S\left(\mathbf{N}, \mathbf{X}, t\right) dS =$$

$$= \frac{1}{\varepsilon}\sum_{i=1}^{3}\int_{\mathcal{S}_i} \psi_S\left(\frac{\mathbf{W}_i}{|\mathbf{W}_i|}, \mathbf{X}, t\right) dS.$$

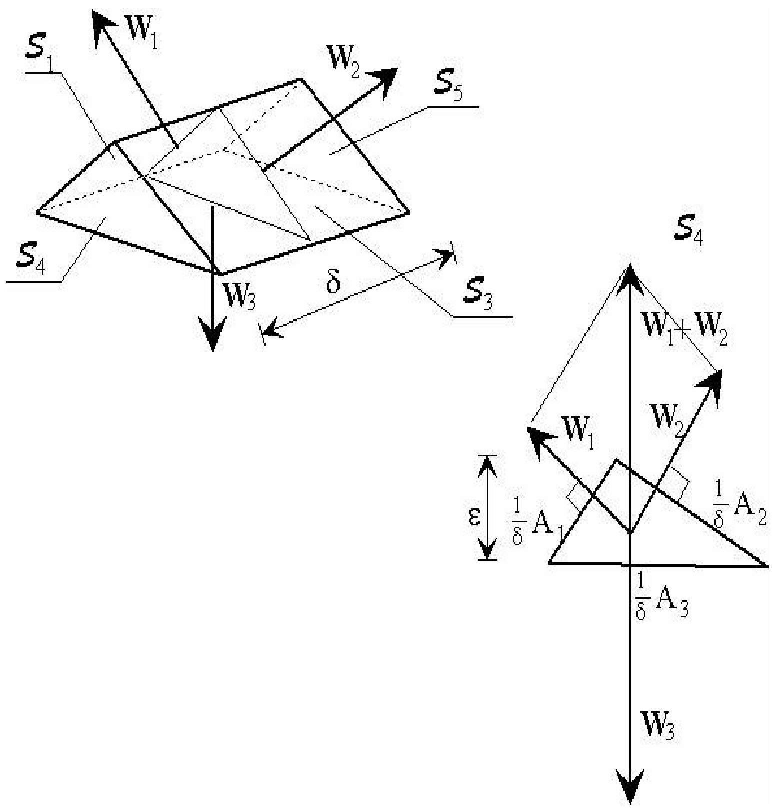

Fig. 4: *Triangular block used in the proof of Cauchy's Theorem*

It is easy to see that $\operatorname{vol}\mathcal{P}_\delta$ and A_4, A_5 are of the order ε^2 whereas $A_i, i = 1,2,3$ is of order ε. Hence, we obtain

$$\lim_{\varepsilon\to 0}\sum_{i=1}^{3}\frac{1}{\varepsilon}\int_{\mathcal{S}_i}\psi_S\left(\frac{\mathbf{W}_i}{|\mathbf{W}_i|},\mathbf{X},t\right)dS = 0.$$

Now let us apply the mean value theorem to the above relation. We have

$$\lim_{\varepsilon\to 0}\sum_{i=1}^{3}\frac{1}{\varepsilon}A_i\psi_S\left(\frac{\mathbf{W}_i}{|\mathbf{W}_i|},\mathbf{X}^{(i)},t\right) = 0,$$

where $\mathbf{X}^{(i)} \in \mathcal{S}_i$. Bearing (44) in mind, we finally arrive at

$$\lim_{\varepsilon\to 0}\sum_{i=1}^{3}|\mathbf{W}_i|\,\psi_S\left(\frac{\mathbf{W}_i}{|\mathbf{W}_i|},\mathbf{X}^{(i)},t\right) =$$

$$= |\mathbf{W}_1|\,\psi_S\left(\frac{\mathbf{W}_1}{|\mathbf{W}_1|},\mathbf{X},t\right) + |\mathbf{W}_2|\,\psi_S\left(\frac{\mathbf{W}_2}{|\mathbf{W}_2|},\mathbf{X},t\right) - |\mathbf{W}_3|\,\psi_S\left(\frac{\mathbf{W}_3}{|\mathbf{W}_3|},\mathbf{X},t\right) = 0,$$

which yields the condition ii/. This completes the proof.

Bearing the above results in mind we can write the general balance equation in the following form

$$\forall_{\mathcal{P}}\ \frac{d}{dt}\int_{\mathcal{P}}\varphi(\mathbf{X},t)\,dV = \oint_{\partial\mathcal{P}}\boldsymbol{\psi}(\mathbf{X},t)\cdot\mathbf{N}(\mathbf{X},t)\,dS + \int_{\mathcal{P}}\left[\psi_V(\mathbf{X},t) + \hat{\varphi}(\mathbf{X},t)\right]dV. \quad (45)$$

This result can be transformed to the *local form.* We consider two special cases of this form – one which holds in *regular points*, i.e. in points $\mathbf{X} \in \mathcal{B}_0$ in which all densities appearing in (45) are continuous and, secondly, in *points of a singular surface* $\mathcal{S}$ which may move through the body with a speed $U\mathbf{N}$. This is the velocity of the points on the surface in direction perpendicular to the surface. As we see further the balance equation does not contribute anything to the description of motion which is tangential to the surface, i.e. gliding of $\mathcal{S}$ along tangential directions is immaterial for our considerations. In points of a singular surface limits of densities of the relation (45) may be different on both sides of the surface, i.e. they may suffer *finite jumps.*

Let us first consider the case of a regular point $\mathbf{X} \in \mathcal{B}_0$. We construct an infinite descending family of subbodies $\{\mathcal{P}_i\}_{i=1}^{\infty}$ with three properties: i/ each set of this family contains the point $\mathbf{X}$, ii/ for each i $\mathcal{P}_{i+1} \subset \mathcal{P}_i$ and iii/ $\lim_{i\to\infty}\operatorname{vol}\mathcal{P}_i = 0$, where $\operatorname{vol}\mathcal{P}_i = \int_{\mathcal{P}_i} dV$ is the volume of $\mathcal{P}_i$. Then using the Stokes Theorem for the surface integral we obtain

$$\lim_{i\to\infty}\frac{1}{\operatorname{vol}\mathcal{P}_i}\int\left[\frac{\partial\varphi}{\partial t} - \operatorname{Div}\boldsymbol{\psi} - \psi_V - \hat{\varphi}\right]dV = 0,$$

and, accounting for the mean value Theorem for integrals,

$$\frac{\partial\varphi}{\partial t} = \operatorname{Div}\boldsymbol{\psi} + \psi_V + \hat{\varphi}, \quad (46)$$

for almost all points of $\mathcal{B}_0$.

In thermomechanics this equation is written for mass, momentum, angular momentum, energy and entropy. We list the corresponding densities in Table 2.

Table 2: *Densities of thermomechanics*

Name	density φ	flux $\boldsymbol{\psi}$	supply ψ_V	source $\hat{\varphi}$
mass density	ρ_0	0	0	0
momentum density	$\rho_0\mathbf{v}$	$\mathbf{P}$	$\rho_0\mathbf{b}$	0
angular momentum density	$\rho_0\mathbf{x}\times\mathbf{v}$	$\varepsilon_{klm}x_l P_{mM}\mathbf{e}_k$	$\rho_0\mathbf{x}\times\mathbf{b}$	0
density of energy	$\rho_0\left(\varepsilon+\frac{1}{2}v^2\right)$	$-\mathbf{Q}+\mathbf{P}^T\mathbf{v}$	$\rho_0\left(\mathbf{v}\cdot\mathbf{b}+r\right)$	0
density of entropy	$\rho_0\eta$	$-\mathbf{H}$	$\rho_0 s$	$\hat{\eta}$

All densities are, of course, referred to the unit volume in the undeformed (reference) configuration $\mathcal{B}_0$. $\mathbf{P}$ is the so-called Piola-Kirchhoff stress tensor, $\mathbf{b}$ is the body force per unit mass, ε denotes the specific internal energy per unit mass, $\frac{1}{2}\rho_0 v^2\equiv\frac{1}{2}\rho_0\mathbf{v}\cdot\mathbf{v}$ is the density of kinetic energy per unit reference volume, $\mathbf{Q}$ is the heat flux vector in the reference configuration, r is the density of energy radiation per unit mass, η is the specific entropy per unit mass, $\mathbf{H}$ is the entropy flux vector in the reference configuration, and $\hat{\eta}$ is the source of entropy per unit mass. We return later to the detailed discussion of the definition and the interpretation of all these quantities.

Let us note that except of entropy all other sources are zero. Such balance equations are called *conservation laws.* We see in the theory of multicomponent systems that for some field quantities of mixtures it does not have to be the case.

Now let us turn our attention to points on a singular surface $\mathcal{S}$. We construct again a descending family of subbodies $\{\mathcal{P}_i\}$ with three properties: i/ for each i $\mathcal{P}_i\cap\mathcal{S}=\mathcal{P}_{i+1}\cap\mathcal{S}$, ii/ for each i $\mathcal{P}_{i+1}\subset\mathcal{P}_i$ and iii/ $\lim_{i\to\infty}\operatorname{vol}\mathcal{P}_i=0$. Such a family is demonstrated in Fig. 5.

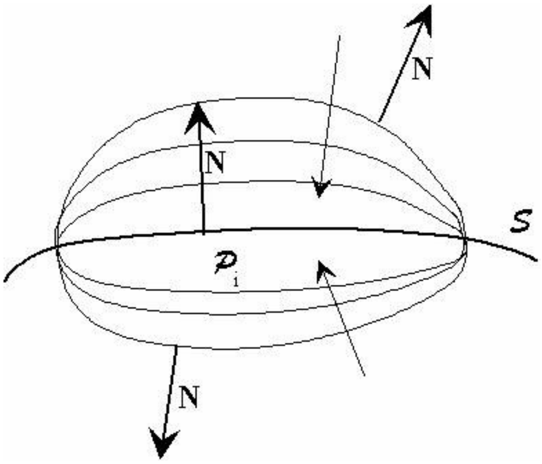

Fig. 5: *Transition to a singular surface*

First we estimate the derivative on the left hand side of the balance equation. We have

$$\begin{aligned}\frac{d}{dt}\int_{\mathcal{P}_i}\varphi dV &= \frac{d}{dt}\int_{\mathcal{P}_i^+}\varphi dV+\frac{d}{dt}\int_{\mathcal{P}_i^-}\varphi dV= \\ &= \int_{\mathcal{P}_i^+}\frac{\partial\varphi}{\partial t}dV-\int_{\mathcal{S}\cap\partial\mathcal{P}_i^+}\varphi^+ UdS+\int_{\mathcal{P}_i^-}\frac{\partial\varphi}{\partial t}dV+\int_{\mathcal{S}\cap\partial\mathcal{P}_i^-}\varphi^- UdS,\end{aligned}$$

where $\mathcal{P}_i^+, \mathcal{P}_i^-$ are the part of $\mathcal{P}_i$ lying above and below the surface $\mathcal{S}$, respectively, φ^+, φ^- are limits of φ calculated from the positive (with respect to the orientation $\mathbf{N}$) and negative sides of $\mathcal{S}$. The difference in sign in surface integrals follows from the opposite orientation of the surfaces $\mathcal{S} \cap \partial\mathcal{P}_i^+$ and $\mathcal{S} \cap \partial\mathcal{P}_i^-$.

In the limit $i \to \infty$ volume integrals vanish. The flux term can be written in the form

$$\oint_{\partial\mathcal{P}_i} \boldsymbol{\psi} \cdot \mathbf{N} dS = \int_{\partial\mathcal{P}_i \cap \partial\mathcal{P}_i^+} \boldsymbol{\psi} \cdot \mathbf{N} dS + \int_{\partial\mathcal{P}_i \cap \partial\mathcal{P}_i^-} \boldsymbol{\psi} \cdot \mathbf{N} dS. \tag{47}$$

Taking the limit in the whole balance equation we obtain

$$\int_{\mathcal{S} \cap \mathcal{P}_i} \left[-\left(\varphi^+ - \varphi^- \right) U - \left(\boldsymbol{\psi}^+ \cdot \mathbf{N} - \boldsymbol{\psi}^- \cdot \mathbf{N} \right) \right] dS = 0.$$

We can localize this relation as well and for an arbitrary point of the surface $\mathcal{S}$ we obtain the following *Kotchine condition*

$$[[\varphi]] \, U + [[\boldsymbol{\psi}]] \cdot \mathbf{N} = 0, \quad [[...]] := (...)^+ - (...)^- . \tag{48}$$

It has been assumed that the source is volume continuous, i.e. that the surface $\mathcal{S}$ does not contribute to the production. It does not have to be the case for some surfaces such as membranes. We discuss this problem later.

For thermomechanical fields the balance equations are collected in Table 3 in the same order as in Table 2.

Table 3: *Balance equations of thermomechanical model in Lagrangian description Left – regular points, right – points of a singular surface*

$\frac{\partial \rho_0}{\partial t} = 0$.	$[[\rho_0]] \, U = 0$.
$\rho_0 \frac{\partial \mathbf{v}}{\partial t} = \operatorname{Div} \mathbf{P} + \rho_0 \mathbf{b}$.	$[[\rho_0 \mathbf{v}]] \, U + [[\mathbf{P}]] \, \mathbf{N} = 0$.
$\mathbf{P}\mathbf{F}^T = \mathbf{F}\mathbf{P}^T$.	identity
$\rho_0 \frac{\partial}{\partial t} \left(\varepsilon + \frac{1}{2} v^2 \right) + \operatorname{Div} \left(\mathbf{Q} - \mathbf{P}^T \mathbf{v} \right) =$ $= \rho_0 \mathbf{v} \cdot \mathbf{b} + \rho_0 r$.	$\left[\left[\rho_0 \left(\varepsilon + \frac{1}{2} v^2 \right) \right]\right] U -$ $- \left[\left[\mathbf{Q} - \mathbf{P}^T \mathbf{v} \right]\right] \cdot \mathbf{N} = 0$.
$\rho_0 \frac{\partial \eta}{\partial t} + \operatorname{Div} \mathbf{H} = \rho_0 s + \hat{\eta}$.	$[[\rho_0 \eta]] \, U - [[\mathbf{H}]] \cdot \mathbf{N} = 0$.

In the evaluation of the second law of thermodynamics it is convenient to work with field equations of the first order. Then neither $\mathbf{F}$ should be considered as the gradient of the function of motion $\mathbf{f}$ nor $\mathbf{v}$ should be the time derivative of this function. The function $\mathbf{f}$ does not appear in such an approach. Its existence is secured by the integrability conditions of $\mathbf{F}$ and $\mathbf{v}$

$$\frac{\partial \mathbf{F}}{\partial t} = \operatorname{Grad} \mathbf{v}, \quad \operatorname{Grad} \mathbf{F} = \left(\operatorname{Grad} \mathbf{F}\right)^{T^{23}} \text{ i.e. } \frac{\partial F_{kK}}{\partial X_L} = \frac{\partial F_{kL}}{\partial X_K}. \tag{49}$$

Clearly, these relations are identically satisfied if we introduce the function $\mathbf{f}$. Otherwise they have to be used in the model in the same way as other field equations. Usually the second condition is directly incorporated in the evaluation of thermodynamical admissibility. However, the first one remains as an additional equation.

It is convenient to write the above integrability condition in the form of balance equation. We have

$$\frac{\partial \mathbf{F}}{\partial t} - \operatorname{Div}\left(\mathbf{v} \otimes \mathbf{1}\right) = 0 \quad \Longrightarrow \quad \frac{d}{dt} \int_{\mathcal{P}} \mathbf{F} dV - \oint_{\partial \mathcal{P}} \mathbf{v} \otimes \mathbf{N} dS = 0. \tag{50}$$

It means that we have an additional kinematical jump condition on singular surfaces

$$[[\mathbf{F}]]\, U + [[\mathbf{v} \otimes \mathbf{N}]] = 0. \tag{51}$$

This is one of the so-called Hadamard kinematic compatibility conditions which form the basis of wave analysis in continua. We return to this problem in further Lectures. It yields two important conclusions: on singular surfaces on which the velocity is continuous also the deformation gradient must be continuous and on material surfaces of contact of two bodies ($U = 0$) the velocity is continuous.

The above form of balance equations related to the reference configuration at a chosen instant of time t_0 is often inconvenient in practical applications. For instance, the fluid mechanics never relies on such a description and it uses a current configuration as the reference. We call the above presented description *Lagrangian* and we proceed now to formulate *Eulerian description* in which the current configuration is used.

Let us begin with the proof of an identity which is frequently used by the transformation of balance equations. Namely[4]

$$\operatorname{Div}\left(J \mathbf{F}^{-T}\right) = 0. \tag{52}$$

We write it in Cartesian coordinates

$$\begin{aligned} \frac{\partial \left(J F_{Kk}^{-1}\right)}{\partial X_K} &= \frac{\partial J}{\partial X_K} F_{Kk}^{-1} + J \frac{\partial F_{Kk}^{-1}}{\partial X_K} = \\ &= J F_{Ll}^{-1} \frac{\partial F_{lL}}{\partial X_K} F_{Kk}^{-1} - J F_{Kl}^{-1} F_{Lk}^{-1} \frac{\partial F_{lL}}{\partial X_K}, \end{aligned}$$

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[4] In a similar way one can prove a dual identity

$$\operatorname{div}\left(J^{-1} \mathbf{F}^{T}\right) = 0.$$

and (52) follows when we use the symmetry $\frac{\partial F_{lL}}{\partial X_K} = \frac{\partial F_{lK}}{\partial X_L}$. In the derivation we have used the identity

$$\frac{\partial \left(F_{Kk}^{-1} F_{kL} \right)}{\partial X_K} = 0 = \frac{\partial F_{Kk}^{-1}}{\partial X_K} F_{kL} + F_{Kk}^{-1} \frac{\partial F_{kL}}{\partial X_K} \quad \Longrightarrow \quad \frac{\partial F_{Kk}^{-1}}{\partial X_K} = -F_{Kl}^{-1} F_{Lk}^{-1} \frac{\partial F_{lL}}{\partial X_K}. \tag{53}$$

The transformation of Lagrangian to Eulerian description relies on the substitution of the inverse function of motion $\mathbf{X} = \mathbf{f}^{-1}(\mathbf{x},t)$. We have, for instance

$$\begin{aligned} \mathbf{v} &= \bar{\mathbf{v}}(\mathbf{x}, \mathbf{t}) = \mathbf{v}\left(\mathbf{f}^{-1}(\mathbf{x},t), t\right), \quad \mathbf{a} = \bar{\mathbf{a}}(\mathbf{x}, \mathbf{t}) = \mathbf{a}\left(\mathbf{f}^{-1}(\mathbf{x},t), t\right), \\ \mathbf{L} &= \bar{\mathbf{L}}(\mathbf{x}, \mathbf{t}) = \mathbf{L}\left(\mathbf{f}^{-1}(\mathbf{x},t), t\right), \\ \mathbf{B} &= \bar{\mathbf{B}}(\mathbf{x}, \mathbf{t}) = \mathbf{F}\left(\mathbf{f}^{-1}(\mathbf{x},t), t\right) \mathbf{F}^T \left(\mathbf{f}^{-1}(\mathbf{x},t), t\right). \end{aligned} \tag{54}$$

Transformation of the velocity gradient $\mathbf{L}$ has a special bearing. We have

$$\mathbf{L} = \frac{\partial \mathbf{F}}{\partial t} \mathbf{F}^{-1} = (\operatorname{Grad} \mathbf{v}) \mathbf{F}^{-1} = \operatorname{grad} \bar{\mathbf{v}}, \tag{55}$$

and this relation explains the name of $\mathbf{L}$.

We have also the following relations for derivatives of J

$$\begin{aligned} \frac{\partial J}{\partial t} &= J \mathbf{F}^{-T} \cdot \frac{\partial \mathbf{F}}{\partial t} = \bar{J} \operatorname{tr} \bar{\mathbf{L}} = \bar{J} \operatorname{div} \bar{\mathbf{v}}, \\ \operatorname{Grad} J &= \bar{\mathbf{F}}^T \operatorname{grad} \bar{J}. \end{aligned} \tag{56}$$

Whenever it will be clear from the context that we work in spatial coordinates $(\mathbf{x}, t)$ we shall skip the bar over Eulerian quantities.

Let us investigate the balance equations. The transformation $\mathbf{X} \to \mathbf{x}$ in (45) yields

$$\begin{aligned} \frac{d}{dt} \int_{\mathcal{P}_t} \bar{\varphi} \bar{J}^{\cdot -1} dv &= \oint_{\partial \mathcal{P}_t} \left(\bar{J}^{-1} \bar{\mathbf{F}} \bar{\boldsymbol{\psi}} \right) \cdot \mathbf{n} ds + \int_{\mathcal{P}_t} \left[\bar{\psi}_V + \hat{\varphi}' \right] \bar{J}^{\cdot -1} dv, \\ \hat{\varphi}' &: = \hat{\varphi}\left(\mathbf{f}^{-1}(\mathbf{x}, t), t\right), \end{aligned} \tag{57}$$

where we have used the formula for the transformation of variables $\mathbf{X} \to \mathbf{x}$ known from the classical analysis. The domain of integration is given by the transformation of the *material* volume $\mathcal{P}_t = \mathbf{f}(\mathcal{P}, t)$, where $\partial \mathcal{P}_t$ is its boundary and $\mathbf{n}$ the unit normal vector given by (10). This formula explains the presence of the contribution $\bar{J}^{-1} \bar{\mathbf{F}}$ in this relation. dv denotes the infinitesimal volume element in the current configuration and ds the infinitesimal surface element in the current configuration. $\bar{J}^{-1} = J^{-1}(\mathbf{x}, t)$ is in this relation, of course, the Jacobian of the transformation.

We introduce the following notation which will be particularly useful in thermodynamics of multicomponent systems

$$\varphi_t = \varphi J^{-1}, \quad \boldsymbol{\psi}_t = J^{-1} \mathbf{F} \boldsymbol{\psi}, \quad \psi_{Vt} = \psi_V J^{-1}, \quad \hat{\varphi}_t = \hat{\varphi}', \tag{58}$$

all of them being functions of $(\mathbf{x}, t)$. Then the general balance equation in Eulerian description has the form

$$\frac{d}{dt} \int_{\mathcal{P}_t} \varphi_t dv = \oint_{\partial \mathcal{P}_t} \boldsymbol{\psi}_t \cdot \mathbf{n} ds + \int_{\mathcal{P}_t} \left[\psi_t + \hat{\varphi}_t \right] dv. \tag{59}$$

As in the Lagrangian description we can derive the local form of this equation in regular points and in points on a singular surface.

In the first case the left hand side has the form

$$\frac{d}{dt}\int_{\mathcal{P}_t}\varphi_t dv=\int_{\mathcal{P}_t}\frac{\partial\varphi_t}{\partial t}dv+\oint_{\partial\mathcal{P}_t}\varphi_t\mathbf{v}\cdot\mathbf{n}ds=\int_{\mathcal{P}_t}\left[\frac{\partial\varphi_t}{\partial t}+\operatorname{div}\left(\varphi_t\mathbf{v}\right)\right]dv, \tag{60}$$

which results from the fact that the domain is material.

Hence by means of Stokes Theorem and the localization procedure discussed before we obtain

$$\frac{\partial\varphi_t}{\partial t}+\operatorname{div}\left(\varphi_t\mathbf{v}-\boldsymbol{\psi}_t\right)=\hat{\varphi}_t, \tag{61}$$

for almost all points of $\mathbf{f}\left(\mathcal{B}_0,t\right)$. This is the Eulerian counterpart of the equation (46) in the Lagrangian description.

We illustrate the above general considerations by the mass balance. We have

$$\frac{d}{dt}\int_{\mathcal{P}}\rho_0 dV=\frac{d}{dt}\int_{\mathbf{f}(\mathcal{P},t)}\bar{\rho}_0\bar{J}^{-1}dv=0.$$

Consequently, it is convenient to introduce the following notion of the *current mass density*

$$\rho\left(\mathbf{x},t\right)=\rho_0\left(\mathbf{f}^{-1}\left(\mathbf{x},t\right)\right)J^{-1}\left(\mathbf{f}^{-1}\left(\mathbf{x},t\right),t\right). \tag{62}$$

It satisfies the following balance law (conservation of mass)

$$\frac{d}{dt}\int_{\mathcal{P}_t}\rho dv=0,\quad \mathcal{P}_t:=\mathbf{f}\left(\mathcal{P},t\right) \tag{63}$$

In regular points, we can transform this relation in the following way

$$\begin{aligned}\frac{d}{dt}\int_{\mathcal{P}_t}\rho dv &= \int_{\mathcal{P}_t}\frac{\partial\rho}{\partial t}dv+\oint_{\partial\mathcal{P}_t}\rho\mathbf{v}\cdot\mathbf{n}dv= \\ &= \int_{\mathcal{P}_t}\left[\frac{\partial\rho}{\partial t}+\operatorname{div}\left(\rho\mathbf{v}\right)\right]dv=0\quad\text{i.e.}\quad\frac{\partial\rho}{\partial t}+\operatorname{div}\left(\rho\mathbf{v}\right)=0.\end{aligned} \tag{64}$$

We have used in these manipulations the fact the surface $\partial\mathcal{P}_t$ of the material domain $\mathcal{P}_t$ (i.e. the domain whose motion in the current configurations is determined by material points forming the domain) moves with the speed $\mathbf{v}\cdot\mathbf{n}$, where $\mathbf{n}$ denotes the outward normal vector of this surface.

Making use of relations (56) it can be easily shown that the relation (62) $\rho=\rho_0J^{-1}$ is the solution of the equation (64) with the initial solution $\rho\left(\mathbf{x},t=t_0\right)=\rho_0\left(\mathbf{f}\left(\mathbf{X},t_0\right)\right)$. This is the reason that, in contrast to fluid mechanics, in solid mechanics in which Lagrangian description is used the continuity equation (i.e. conservation of mass (64)) is not included in the set of fundamental field equations.

For a singular surface $\mathcal{S}_t$ which moves with the speed $c\mathbf{n}$ we can derive the jump condition. The procedure is similar to this used in the Lagrangian description. We have

$$\frac{d}{dt}\int_{\mathcal{P}_t}\rho dv=\int_{\mathcal{P}_t^+\cup\mathcal{P}_t^-}\frac{\partial\rho}{\partial t}dv+\oint_{\partial\mathcal{P}_t^+}\rho\mathbf{w}\cdot\mathbf{n}ds+\oint_{\partial\mathcal{P}_t^-}\rho\mathbf{w}\cdot\mathbf{n}ds, \tag{65}$$

where $\mathbf{w}\cdot\mathbf{n}=\mathbf{v}\cdot\mathbf{n}$ on material surfaces $\partial\mathcal{P}_t^+\cap\partial\mathcal{P}_t$ and $\partial\mathcal{P}_t^-\cap\partial\mathcal{P}_t$ and $\mathbf{w}\cdot\mathbf{n}=\pm c$ on the singular surface $\mathcal{S}_t\cap\partial\mathcal{P}_t^\pm$. The difference in sign appears again due to the difference in the orientation. As before we form a descending family of subsets and taking the limit of balance equations we obtain

$$\begin{aligned}
&\int_{\mathcal{S}_t\cap\mathcal{P}_t}\left[\rho^+\left(\mathbf{v}^+\cdot\mathbf{n}-c\right)-\rho^-\left(\mathbf{v}^-\cdot\mathbf{n}-c\right)\right]ds=0 \quad\Longrightarrow\\
&\Longrightarrow \quad [[\rho\left(\mathbf{v}\cdot\mathbf{n}-c\right)]]=0.
\end{aligned} \tag{66}$$

This Eulerian jump condition (continuity of mass through the singular surface) is the counterpart of the Lagrangian relation quoted in Table 3.

In the case of momentum balance, we have

$$\frac{d}{dt}\int_{\mathcal{P}_t}\rho\mathbf{v}dv=\oint_{\partial\mathcal{P}_t}\mathbf{T}\mathbf{n}ds+\int_{\mathcal{P}_t}\rho\mathbf{b}dv, \tag{67}$$

In order to find the relation between the tensor $\mathbf{T}$ and the Piola-Kirchhoff stress tensor $\mathbf{P}$ of the Lagrangian description one can use either the general relation (57) or transform directly the local momentum balance in a regular point

$$\begin{aligned}
\frac{\partial\left(\rho_0 J^{-1}J\mathbf{v}\right)}{\partial t} &= J\frac{\partial\left(\rho\mathbf{v}\right)}{\partial t}+\rho\mathbf{v}\frac{\partial J}{\partial t}=\bar{J}\left[\frac{\partial\left(\bar{\rho}\bar{\mathbf{v}}\right)}{\partial t}+\bar{\mathbf{v}}\cdot\operatorname{grad}\bar{\mathbf{v}}\right]+\bar{\rho}\bar{\mathbf{v}}\bar{J}\operatorname{div}\bar{\mathbf{v}}=\\
&= \bar{J}\left[\frac{\partial\left(\bar{\rho}\bar{\mathbf{v}}\right)}{\partial t}+\operatorname{div}\left(\bar{\rho}\bar{\mathbf{v}}\otimes\bar{\mathbf{v}}\right)\right]=\\
&= \bar{J}\operatorname{div}\left(\bar{J}^{-1}\bar{\mathbf{P}}\bar{\mathbf{F}}^T\right)+\rho_0 J^{-1}J\mathbf{b}=\bar{J}\left(\operatorname{div}\bar{\mathbf{T}}+\bar{\rho}\bar{\mathbf{b}}\right),
\end{aligned}$$

i.e. skipping the bar for Eulerian quantities

$$\frac{\partial\left(\rho\mathbf{v}\right)}{\partial t}+\operatorname{div}\left(\rho\mathbf{v}\otimes\mathbf{v}-\mathbf{T}\right)=\rho\mathbf{b}, \quad \mathbf{T}=J^{-1}\mathbf{P}\mathbf{F}^T. \tag{68}$$

This is the local form of momentum conservation law. $\mathbf{T}$ is called the *Cauchy stress tensor*.

Inspection of the above relations shows that the transformation from Lagrangian to Eulerian description in regular points requires the following transformation of operators

$$\frac{\partial}{\partial t}\rightarrow\frac{\partial}{\partial t}+\mathbf{v}\cdot\operatorname{grad}, \quad \operatorname{Grad}\rightarrow\bar{\mathbf{F}}^T\operatorname{grad}. \tag{69}$$

The time derivative appearing in the above relations is called *material* and it is sometimes denoted by a dot on top of the symbol.

In Table 4 we have collected the balance equations in Eulerian description.

We complete the considerations of balance equations with a few remarks concerning particular cases of jump conditions (conditions on a singular surface).

We have already mentioned that a singular surface which is *material*, i.e. a surface of contact between two bodies does not move in the Lagrangian description ($U=0$) and it means that $c=\mathbf{v}\cdot\mathbf{n}$ in the Eulerian description. The jump of the mass density can be in such cases arbitrary and the remaining conditions have the following form

$$[[\mathbf{T}]]\,\mathbf{n}=0, \quad [[\mathbf{q}]]\cdot\mathbf{n}=0, \quad [[\mathbf{h}]]\cdot\mathbf{n}=0. \tag{70}$$

We have used the fact that on material surfaces not only the normal component of velocity $\mathbf{v}\cdot\mathbf{n}$ but the full velocity $\mathbf{v}$ is continuous. This is the consequence of the Hadamard condition (51).

Table 4: *Balance equations of thermomechanical model in Eulerian description*
Left – regular points, right – points of a singular surface

$\frac{\partial\rho}{\partial t}+\operatorname{div}(\rho\mathbf{v})=0, \quad \rho=\rho_0\bar{J}^{-1}$.	$[[\rho(\mathbf{v}\cdot\mathbf{n}-c)]]=0$.
$\frac{\partial(\rho\mathbf{v})}{\partial t}+\operatorname{div}(\rho\mathbf{v}\otimes\mathbf{v}-\mathbf{T})=\rho\mathbf{b}, \quad \mathbf{T}=\bar{J}^{-1}\bar{\mathbf{P}}\bar{\mathbf{F}}^T$.	$[[\rho(\mathbf{v}\cdot\mathbf{n}-c)\,\mathbf{v}]]-[[\mathbf{T}]]\,\mathbf{n}=0$.
$\mathbf{T}=\mathbf{T}^T$.	identity
$\frac{\partial}{\partial t}\left[\rho\left(\varepsilon+\frac{1}{2}v^2\right)\right]+\operatorname{div}\left(\rho\left(\varepsilon+\frac{1}{2}v^2\right)\mathbf{v}+\mathbf{q}-\mathbf{T}\mathbf{v}\right)=$ $=\rho\mathbf{v}\cdot\mathbf{b}+\rho r, \quad \mathbf{q}=\bar{J}^{-1}\bar{\mathbf{F}}\bar{\mathbf{Q}}$.	$\left[\left[\rho(\mathbf{v}\cdot\mathbf{n}-c)\left(\varepsilon+\frac{1}{2}v^2\right)\right]\right]+$ $+[[\mathbf{q}-\mathbf{T}\mathbf{v}]]\cdot\mathbf{n}=0$.
$\frac{\partial(\rho\eta)}{\partial t}+\operatorname{div}\mathbf{h}=\rho s+\hat{\eta}_t, \quad \hat{\eta}_t=\bar{J}^{-1}\hat{\eta}$.	$[[\rho(\mathbf{v}\cdot\mathbf{n}-c)\,\eta]]+[[\mathbf{h}]]\cdot\mathbf{n}=0$.

The first two relations play an important role in the formulation of boundary conditions for continua. The first one – continuity of tractions, means that we may prescribe forces on the boundary and these will be transmitted into the body by the stress vector $\mathbf{Tn}$. The second one – continuity of the heat flux is used as one of the boundary conditions in the theory of heat conduction. The second two conditions have the great importance for properties of the so-called *ideal walls* which are a part of the second law of thermodynamics. We discuss them further.

On surfaces carrying jump of velocity, we can write the above conditions in the alternative form

$$\begin{aligned} &m := \rho^+\left(c-\mathbf{v}^+\cdot\mathbf{n}\right)\equiv\rho^-\left(c-\mathbf{v}^-\cdot\mathbf{n}\right), \\ &m\,[[\mathbf{v}]]+[[\mathbf{T}]]\cdot\mathbf{n}=0, \qquad (71) \\ &m\left[\left[\varepsilon+\frac{1}{2}v^2\right]\right]-[[\mathbf{q}-\mathbf{T}\mathbf{v}]]\cdot\mathbf{n}=0. \end{aligned}$$

These equations for the stress tensor reduced to pressure $\mathbf{T}=-p\mathbf{1}$, which is characteristic for gas dynamics, are called *Rankine-Hugoniot conditions* and they form a foundation for the theory of shock waves in gases. The coefficient m – the mass transport coefficient is related to the *Mach number.*

We close this lecture with a few remarks on the formulation of field equations for a particular material which frequently appears in engineering applications. *Thermoelasticity* is the theory which describes changes of two fields: the function of motion $\mathbf{f}$ describing time dependent large deformations of the material and the temperature T responsible for the energy transfer in the material in the form of heat conduction. Further we discuss in details the notion of temperature. For the purpose of this example we do not go into any details concerning this field. In the Lagrangian description we do not need to consider the mass density ρ_0 because, according to the mass conservation, it does not change in time. In the case of homogeneous materials it is even constant.

For the fields $\{\mathbf{f}, T\}$ as functions of variables $(\mathbf{X}, t) \in \mathcal{B}_0 \times \mathcal{T}$ we must formulate *field equations*. As we require from the model that it satisfies the conservation laws of momentum, moment of momentum and energy, these laws are chosen as the foundation for the construction of field equations

$$\rho_0 \frac{\partial^2 \mathbf{f}}{\partial t^2} = \operatorname{Div} \mathbf{P} + \rho_0 \mathbf{b}, \quad \rho_0 \frac{\partial \varepsilon}{\partial t} + \operatorname{Div} \mathbf{Q} = \mathbf{P} \cdot \operatorname{Grad} \frac{\partial \mathbf{f}}{\partial t} + \rho r. \tag{72}$$

In addition we have the restriction $\mathbf{P} \left(\operatorname{Grad} \mathbf{f}\right)^T = \left(\operatorname{Grad} \mathbf{f}\right) \mathbf{P}^T$. The energy conservation law was reduced by means of the momentum conservation. Consequently, we obtain the balance energy for the internal energy ε which does not have the form of the conservation law (the so-called divergent form). There appears a source term which describes the power of stresses $\mathbf{P} \cdot \operatorname{Grad} \frac{\partial \mathbf{f}}{\partial t}$.

Equations (72) are not yet field equations. We must perform the so-called *closure* which defines the Piola-Kirchhoff stress tensor $\mathbf{P}$, the internal energy ε, and the heat flux $\mathbf{Q}$ in terms of the fields $\mathbf{f}$, T. This is done in the form of *constitutive relations* which limit the applicability of the model to a particular class of materials. For thermoelastic materials it is *assumed* that constitutive relations have the following form

$$\begin{aligned} \mathbf{P} &= \mathbf{P}\left(\mathbf{v}, \mathbf{F}, T, \mathbf{G}\right), \quad \varepsilon = \varepsilon\left(\mathbf{v}, \mathbf{F}, T, \mathbf{G}\right), \\ \mathbf{Q} &= \mathbf{Q}\left(\mathbf{v}, \mathbf{F}, T, \mathbf{G}\right), \quad \mathbf{G} := \operatorname{Grad} T, \end{aligned} \tag{73}$$

These are the simplest possible relations which do not yield a triviality of the model. They possess a few features characteristic for such a construction

> i/ among variables we have the first gradients of the fields $\mathbf{F} = \operatorname{Grad} \mathbf{f}$, $\mathbf{G} = \operatorname{Grad} T$ which account for the influence of a neighborhood of a point $\mathbf{X} \in \mathcal{B}_0$ on the properties of the material at this point,
>
> ii/ they do not contain a dependence on the function of motion $\mathbf{f}$. This is related to the *principle of material objectivity* which we discuss further; as a mater of fact the same principle eliminates a dependence on the velocity $\mathbf{v}$ as well,
>
> iii/ the constitutive relations are *functions* and not functionals which would be able to account for the dependence on the past history of processes. Such functionals would appear, for instance, in cases in which at least one of the constitutive quantities $\mathbf{P}$,ε, $\mathbf{Q}$ would be given by an *evolution equation*. We discuss such classes of materials (e.g. viscoelastic solids) further in this course.

The constitutive relations must be further restricted by, for example, a condition of thermodynamical admissibility. This will be the subject of the next lecture. However, if we are lucky we may formulate the above relations on the basis of experiments and then no further restrictions would be needed. This does not seem to be the case ever. At least some hints from a general model how to conduct experiments are always needed and this is the motivation for the thermodynamical construction of models.

We close this example with an alternative formulation of the thermoelastic model which is more convenient for thermodynamical considerations. It has been mentioned already that the field $\mathbf{f}$ can be replaced by two fields $\mathbf{F}, \mathbf{v}$ and then we have to require certain integrability conditions in order to be able to integrate $\mathbf{F}$ and $\mathbf{v}$ *a posteriori* in order to find the motion $\mathbf{f}$. The model in this setting has the following form

i/ fields $\{\mathbf{v}, \mathbf{F}, T\}$

ii/ conservation laws

$$\begin{aligned} \rho_0 \frac{\partial \mathbf{v}}{\partial t} - \operatorname{Div} \mathbf{P} &= \rho_0 \mathbf{b}, \quad \frac{\partial \mathbf{F}}{\partial t} - \operatorname{Grad} \mathbf{v} = 0, \\ \rho_0 \frac{\partial \varepsilon}{\partial t} + \operatorname{Div} \mathbf{Q} &= \mathbf{P} \cdot \operatorname{Grad} \mathbf{v} + \rho_0 r, \end{aligned} \tag{74}$$

iii/ constitutive relations

$$\mathbf{P} = \mathbf{P}(\mathbf{v}, \mathbf{F}, T, \mathbf{G}), \quad \varepsilon = \varepsilon(\mathbf{v}, \mathbf{F}, T, \mathbf{G}), \quad \mathbf{Q} = \mathbf{Q}(\mathbf{v}, \mathbf{F}, T, \mathbf{G}). \tag{75}$$

This problem still contains a dependence on the temperature gradient $\mathbf{G}$ which yields the set of the second order equations. This can be changed as well by exchanging the role of $\mathbf{G}$ and $\mathbf{Q}$. We demonstrate further this way of constructing field equations which is known as the *extended thermodynamics.*

Lecture 3: Second law of thermodynamics: entropy inequality, thermodynamic admissibility

Since a long time it has been clear to scientists that macroscopic processes are **irreversible**. This means that there exists no macroscopic systems which, when disturbed, return spontaneously (i.e. without any influence of the external world) to their initial state. Since XIXth century there exist models of physical systems in which macroscopic properties of processes are being derived from microscopic description, in most cases stemming from the classical mechanics of discrete systems. It has been observed that such a construction of models yields the contradiction. Microscopic mechanical models are reversible, i.e. all processes possible for a given choice of the time variable are also possible after a reversal of time. This contradicts the macroscopic irreversibility. It can be shown rigorously, for example, that equations of dynamics of many interacting particles lead to solutions in which after a sufficiently long time the system *spontaneously* returns to an arbitrarily small neighborhood of its initial state. This time is called the *recurrence time* of Poincare's cycle. One can estimate this time and for large systems containing, say 10^{23} particles (the order of magnitude of the Avogadro number), the recurrence time exceeds the time of existence of the Universe by many orders of magnitude.

The above described properties of large systems led to vehement discussions among physicists of the end of XIXth century and the beginning of XXth century. L. Boltzmann proposed a model of gases – the so-called **kinetic theory**, in which the microscopic model was reversible (noninteracting particles flying free in space and exchanging momentum and energy in elastic collisions) and the macroscopic result described by the so-called H-Theorem, was irreversible. This result has been opposed by many physicists who were using, for instance, the argument based on the Poincare cycle, that the model must contain some flaws. On Zermelo's criticism pointing out the existence of the recurrence time Boltzmann supposedly replied: "You should wait that long!" However for Boltzmann the result of this discussion has a tragic end. He committed suicide.

Before we present the modern version of the principle of macroscopic irreversibility we discuss briefly two simple models motivating this principle on the basis of microscopic considerations.

The first example has been constructed by P. and T. Ehrenfest in 1907 and it is called "Dog and flea model" or "urn model". We present the idea of this model in Figure 6.

For urn model we consider the dynamics of two urns containing N balls labelled from 1 to N. For simplicity, let us assume that initially all balls are in the urn (1) and the urn (2) is empty. The motion of balls is given by random drawing a number between 1 and N and then moving a ball with this number from one urn to the other. In the dog-flea model the motion occurs because fleas are jumping from one dog to the other looking for better breeding conditions. It is obvious that the "flux" must start from the urn (1) in direction of urn (2). It may happen that we draw the same number again and the ball then returns to the urn (1). However, for a very large N, say $N = 10^{23}$, it is much more probable that we get a different number and another ball moves from the urn (1) to the urn (2). Hence, despite small fluctuations, an average flux of balls has a definite direction until we reach the macrostate in which both urns have almost equal number of balls $N/2$. Although it cannot be excluded that we draw the sequence of numbers which would make the urn (2) empty again, it is clear that such a process is extremely exceptional. This is connected to the fact that the state with all balls in one urn is only one while the state of equally distributed balls may appear in $W = 2^N$ variations if we ignore the numbering of balls. It is said that the equal distribution between two urns yields the *maximum of the entropy* $S = \ln W$. We shall return to this definition later.

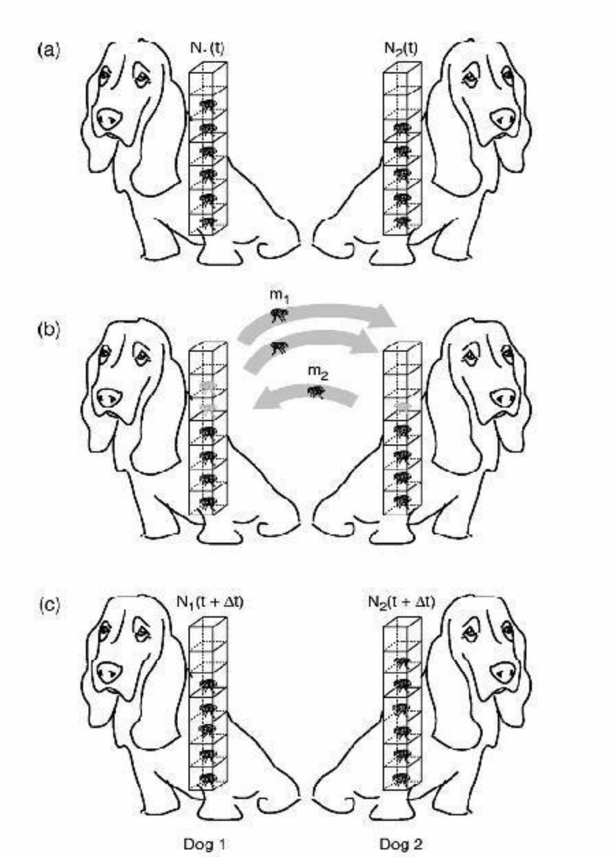

Fig. 6: *Ehrenfest's dog-flea (urn) model (1907)*
a/ state of the system at time t; b/ a particular microtrajectory to which two fleas jump from the dog on the left and one flea jumps from the dog on the right; c/ occupancies of the dogs at time $t + \Delta t$
(K. Gosh at al., Am. J. Phys. 74(2), 2006)

Let us note that the above analysis assumes a very large number of possible states of the system. It is still a matter of dispute how small a system may be in order to admit a macroscopic modelling. For instance, the diffusion process of DNA particles within cells (translation through nanopores) is described by a variation between a few hundred states. Still some macroscopic thermodynamical arguments are applied to such systems.

We proceed to present an ingenious model of Marc Kac which illustrates the problem of irreversibility of Boltzmann's kinetic theory. Simple calculations presented below demonstrate that the irreversibility results from a certain assumption on randomness of the system ("**Stoßzahlansatz**") and this is, of course, related to the large number properties of the above presented dog-flea model.

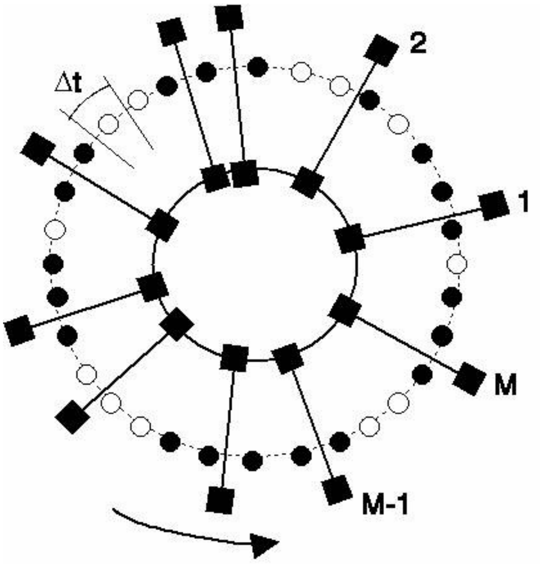

Fig.7: *Irreversibility and Stoßzahlansatz – model of M. Kac (1956).*

The system consists of N white or black circles distributed in the equal distance Δt on the circumference of a large circle (Fig. 7). Dynamics of the system is introduced by the rotation of the wheel with the set, S, of M spokes distributed at random in different middle positions between small circles. Whenever the wheel rotates on the angle Δt the color of the small circle through which the spoke passes changes the color. We assume that both N and M are very large but simultaneously $M \ll N$. The instantaneous number of white and black circles is described by the following "equation of motion" with the discrete time

$$N_w\left(t+\Delta t\right)=N_w\left(t\right)+N_b\left(S,t\right)-N_w\left(S,t\right), \tag{76}$$

with

$$\forall_t\ N_w\left(t\right)+N_b\left(t\right)=N, \quad N_w\left(S,t\right)+N_b\left(S,t\right)=M. \tag{77}$$

Certainly, $N_b\left(S,t\right)$ denotes the number of black circles which change color in the step $t\rightarrow t+\Delta t$, and $N_w\left(S,t\right)$ the number of white circles which change color in this step.

Equation (76) constitutes the counterpart of the *Liouville equation* for N particles and describes reversible processes on the microlevel: after two full rotations of the wheel the systems returns to its initial state. This means that the recurrence time of Poincare's cycle is equal for this model to $t_P=2N\Delta t$.

The change in the surplus of white circles at the instant of time $t+\Delta t$ is, according to the equation of motion, given by the following equation

$$\left[N_w\left(t+\Delta t\right)-N_b\left(t+\Delta t\right)\right]=\left[N_w\left(t\right)-N_b\left(t\right)\right]-2\left[N_w\left(S,t\right)-N_b\left(S,t\right)\right]. \tag{78}$$

Now, we make the *reasonable assumption* that, owing to the randomness of the set S, after sufficiently many time steps the black and white circles will be regularly distributed, i.e.

$$N_w\left(S,t\right)=\frac{M}{N}N_w\left(t\right), \quad N_b\left(S,t\right)=\frac{M}{N}N_b\left(t\right). \tag{79}$$

Substitution of this assumption in (78) yields the following difference equation

$$\left[N_w\left(t+\Delta t\right)-N_b\left(t+\Delta t\right)\right]=\left(1-2\frac{M}{N}\right)\left[N_w\left(t\right)-N_b\left(t\right)\right]. \tag{80}$$

This equation can be solved immediately and we obtain

$$\left[N_w\left(t\right)-N_b\left(t\right)\right]=N\left(1-2\frac{M}{N}\right)^t. \tag{81}$$

Let us assume that the initial state of the system was $N_w\left(t=0\right)=N$, $N_b\left(t=0\right)=0$. Then it follows

$$\frac{N_w\left(t\right)}{N}=\frac{1}{2}+\frac{1}{2}\left(1-2\frac{M}{N}\right)^t. \tag{82}$$

Consequently

$$\frac{N_w\left(t=0\right)}{N}=1,\quad \lim_{t\to\infty}\frac{N_w\left(t\right)}{N}=\frac{1}{2}. \tag{83}$$

The most important property of the solution (82) is its irreversibility. It can be easily checked that, independently of the initial state, we obtain always the same asymptotic end state with equal number of white and black circles. There is no trace left of the microscopical periodicity of processes. The reason for this behavior is hidden in the only assumption which we made (79) which corresponds to the Stoßzahlansatz of Boltzmann's theory. We see that conditions under which the solution (82) makes sense are the randomness of the set S and long, but not too long times of observations: $1\ll t\ll t_P$.

The above examples motivate the following formulation of macroscopic models. Constitutive equations which define a particular class of materials should have such a form that solutions of field equations will be not invariant with respect to the time reversal (**irreversibility**) and, secondly, that disturbances of finite time duration should produce solutions which relax (i.e. possess a time limit in infinity) to an **equilibrium state** characteristic for a given class of materials and for given boundary conditions.

This program is usually realized by means of an additional scalar inequality which constraints the class of solutions. Its form has been varying since XIXth century. Clausius and Duhem proposed the first continuous version of such an inequality and this inequality has been very intensively investigated in the 1960th. It has been found that results of classical thermostatics obtained by Gibbs, Caratheodory and many others follow as a particular case (equilibrium properties) from this inequality. It has been also proved that the linear nonequilibrium thermodynamics proposed by Onsager is a particular case of this inequality for single component systems. Simultaneously, it has been shown that the Clausius-Duhem inequality is inadequate in description of multicomponent systems as well as for some nonmechanical (e.g. electromagnetic) fields. The extension of this inequality has been proposed in 1968 by I. Müller. It is usually called the entropy inequality and this seems to be the most general formulation of the continuous second law of thermodynamics which has been proposed up to now.

There is an alternative approach to the formulation of the second law of thermodynamics which stems from the classical XIXth century works of S. Carnot and F. Reech on *cyclic processes.* This notion has been extended and applied to nonequilibrium thermodynamics by J. Serrin and M. Šilhavý and then summarized by C. Truesdell and S. Bharatha.

We discuss further in this course various applications of the entropy inequality. We begin with a formulation appropriate for all models which we discuss further and, for the purpose of this lecture we assume that the notion of temperature is known. However, we return in the next lecture to the discussion of notions of empirical and absolute temperatures and various problems which they may create, particularly for multicomponent systems.

The strategy of continuum thermodynamics in construction of macroscopic models relies on the assumption that solutions of the field equations identically satisfy the **second law of thermodynamics** called also the **entropy principle**. This law consists of four parts. We formulate them in Lagrangian description and then, when needed, change variables to Eulerian description.

Entropy principle:

i/ There exist a nontrivial entropy density function η and the entropy flux $\mathbf{H}$ which are both dependent on the same constitutive variables as other constitutive functions of the model.

ii/ The entropy density satisfies the balance equation whose form in regular points is as follows

$$\rho_0 \frac{\partial \eta}{\partial t} + \operatorname{Div} \mathbf{H} = \hat{\eta}, \tag{84}$$

where $\hat{\eta}$ denotes the entropy source.

iii/ The entropy source is nonnegative for all *solutions* of field equations, i.e. for all *thermodynamic processes.* Consequently, the following inequality holds

$$\forall_{\text{all thermodynamic processes}} \rho_0 \frac{\partial \eta}{\partial t} + \operatorname{Div} \mathbf{H} \geq 0. \tag{85}$$

iv/ There exist *ideal walls* on which there is no entropy production, i.e.

$$[[\mathbf{H} \cdot \mathbf{N}]] + [[\eta]]\, \rho_0 U = 0, \tag{86}$$

these walls are assumed to be material, i.e. $U = 0$.

The last condition is modified for multicomponent systems and concerns the existence of semipermeable membranes. We discuss this notion further in this course.

I-Shih Liu has proposed in 1973 a method of exploitation of the inequality (84) which reminds the classical method of Lagrange multipliers in mechanics[5]. Namely, instead of this inequality restricting the *solutions of field equations* we consider solutions of an extended inequality which should hold for *all fields.* This can be done if we consider field equations as constraints on solutions of the entropy inequality.

Before we formulate Liu's Theorem we again consider a simple example of the thermoelastic material which has been introduced in the previous lecture. The set of governing equations is as follows (compare (74), (75))

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[5] It has been pointed out by R. A. Hauser and N. P. Kirchner (*A historical note on the entropy principle of Müller and Liu, Cont. Mech. Thermodyn.,* **14**, 2, 2002) that the result of I-Shih Liu is a particular case of Farkas-Minkowski Theorem known in the duality theory of linear programming.

i/ fields $\{\mathbf{v},\mathbf{F},T\}$
ii/ conservation laws

$$\begin{aligned}\rho_0\frac{\partial\mathbf{v}}{\partial t}-\operatorname{Div}\mathbf{P}&=0,\quad \frac{\partial\mathbf{F}}{\partial t}-\operatorname{Grad}\mathbf{v}=0,\\ \rho_0\frac{\partial\varepsilon}{\partial t}+\operatorname{Div}\mathbf{Q}&=\mathbf{P}\cdot\operatorname{Grad}\mathbf{v},\end{aligned}\tag{87}$$

iii/ constitutive relations

$$\mathbf{P}=\mathbf{P}\left(\mathbf{F},T,\mathbf{G}\right),\quad \varepsilon=\varepsilon\left(\mathbf{F},T,\mathbf{G}\right),\quad \mathbf{Q}=\mathbf{Q}\left(\mathbf{F},T,\mathbf{G}\right).\tag{88}$$

We have left out the constitutive dependence on the velocity $\mathbf{v}$. Also body forces $\mathbf{b}$ and radiation r have been assumed to be zero. This assumption follows from the fact that the entropy inequality should hold for arbitrary external sources. It means that constitutive restrictions which follow from the second law should be independent of such sources. Consequently, restrictions which we obtain without sources must be identical as these when those sources are present. This argument is different from the argument used, for example, in a series of papers of B. D. Coleman and his followers.

The above problem should satisfy the entropy inequality of the following form

$$\forall_{\text{all thermodynamic processes}}\rho_0\frac{\partial\eta}{\partial t}+\operatorname{Div}\mathbf{H}\geq 0,\quad \eta=\eta\left(\mathbf{F},T,\mathbf{G}\right),\quad \mathbf{H}=\mathbf{H}\left(\mathbf{F},T,\mathbf{G}\right).\tag{89}$$

Using the chain rule of differentiation, we can write this inequality in the explicit form

$$\begin{aligned}&\forall_{\text{all fields}}\rho_0\left[\frac{\partial\eta}{\partial F_{kK}}\frac{\partial F_{kK}}{\partial t}+\frac{\partial\eta}{\partial T}\frac{\partial T}{\partial t}+\frac{\partial\eta}{\partial G_K}\frac{\partial G_K}{\partial t}\right]+\\ &+\frac{\partial H_K}{\partial F_{lL}}\frac{\partial F_{lL}}{\partial X_K}+\frac{\partial H_K}{\partial T}G_K+\frac{\partial H_K}{\partial G_L}\frac{\partial G_L}{\partial X_K}\geq 0\end{aligned}\tag{90}$$

where

$$\begin{aligned}\frac{\partial F_{kK}}{\partial t}&=\frac{\partial v_k}{\partial X_K},\\ \frac{\partial T}{\partial t}&=\left(\frac{\partial\varepsilon}{\partial T}\right)^{-1}\left[-\frac{\partial\varepsilon}{\partial F_{kK}}\frac{\partial F_{kK}}{\partial t}-\frac{\partial\varepsilon}{\partial G_K}\frac{\partial G_K}{\partial t}-\right.\\ &\left.-\frac{1}{\rho_0}\left(\frac{\partial Q_K}{\partial F_{lL}}\frac{\partial F_{lL}}{\partial X_K}+\frac{\partial Q_K}{\partial T}G_K+\frac{\partial Q_K}{\partial G_L}\frac{\partial G_L}{\partial X_K}-P_{kK}\frac{\partial v_k}{\partial X_K}\right)\right],\end{aligned}\tag{91}$$

and these derivatives are eliminated from (90).

Clearly, this inequality is linear with respect to the following derivatives

$$\left\{\frac{\partial F_{kK}}{\partial t},\frac{\partial G_K}{\partial t},\frac{\partial F_{lL}}{\partial X_K},\frac{\partial G_L}{\partial X_K},\frac{\partial v_k}{\partial X_K}\right\}.\tag{92}$$

As the inequality must hold for **ALL** fields – we have eliminated constraints imposed by field equations (note that linearity of the momentum equation with respect to the acceleration $\frac{\partial v_k}{\partial t}$ does not impose any restrictions because the acceleration does not appear in the entropy inequality) coefficients of the above derivatives have to vanish identically. Otherwise we could choose the fields in such a way that one negative term would dominate all others and the inequality would be violated. Hence, we obtain

$$\begin{aligned}
\frac{\partial \eta}{\partial F_{kK}} - \Lambda^{\varepsilon}\frac{\partial \varepsilon}{\partial F_{kK}} + \frac{1}{\rho_0}P_{kK} &= 0, \quad \Lambda^{\varepsilon} := \frac{\partial \eta}{\partial T}\left(\frac{\partial \varepsilon}{\partial T}\right)^{-1} \\
\frac{\partial \eta}{\partial G_K} - \Lambda^{\varepsilon}\frac{\partial \varepsilon}{\partial G_K} &= 0, \\
\frac{\partial H_{(K}}{\partial F_{lL)}} - \Lambda^{\varepsilon}\frac{\partial Q_{(K}}{\partial F_{lL)}} &= 0, \\
\frac{\partial H_{(K}}{\partial G_{L)}} - \Lambda^{\varepsilon}\frac{\partial Q_{(K}}{\partial G_{L)}} &= 0,
\end{aligned} \tag{93}$$

where the parenthesis denotes the symmetric part, e.g. $\frac{\partial Q_{(K}}{\partial G_{L)}} = \frac{1}{2}\left(\frac{\partial Q_K}{\partial G_L} + \frac{\partial Q_L}{\partial G_K}\right)$. We have made the assumption $\frac{\partial \varepsilon}{\partial T} \neq 0$ which is physically justified as this derivative defines the specific heat in thermodynamical equilibrium.

There remains the **residual inequality** which does not contain linear contributions anymore

$$\mathcal{D} := \left(\frac{\partial H_K}{\partial T} - \Lambda^{\varepsilon}\frac{\partial Q_K}{\partial T}\right) G_K \geq 0. \tag{94}$$

The exploitation of identities (93) requires certain additional techniques which we present in the next lecture. They are either based on a simplifying assumption that the material is isotropic or, in more general cases, one has to use a Theorem proved by I-Shih Liu in 1996 on the relation between the entropy flux and heat flux[6]. Under rather general conditions this Theorem states that in our case identities $(93)_{3,4}$ yield

$$H_K = \Lambda^{\varepsilon} Q_K. \tag{95}$$

Then the substitution of the above relation in $(93)_{3,4}$ yields

$$\Lambda^{\varepsilon} = \Lambda^{\varepsilon}(T). \tag{96}$$

Let us consider a contact surface between a poroelastic material and an ideal gas. For the latter we have the relation $\mathbf{H} = (1/T)\,\mathbf{Q}$ which we motivate in a further lecture by microscopic (kinetic) considerations. Bearing the continuity of fluxes on the surface of contact in mind (jump conditions and the last part of the second law of thermodynamics) we obtain

$$[[\mathbf{H}]] \cdot \mathbf{N} = 0, \quad [[\mathbf{Q}]] \cdot \mathbf{N} = 0 \quad \Longrightarrow \quad \Lambda^{\varepsilon} = \frac{1}{T}. \tag{97}$$

Consequently, we obtain the classical Fourier result for fluxes

$$\mathbf{H} = \frac{1}{T}\mathbf{Q}. \tag{98}$$

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[6] I-Shih Liu; *On entropy flux – heat flux relation in thermodynamics with Lagrange multipliers, Cont. Mech. Thermodyn.*, **7**, 247-256, 1996.

Substitution in the definition of Λ^{ε} $(93)_1$ leads to the classical thermodynamical identity

$$\frac{\partial \varepsilon}{\partial T} - T\frac{\partial \eta}{\partial T} = 0. \tag{99}$$

It is useful to define the following function

$$\psi = \varepsilon - T\eta. \tag{100}$$

Then differentiation with respect to the temperature T yields immediately

$$\eta = -\frac{\partial \psi}{\partial T}, \quad \varepsilon = \psi - T\frac{\partial \psi}{\partial T}, \quad \psi = \psi\left(T, \mathbf{F}\right), \tag{101}$$

where the identity $(93)_2$ has been exploited. The function ψ is called the *Helmholtz free energy.* If we use it in $(93)_1$ we obtain

$$\mathbf{P} = \rho_0 \frac{\partial \psi}{\partial \mathbf{F}}. \tag{102}$$

Hence, if the constitutive relation for the Helmholtz free energy $\psi = \psi\left(T, \mathbf{F}\right)$ is known it determines constitutive relations for $\varepsilon, \eta, \mathbf{P}$. This is one of the main results of the second law of thermodynamics: it yields the existence of *thermodynamical potentials* which reduce the number of required constitutive relations.

By means of the above results we can immediately show that the following differential relation holds

$$d\eta = \frac{1}{T}\left(d\varepsilon - \frac{1}{\rho_0}\mathbf{P}\cdot \mathbf{dF}\right). \tag{103}$$

In classical thermodynamics this relation is called the *Gibbs equation* and it is often mistakenly called the second law of thermodynamics. Obviously, it yields relations (99) and (102). However, it does not contain the residual inequality (94) which also follows from the second law. In other words, Gibbs equation cannot determine the *dissipation* $\mathcal{D}$ in the system. Bearing the above results in mind we can write the dissipation in the following form

$$\mathcal{D} = -\frac{1}{T^2}\mathbf{Q}\cdot \mathbf{G} \geq 0. \tag{104}$$

This is, of course, the requirement that heat cannot flow from colder to hotter regions. If we assume the linear Fourier law for heat conduction we obtain the classical result for the heat conductivity

$$\mathbf{Q} = -K\mathbf{G} \quad \Longrightarrow \quad K \geq 0. \tag{105}$$

This is related to the so-called stability of the thermodynamical equilibrium. Namely, we define the *thermodynamical equilibrium* as a state in which the dissipation $\mathcal{D}$ vanishes. In our case it means that the temperature gradient in equilibrium must be zero. Hence, all isothermal processes $T = const$ of arbitrary large deformations contain only equilibrium states, i.e. these are *equilibrium processes.* Simultaneously, the inequality (104) shows that equilibrium states are states of *minimum* of the dissipation function. Consequently the following condition must hold

$$\forall_{\mathbf{Z}} \quad \mathbf{Z} \cdot \frac{\partial^2 \mathcal{D}}{\partial \mathbf{G} \partial \mathbf{G}} \mathbf{Z} > 0, \tag{106}$$

i.e. the Hessian matrix of $\mathcal{D}$ is positive definite. This is the so-called *stability condition of equilibrium.*

The above results show how powerful is the entropy inequality. However, we can essentially improve the method of derivation of these results. Instead of directly eliminating some derivatives by means of field equations we can use the I-Shih Liu Theorem on the existence of Lagrange multipliers which help to eliminate the constraints imposed by field equations on the entropy inequality.

Inspection of the above derivation shows that we are solving an *algebraic* problem. Constitutive relations and the chain rule of differentiation yield the entropy inequality whose part is a linear function of some derivatives, in our example listed in (92) and a nonlinear part which leads to the residual inequality. If we eliminate restrictions imposed by field equations we have to solve an inequality for *arbitrary independent* linear contributions.

We formulate the general problem in the following abstract way.

We construct a continuous model for fields which form an n-dimensional vector $\mathbf{w} \equiv \{w_\gamma\}_{\gamma=1}^{n} \in \mathcal{V}^n$. The set of field equations for $\mathbf{w}$ is of the following form

$$\frac{\partial F_{0\gamma}}{\partial t} + \frac{\partial F_{K\gamma}}{\partial X_K} = \hat{f}_\gamma, \quad \{F_{0\gamma}\}_{\gamma=1}^{n} \in \mathcal{V}^n, \quad \{F_{K\gamma}\}_{\gamma=1}^{n} \in \mathcal{V}^n, K = 1, 2, 3, \quad \hat{f}_\gamma \in \mathcal{V}^n, \tag{107}$$

where the following differentiable constitutive relations are fulfilled

$$F_{0\gamma} = F_{0\gamma}(\mathfrak{w}), \quad F_{K\gamma} = F_{K\gamma}(\mathfrak{w}), \quad \hat{f}_\gamma = \hat{f}_\gamma(\mathfrak{w}), \quad \mathfrak{w} \in \mathcal{V}^N. \tag{108}$$

The choice of constitutive variables $\mathfrak{w}$ defines the class of materials to be described. The constitutive relations (108) must be such that solutions of field equations identically satisfy the entropy inequality

$$\rho_0 \frac{\partial \eta}{\partial t} + \frac{\partial H_K}{\partial X_K} \geq 0, \quad \eta = \eta(\mathfrak{w}), \quad H_K = H_K(\mathfrak{w}). \tag{109}$$

Obviously the constitutive variables $\mathfrak{w}$ may contain both fields $\mathbf{w}$ as well as their various temporal and spatial derivatives.

Let us introduce the following notation

$$\mathfrak{a} = \left\{ \rho_0 \frac{\partial \eta}{\partial \mathfrak{w}_1}, ..., \rho_0 \frac{\partial \eta}{\partial \mathfrak{w}_N}, \frac{\partial H_1}{\partial \mathfrak{w}_1}, ..., \frac{\partial H_3}{\partial \mathfrak{w}_N} \right\} \in \Re^{4N}, \tag{110}$$

$$\mathfrak{X} = \left\{ \frac{\partial \mathfrak{w}_1}{\partial t}, ..., \frac{\partial \mathfrak{w}_N}{\partial t}, \frac{\partial \mathfrak{w}_1}{\partial X_1}, ..., \frac{\partial \mathfrak{w}_N}{\partial X_3} \right\}^T \in \Re^{4N}, \tag{111}$$

where $\mathfrak{w}_a, a = 1, ..., N$ are components of the vector $\mathfrak{w}$. Then the field equations can be written in the form

$$\mathsf{A}\mathfrak{X} - \hat{\mathbf{f}} = 0, \quad \hat{\mathbf{f}} \equiv \left\{ \hat{f}_\gamma \right\}_{\gamma=1}^{n} \tag{112}$$

where

$$\mathsf{A} = \begin{pmatrix} \frac{\partial F_{01}}{\partial \mathfrak{w}_1} & \frac{\partial F_{01}}{\partial \mathfrak{w}_2} & \dots & \frac{\partial F_{31}}{\partial \mathfrak{w}_N} \\ \frac{\partial F_{02}}{\partial \mathfrak{w}_1} & \frac{\partial F_{02}}{\partial \mathfrak{w}_2} & \dots & \frac{\partial F_{32}}{\partial \mathfrak{w}_N} \\ \vdots & \vdots & & \vdots \\ \frac{\partial F_{0n}}{\partial \mathfrak{w}_1} & \frac{\partial F_{0n}}{\partial \mathfrak{w}_2} & \dots & \frac{\partial F_{3n}}{\partial \mathfrak{w}_N} \end{pmatrix} \in \Re^n \times \Re^{4N}. \tag{113}$$

Then we can formulate the following Theorem:

Theorem (*I-Shih Liu: on the existence of Lagrange multipliers*). Let A be given by (113) and $\mathfrak{X}$ by (111), and

$$\mathsf{S} = \left\{ \mathfrak{X} \in \Re^{4N} \middle| \, \mathsf{A}\mathfrak{X} - \hat{\mathbf{f}} = 0 \right\} \neq \emptyset. \tag{114}$$

Then, the following conditions are equivalent:

$$\text{i/} \quad \forall \mathfrak{X} \in \mathsf{S} : \quad \mathfrak{a} \cdot \mathfrak{X} \geq 0, \tag{115}$$

where $\mathfrak{a}$ is given by (110),

$$\text{ii/} \quad \exists \boldsymbol{\Lambda} \in \Re^n, \boldsymbol{\Lambda} \neq \mathbf{0} \quad \forall \mathfrak{X} \in \Re^{4N} : \quad \mathfrak{a} \cdot \mathfrak{X} - \boldsymbol{\Lambda} \cdot \left(\mathsf{A}\mathfrak{X} - \hat{\mathbf{f}} \right) \geq 0, \tag{116}$$

$$\text{iii/} \quad \exists \boldsymbol{\Lambda} \in \Re^n, \boldsymbol{\Lambda} \neq \mathbf{0} : \quad \mathfrak{a} - \mathsf{A}^T \boldsymbol{\Lambda} = \mathbf{0}, \quad \boldsymbol{\Lambda} \cdot \hat{\mathbf{f}} \geq 0. \tag{117}$$

We prove the following implications

$$\text{i/} \Longleftarrow \text{ii/} \Longleftrightarrow \text{iii/} \Longleftarrow \text{i/}. \tag{118}$$

1. The implication ii/$\Longrightarrow$i/ is immediate.

2. We shall prove the equivalence of ii/ and iii/. The relation (116) can be written in the form

$$\forall \mathfrak{X} \in \Re^{4N} : \quad \left(\mathfrak{a} - \mathsf{A}^T \cdot \boldsymbol{\Lambda} \right) \cdot \mathfrak{X} + \boldsymbol{\Lambda} \cdot \hat{\mathbf{f}} \geq 0. \tag{119}$$

Since this inequality holds for arbitrary $\mathfrak{X}$, it follows necessarily that

$$\left(\mathfrak{a} - \mathsf{A}^T \cdot \boldsymbol{\Lambda} \right) = 0 \quad \Longrightarrow \quad \boldsymbol{\Lambda} \cdot \hat{\mathbf{f}} \geq 0. \tag{120}$$

3. It remains to prove the implication i/$\Longrightarrow$iii/. With this aim, we define the following sets:

$$\begin{aligned} \mathsf{H} &\equiv \left\{ \mathfrak{X} \in \Re^{4N} \middle| \, \mathfrak{a} \cdot \mathfrak{X} \geq 0 \right\}, \\ \mathsf{H}_0 &\equiv \left\{ \mathfrak{X} \in \Re^{4N} \middle| \, \mathfrak{a} \cdot \mathfrak{X} = 0 \right\}, \quad \mathsf{S}_0 \equiv \left\{ \mathfrak{X} \in \Re^{4N} \middle| \, \mathsf{A}\mathfrak{X} = 0 \right\}, \\ \mathsf{H}_0^{\perp} &\equiv \left\{ \mathfrak{Y} \in \Re^{4N} \middle| \, \forall \mathfrak{X} \in \mathsf{H}_0 : \mathfrak{Y} \cdot \mathfrak{X} = 0 \right\}, \\ \mathsf{S}_0^{\perp} &\equiv \left\{ \mathfrak{Y} \in \Re^{4N} \middle| \, \forall \mathfrak{X} \in \mathsf{S}_0 : \mathfrak{Y} \cdot \mathfrak{X} = 0 \right\}. \end{aligned} \tag{121}$$

To prove the assertion we show first that

$$\mathsf{H}_0^{\perp} \subset \mathsf{S}_0^{\perp}. \tag{122}$$

Let us first motivate the purpose of this relation. It is easy to see from definitions (121) that the set of derivatives of the entropy and entropy flux with respect to the constitutive variables $\mathfrak{w}$, i.e. the vector $\mathfrak{a}$ belongs to the subspace $\mathsf{H}_0^{\perp}$ because it is orthogonal to all vectors belonging to H_0. Consequently, if we prove (122) we can claim that this vector belong to $\mathsf{S}_0^{\perp}$. Simultaneously, we can introduce a special representation of such vectors based on the matrix A which has a physical bearing. Components of $\mathfrak{a}$ in this representation form the vector of Lagrange multipliers $\mathbf{\Lambda}$.

It is easy to notice that $\mathsf{H}_0, \mathsf{H}_0^{\perp}, \mathsf{S}_0^{\perp}$ are subspaces of $\Re^{4N}$. Simultaneously, i/ implies that $\mathsf{S} \subset \mathsf{H}$; we obtain $\mathsf{S}_0 \subset \mathsf{H}_0$.

Suppose that the above relation does not hold. Then

$$\exists \mathfrak{Y} \in \mathsf{S}_0 : \quad \mathfrak{a} \cdot \mathfrak{Y} \neq 0.$$

However, S_0 is the linear subspace of $\Re^{4N}$. Therefore

$$\forall a \in \Re : \quad a\mathfrak{Y} \in \mathsf{S}_0 \quad \Longrightarrow \quad \forall \mathfrak{Z} \in \mathsf{S} : \quad \mathfrak{Z} + a\mathfrak{Y} \in \mathsf{S}.$$

On the other hand

$$\mathfrak{a} \cdot (\mathfrak{Z} + a\mathfrak{Y}) = a\mathfrak{a} \cdot \mathfrak{Y} + \mathfrak{a} \cdot \mathfrak{Z}.$$

Hence

$$\exists a \in \Re : \quad a\mathfrak{a} \cdot \mathfrak{Y} \leq -\mathfrak{a} \cdot \mathfrak{Z} \quad \Longrightarrow \quad \mathfrak{Z} + a\mathfrak{Y} \notin \mathsf{H},$$

which is a contradiction. Hence, $\mathsf{S}_0 \subset \mathsf{H}_0$.

We proceed to prove the implication i/$\Longrightarrow$iii/. By definition, we have $\mathfrak{a} \in \mathsf{H}_0^{\perp}$ and consequently, $\mathfrak{a} \in \mathsf{S}_0^{\perp}$. Let us construct, from the matrix A, the sequence of vectors $\{\mathsf{A}_1, ..., \mathsf{A}_n\}$ whose coordinates coincide with the rows of A. Then

$$\forall 1 \leq \gamma \leq n : \quad \mathsf{A}_\gamma \in \mathsf{S}_0^{\perp}. \tag{123}$$

On the other hand, we have

$$\dim \mathsf{S}_0^{\perp} = \operatorname{rank} \mathsf{A}, \tag{124}$$

and, consequently, the vectors $\{\mathsf{A}_\gamma\}_{\gamma=1}^n$ span the space $\mathsf{S}_0^{\perp}$. It follows that

$$\exists \mathbf{\Lambda} \in \Re^n, \mathbf{\Lambda} \neq \mathbf{0} : \quad \mathfrak{a} = \sum_{\gamma=1}^{n} \mathsf{A}_\gamma \Lambda^\gamma = \mathsf{A}^T \mathbf{\Lambda}. \tag{125}$$

Finally,

$$\forall \mathfrak{X} \in \mathsf{S} : \quad \mathfrak{a} \cdot \mathfrak{X} = \left(\mathsf{A}^T \mathbf{\Lambda}\right) \cdot \mathfrak{X} = \mathbf{\Lambda} \cdot (\mathsf{A}\mathfrak{X}) = \mathbf{\Lambda} \cdot \hat{\mathbf{f}}; \tag{126}$$

since $\mathsf{S} \subset \mathsf{H}$, i.e. $\mathfrak{a} \cdot \mathfrak{X} \geq 0$, we obtain

$$\mathbf{\Lambda} \cdot \hat{\mathbf{f}} \geq 0, \tag{127}$$

which completes the proof.

For the example of thermoelastic materials the objects appearing in the above theorem have the following form

$$\begin{aligned}
&\mathbf{w} = \{\mathbf{v}, \mathbf{F}, T\} \in \mathcal{V}^{13}, \quad n = 13, \\
&\mathfrak{w} := \{\mathbf{v}, \mathbf{F}, T, \mathbf{G}\} \in \mathcal{V}^{16}, \quad N = 16, \\
&\{F_{0\gamma}\}_{\gamma=1}^{13} = \{\rho_0 v_k, F_{kK}, \rho_0 \varepsilon\} \in \mathcal{V}^{13}, \\
&\{F_{K\gamma}\}_{\gamma=1}^{13} = \{P_{kK}, v_k \delta_{LK}, Q_K\}, \quad K = 1, 2, 3, \\
&\left\{\hat{f}_\gamma\right\}_{\gamma=1}^{13} = \left\{\mathbf{0}, \mathbf{0}, P_{kK} \frac{\partial v_k}{\partial X_K}\right\}.
\end{aligned} \tag{128}$$

The Lagrange multipliers have been shown to be

$$\{\Lambda_\gamma\}_{\gamma=1}^{n} = \left\{\mathbf{0}, \Lambda_{kK}, \frac{1}{T}\right\}, \tag{129}$$

where Λ_{kK} has not been derived in the explicit form because the constraint due to the condition $(87)_2$ has been eliminated by substitution. The multiplies of momentum equations are zero because these equations contain a linear contribution of the acceleration. Further we show various generalizations of this model and demonstrate the full exploitation of the Liu Theorem.

Lecture 4: Second law of thermodynamics, isotropy, material objectivity; example - rigid heat conductor

Before we present technical tools for the exploitation of thermodynamical identities we discuss briefly a very simple classical problem of the heat conduction in a rigid heat conductor. This example demonstrates all basic features of the exploitation of the second law of thermodynamics without many technical details.

We consider the problem defined by a single scalar field of the absolute temperature T on the domain $\mathcal{B}_0$ of the rigid heat conductor (undeformable body). The function $T(\mathbf{X}, t)$ is assumed to follow from the energy conservation law

$$\rho_0 \frac{\partial \varepsilon}{\partial t} + \operatorname{Div} \mathbf{Q} = 0, \tag{130}$$

where ρ_0 is the constant mass density, and we have left out the energy radiation r. The latter contribution is immaterial for the exploitation of the second law. We assume that the internal energy density ε and the heat flux $\mathbf{Q}$ satisfy the constitutive relations

$$\varepsilon = \varepsilon(T, \mathbf{G}), \quad \mathbf{Q} = \mathbf{Q}(T, \mathbf{G}), \quad \mathbf{G} = \operatorname{Grad} T, \tag{131}$$

which are sufficiently smooth functions of both variables.

The second law of thermodynamics is given in the form of entropy inequality

$$\rho_0 \frac{\partial \eta}{\partial t} + \operatorname{Div} \mathbf{H} \geq 0, \quad \eta = \eta(T, \mathbf{G}), \quad \mathbf{H} = \mathbf{H}(T, \mathbf{G}), \tag{132}$$

which must hold for all thermodynamical processes, i.e. for all solutions of the field equation which follows from (130).

According to Liu's Theorem there exists a Lagrange multiplier $\Lambda^\varepsilon(T, \mathbf{G})$ which allows to write the above inequality in the following modified form

$$\rho_0 \frac{\partial \eta}{\partial t} + \operatorname{Div} \mathbf{H} - \boldsymbol{\Lambda}^\varepsilon \left(\rho_0 \frac{\partial \varepsilon}{\partial t} + \operatorname{Div} \mathbf{Q} \right) \geq 0, \tag{133}$$

and this inequality must hold for **all** fields T and not only for the solutions of field equations. Chain rule of differentiation yields the explicit form of this inequality

$$\begin{aligned} &\rho_0 \left(\frac{\partial \eta}{\partial T} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial T} \right) \frac{\partial T}{\partial t} + \rho_0 \left(\frac{\partial \eta}{\partial \mathbf{G}} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{G}} \right) \cdot \frac{\partial \mathbf{G}}{\partial t} + \\ &+ \left(\frac{\partial \mathbf{H}}{\partial T} - \Lambda^\varepsilon \frac{\partial \mathbf{Q}}{\partial T} \right) \cdot \mathbf{G} + \left(\frac{\partial H_K}{\partial G_L} + \Lambda^\varepsilon \frac{\partial Q_K}{\partial G_L} \right) \frac{\partial^2 T}{\partial X_K X_L} \geq 0. \end{aligned} \tag{134}$$

The last contribution has been written in coordinates in order to reveal the symmetry. The above inequality is linear with respect to the following derivatives

$$\mathfrak{X} := \left\{ \frac{\partial T}{\partial t}, \frac{\partial \mathbf{G}}{\partial t}, \frac{\partial^2 T}{\partial X_K X_L} \right\}. \tag{135}$$

Obviously, the fourth contribution proportional to $\mathbf{G}$ is nonlinear. Hence, Liu's Theorem implies

$$\frac{\partial \eta}{\partial T} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial T} = 0, \quad \frac{\partial \eta}{\partial \mathbf{G}} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{G}} = 0,$$

$$\frac{\partial H_{(K}}{\partial G_{L)}} + \Lambda^{\varepsilon}\frac{\partial Q_{(K}}{\partial G_{L)}} = 0. \tag{136}$$

There remains the *residual inequality*

$$\mathcal{D} = \left(\frac{\partial \mathbf{H}}{\partial T} - \Lambda^{\varepsilon}\frac{\partial \mathbf{Q}}{\partial T}\right)\cdot \mathbf{G} \geq 0, \tag{137}$$

which defines the *dissipation* $\mathcal{D}(T, \mathbf{G})$ in the rigid heat conductor.

We begin the exploitation of the above identities from $(136)_3$. In the case of *isotropic heat conductors* the vector functions $\mathbf{Q}, \mathbf{H}$ must have the following form

$$\mathbf{Q} = Q\left(T, G^2\right)\mathbf{G}, \quad \mathbf{H} = H\left(T, G^2\right)\mathbf{G}, \tag{138}$$

where Q, H are arbitrary scalar functions of T and of the *invariant* of $\mathbf{G}$, i.e. its length $G = \sqrt{\mathbf{G}\cdot\mathbf{G}}$. For convenience we use the square of this variable. Then the identity (136) has the form

$$2\left(\frac{\partial H}{\partial G^2} - \Lambda^{\varepsilon}\frac{\partial Q}{\partial G^2}\right)G_K G_L + \left(H - \Lambda^{\varepsilon} Q\right)\delta_{KL} = 0. \tag{139}$$

Taking the deviatoric part of this identity

$$2\left(\frac{\partial H}{\partial G^2} - \Lambda^{\varepsilon}\frac{\partial Q}{\partial G^2}\right)\left(G_K G_L - \frac{1}{3}G^2\delta_{KL}\right) = 0,$$

we obtain that the first contribution should be zero, and, consequently, the second contribution must vanish as well

$$\frac{\partial H}{\partial G^2} - \Lambda^{\varepsilon}\frac{\partial Q}{\partial G^2} = 0, \quad H - \Lambda^{\varepsilon} Q = 0. \tag{140}$$

Hence the substitution of the second identity in the first one gives the following result

$$\mathbf{H} = \Lambda^{\varepsilon}\mathbf{Q}, \quad \Lambda^{\varepsilon} = \Lambda^{\varepsilon}(T). \tag{141}$$

There are only few results of this type for anisotropic materials. In the case of the rigid heat conductor which is *linear* with respect to the temperature gradient we can prove it easily. Namely, if we assume

$$H_K = \mathrm{H}_{KL}\frac{\partial T}{\partial X_L}, \quad Q_K = \mathrm{Q}_{KL}\frac{\partial T}{\partial X_L}, \quad \mathrm{H}_{KL} = \mathrm{H}_{KL}(T), \quad \mathrm{Q}_{KL} = \mathrm{Q}_{KL}(T), \tag{142}$$

where $\mathrm{H}_{KL}, \mathrm{Q}_{KL}$ are *conductivity matrices*, then the identity $(136)_3$ has the form

$$\mathrm{H}_{(KL)} - \Lambda \mathrm{Q}_{(KL)} = 0. \tag{143}$$

The skew symmetric parts of matrices $\mathrm{H}_{KL}, \mathrm{Q}_{KL}$ are not restricted. If we assume that they are indentically zero then we obtain again the result (141). For these matrices dependent on the temperature gradient there are no general results.

The question is if the result (141) is characteristic only for materials of a single vectorial constitutive variable. We shall see that differential identities of the form $(136)_3$ give rise to the similar result also for much more general cases of materials. This is the subject of the next Liu Theorem.

We use now the assumption on the existence of ideal walls. According to jump conditions on such walls we have

$$[[\mathbf{H}]]\cdot\mathbf{N}=0,\quad [[\mathbf{Q}]]\cdot\mathbf{N}=0\quad\Longrightarrow\quad [[\Lambda^{\varepsilon}(T)]]=0. \tag{144}$$

There exists one system for which we can calculate the relation between the heat flux $\mathbf{Q}$ and the entropy flux $\mathbf{H}$ from a microscopic model (kinetic theory). This is the ideal gas. For this material the relation has the form $\mathbf{H}=\frac{1}{T}\mathbf{Q}$, where T is the absolute temperature[7]. We return frequently to this relation further in this course. Consequently, if we bring the rigid heat conductor to the contact with the ideal gas through the ideal wall we obtain

$$\Lambda^{\varepsilon}(T)=\frac{1}{T}. \tag{145}$$

This relation holds true in all points of $\mathcal{B}_0$ and not only on the contact surface because the multiplier Λ^{ε} does not depend on $\mathbf{X}$ in the explicit manner. Hence, the relation between fluxes has for isotropic rigid heat conductors the classical form

$$\mathbf{H}=\frac{1}{T}\mathbf{Q}. \tag{146}$$

It is appropriate to make a comment on this relation. In many works on continuum thermodynamics this relation is **assumed** from the beginning and then the bulk entropy inequality has the following form

$$\frac{d}{dt}\int_{\mathcal{P}}\rho\eta dV+\oint_{\partial\mathcal{P}}\frac{\mathbf{Q}\cdot\mathbf{N}}{T}dS-\int_{\mathcal{P}}\rho s dV\geq 0. \tag{147}$$

This is the so-called *Clausius-Duhem inequality.* It has been very extensively used in works of Coleman, Eringen, Noll, Serrin, Šilhavý, Williams, Truesdell and many others. This form of the entropy inequality follows indeed in many cases of single component materials from the more general inequality used in these notes. However, multicomponent systems which we consider further are an example that the Calusius-Duhem inequality is too restrictive.

We return to the remaining identities $(136)_{1,2}$. They can be written in the form

$$\eta=-\frac{1}{T}\frac{\partial\psi}{\partial T},\quad \varepsilon=\psi-T\frac{\partial\psi}{\partial T},\quad \psi:=\varepsilon-T\eta,\quad \psi=\psi(T), \tag{148}$$

where ψ is the trivial example of the Helmholtz free energy. Consequently, neither the free energy ψ nor the internal energy ε, nor the entropy η can depend on the temperature gradient.

Finally, bearing the relation (146) in mind we obtain the residual inequality

$$\mathbf{Q}\cdot\mathbf{G}\leq 0. \tag{149}$$

This is the classical statement of the second law of thermodynamics which says that the heat flux has the orientation opposite to the temperature gradient, i.e. the energy flows

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[7] This relation follows also from the macroscopic thermodynamics of homogeneous systems based on the so-called Caratheodory principle. We show some results of this approach in the next lecture.

from hot to cold regions. This inequality can be written for isotropic heat conductors as follows

$$K \geq 0, \quad K \equiv -Q. \tag{150}$$

Substitution of all above results in the energy conservation equation (130) yields the classical heat conduction equation

$$\rho_0 c_v \frac{\partial T}{\partial t} = \operatorname{Div}\left(K \operatorname{Grad} T \right), \quad c_v := \frac{\partial \varepsilon}{\partial T}, \tag{151}$$

where c_v is the *specific heat* under the constant volume. This quantity is positive and this follows from the stability condition of thermodynamical equilibrium. We discuss this problem in the next lecture. The **thermodynamical equilibrium** is defined as a state in which the dissipation vanishes. For the rigid heat conductors it is the case when the distribution of temperature is homogeneous in space: $\operatorname{Grad} T = 0$.

We return now to certain general properties of constitutive relations which are helpful in the evaluation of identities following from the second law of thermodynamics.

As indicated above in the majority of cases we have to assume the *isotropy of materials.* For anisotropic materials results are scarce and usually extensions from isotropic to anisotropic properties are made *ad hoc.*

Isotropy of materials is one of the properties related to the behavior of models under the transformation of frames. However, we can perform such a transformation either on the reference configuration or in the current configuration. In the first case invariance properties specify the **symmetry** of the material and the corresponding group of transformations is the so-called *symmetry group of the material.* In the particular case when the group is the *full orthogonal group* the material is called *isotropic.* In the second case the transformation is specified by the isometry of the space of motions which we have discussed before. This yields the *principle of frame of indifference* or *the principle of material objectivity.* It plays an important role in the continuum mechanics and thermodynamics by delivering general restrictions of the formulation of constitutive functions of material bodies. It reflects the idea that material properties should be independent of observations made by different observers. Obviously, different observers, as we pointed out in Lecture 1, are related by time-dependent Euclidean transformation of frames. For this reason material frame-indifference is sometimes interpreted as invariance under superimposed **rigid body motions**.

We present further many examples of invariance properties related to both transformations. In order to investigate such invariance properties we have to introduce the mathematical description of isotropic functions. We proceed to do so.

■**Technical part concerning isotropic functions**

We limit our attention to the full orthogonal group which consists of orthogonal tensors $\mathbf{O}$, $\det \mathbf{O} = \pm 1$. We consider a scalar φ, a vector $\mathbf{h}$, and a symmetric tensor $\mathbf{T}$ which transform in the following (objective) way

$$\varphi^* = \varphi, \quad \mathbf{h}^* = \mathbf{O}\mathbf{h}, \quad \mathbf{T}^* = \mathbf{O}\mathbf{T}\mathbf{O}^T. \tag{152}$$

In the particular case of the single vector variable which transforms according to the rule $\mathbf{w}^* = \mathbf{O}\mathbf{w}$, where $\mathbf{O}$ is orthogonal, $\mathbf{w}$ is an arbitrary vector and $\mathbf{w}^*$ is its transformation, arbitrary scalar function $\varphi\left(\mathbf{w}\right)$, vector function $\mathbf{h}\left(\mathbf{w}\right)$, second order symmetric tensor function $\mathbf{T}(\mathbf{w})$ of a single vector variable $\mathbf{w}$ are said to be *isotropic* if for an arbitrary orthogonal tensor $\mathbf{O}$ the following conditions are satisfied

$$\varphi(\mathbf{w}^*) = \varphi(\mathbf{w}), \quad \mathbf{h}(\mathbf{w}^*) = \mathbf{O}\mathbf{h}(\mathbf{w}), \quad \mathbf{T}(\mathbf{w}^*) = \mathbf{O}\mathbf{T}(\mathbf{w})\,\mathbf{O}. \tag{153}$$

It is essential in these relations that functions $\varphi(...), \mathbf{h}(...), \mathbf{T}(...)$ remain the same and only their coordinates change in the new reference.

For the scalar function the representation result is immediate. As the orthogonal transformation changes only the direction but not the length of an arbitrary vector, a scalar function may satisfy the condition $(153)_1$ only if it depends only on the length of the vector, i.e.

$$\varphi(\mathbf{w}) = \varphi(w), \quad w \equiv |\mathbf{w}| = \sqrt{\mathbf{w}\cdot\mathbf{w}}, \quad w^* = w. \tag{154}$$

The representation for the vector function has the following form

$$\mathbf{h}(\mathbf{w}) = h(w)\,\mathbf{w}. \tag{155}$$

This relation has been used in the previous considerations. We proceed to prove it.

For $\mathbf{w} = 0$ we have

$$\forall\mathbf{O}: \quad \mathbf{h}(\mathbf{0}) = \mathbf{O}\mathbf{h}(\mathbf{0}) \quad \Longrightarrow \quad \mathbf{h}(\mathbf{0}) = \mathbf{0}, \tag{156}$$

and (155) is satisfied. Let us assume that $\mathbf{w} \neq \mathbf{0}$. Then

$$\mathbf{h}(\mathbf{w}) = \left[\frac{1}{w^2}\mathbf{w}\cdot\mathbf{h}(\mathbf{w})\right]\mathbf{w} + \left[\mathbf{h}(\mathbf{w}) - \left(\frac{1}{w^2}\mathbf{w}\cdot\mathbf{h}(\mathbf{w})\right)\mathbf{w}\right]. \tag{157}$$

Obviously, the second vector on the right-hand side is orthogonal to $\mathbf{w}$. After the transformation this relation has the following form

$$\begin{aligned}
\mathbf{h}(\mathbf{w}^*) &= \left[\frac{1}{w^2}\mathbf{O}\mathbf{w}\cdot(\mathbf{h}(\mathbf{O}\mathbf{w}))\right]\mathbf{O}\mathbf{w} + \left[\mathbf{h}(\mathbf{O}\mathbf{w}) - \left(\frac{1}{w^2}\mathbf{O}\mathbf{w}\cdot(\mathbf{h}(\mathbf{O}\mathbf{w}))\right)\mathbf{O}\mathbf{w}\right] = \\
&= \left[\frac{1}{w^2}\mathbf{O}\mathbf{w}\cdot\mathbf{O}\mathbf{h}(\mathbf{w})\right]\mathbf{O}\mathbf{w} + \left[\mathbf{O}\mathbf{h}(\mathbf{w}) - \left(\frac{1}{w^2}\mathbf{O}\mathbf{w}\cdot\mathbf{O}\mathbf{h}(\mathbf{w})\right)\mathbf{O}\mathbf{w}\right] = \\
&= \left[\frac{1}{w^2}\mathbf{w}\cdot\mathbf{h}(\mathbf{w})\right]\mathbf{O}\mathbf{w} + \mathbf{O}\left[\mathbf{h}(\mathbf{w}) - \left(\frac{1}{w^2}\mathbf{w}\cdot\mathbf{h}(\mathbf{w})\right)\mathbf{w}\right].
\end{aligned}$$

Let us consider a particular case of the transformation which is the rotation by 180^0 about the vector $\mathbf{w}$, i.e. $\mathbf{w} = \mathbf{O}\mathbf{w}$. In this case the second contribution perpendicular to $\mathbf{w}$ changes the sign

$$\mathbf{h}(\mathbf{w}) = \left[\frac{1}{w^2}\mathbf{w}\cdot\mathbf{h}(\mathbf{w})\right]\mathbf{w} - \left[\mathbf{h}(\mathbf{w}) - \left(\frac{1}{w^2}\mathbf{w}\cdot\mathbf{h}(\mathbf{w})\right)\mathbf{w}\right]. \tag{158}$$

Comparison of (157) and (158) shows that the second term must vanish, i.e.

$$\mathbf{h}(\mathbf{w}) = \left[\frac{1}{w^2}\mathbf{w}\cdot\mathbf{h}(\mathbf{w})\right]\mathbf{w}. \tag{159}$$

The coefficient is obviously an objective scalar. This completes the proof.

For the symmetric tensor we find the representation by investigation of the following auxiliary function

$$\mathbf{h}(\mathbf{w}) = \mathbf{T}(\mathbf{w})\,\mathbf{w}. \tag{160}$$

This function is isotropic. Namely

$$\mathbf{h}(\mathbf{O}\mathbf{w}) = \mathbf{T}(\mathbf{O}\mathbf{w})\,\mathbf{O}\mathbf{w} = \mathbf{O}\mathbf{T}(\mathbf{w})\,\mathbf{O}^T\mathbf{O}\mathbf{w} = \mathbf{O}\mathbf{h}(\mathbf{w}).$$

Therefore, there exists a scalar function $h(w)$ such that

$$\mathbf{h}(\mathbf{w}) = h(w)\,\mathbf{w} \quad \Longrightarrow \quad [\mathbf{T}(\mathbf{w}) - h(w)\,\mathbf{1}]\,\mathbf{w} = \mathbf{0}. \tag{161}$$

Hence, $\mathbf{w}$ is the eigenvector of $\mathbf{T}$. Since the tensor $\mathbf{T}$ is symmetric we have the following spectral representation

$$\mathbf{T}(\mathbf{w}) = \alpha^{(1)}(\mathbf{w})\,\mathbf{w}\otimes\mathbf{w} + \alpha^{(2)}(\mathbf{w})\,\mathbf{u}^{(1)}\otimes\mathbf{u}^{(1)} + \alpha^{(3)}(\mathbf{w})\,\mathbf{u}^{(2)}\otimes\mathbf{u}^{(2)}, \tag{162}$$

where $\mathbf{u}^{(1)}, \mathbf{u}^{(2)}$ are the remaining unit eigenvectors of $\mathbf{T}$. Now let us choose a rotation about the vector $\mathbf{w}$ which satisfies the conditions[8]

$$\mathbf{O}\mathbf{w} = \mathbf{w}, \quad \mathbf{O}\mathbf{u}^{(1)} = \mathbf{u}^{(2)}, \quad \mathbf{O}\mathbf{u}^{(2)} = \mathbf{u}^{(1)}. \tag{163}$$

Then it follows from the spectral decomposition

$$\mathbf{T}(\mathbf{w}) = \alpha^{(1)}(\mathbf{w})\,\mathbf{w}\otimes\mathbf{w} + \alpha^{(3)}(\mathbf{w})\,\mathbf{u}^{(1)}\otimes\mathbf{u}^{(1)} + \alpha^{(2)}(\mathbf{w})\,\mathbf{u}^{(2)}\otimes\mathbf{u}^{(2)},$$

which yields

$$\alpha^{(2)}(\mathbf{w}) = \alpha^{(3)}(\mathbf{w}).$$

Therefore the spectral representation of $\mathbf{T}$ reduces to the following form

$$\mathbf{T}(\mathbf{w}) = \tau_0(w)\,\mathbf{1} + \tau_1(w)\,\mathbf{w}\otimes\mathbf{w}, \quad \tau_1(w) \equiv \alpha^{(1)}(\mathbf{w}) - \frac{1}{w^2}\alpha^{(2)}(\mathbf{w}). \tag{164}$$

This relation specifies the representation of the isotropic symmetric tensor function of one vector variable.

Due to its practical importance we present in some details another special case of isotropic functions of a single symmetric second rank tensors. Then we have

Representation Theorem (Rivlin, Ericksen).

Let $\varphi, \mathbf{h}, \mathbf{T}$ be isotropic scalar-, vector-, and symmetric tensor-valued functions of a symmetric tensor variable $\mathbf{A}$. Then it is necessary and sufficient that they have the following representations

$$\begin{array}{rrcl} 1. & \varphi(\mathbf{A}) & = & \varphi\left(a^{(1)}, a^{(2)}, a^{(3)}\right), \\ 2. & \mathbf{h}(\mathbf{A}) & = & 0, \\ 3. & \mathbf{T}(\mathbf{A}) & = & \tau_0\mathbf{1} + \tau_1\mathbf{A} + \tau_2\mathbf{A}^2, \end{array} \tag{165}$$

where $\varphi, \tau_0, \tau_1, \tau_2$ are scalar functions of the three eigenvalues $a^{(1)}, a^{(2)}, a^{(3)}$ of $\mathbf{A}$.

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[8] i.e. in the basis $\left\{\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{w}\right\}$ $\mathbf{O}$ ($\det\mathbf{O} = -1$) is given by the matrix $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

Proof. The sufficiency is trivial. We prove the necessity. For the vector function we have

$$\mathbf{h}\left(\mathbf{OAO}^{T}\right)=\mathbf{Oh}\left(\mathbf{A}\right),$$

and, choosing $\mathbf{O}=-\mathbf{1}$, we obtain $\mathbf{h}\left(\mathbf{A}\right)=-\mathbf{h}\left(\mathbf{A}\right)$, which proves the Theorem.

For the scalar function, we have to show that whenever two tensors $\mathbf{A}$ and $\mathbf{B}$ have the same eigenvalues, say $\left\{a^{(i)}\right\}_{i=1}^{3}$ then $\varphi\left(\mathbf{A}\right)=\varphi\left(\mathbf{B}\right)$. Using the spectral representation we obtain

$$\mathbf{A}=\sum_{i=1}^{3}a^{(i)}\mathbf{u}^{(i)}\otimes\mathbf{u}^{(i)},\quad \mathbf{B}=\sum_{i=1}^{3}a^{(i)}\mathbf{v}^{(i)}\otimes\mathbf{v}^{(i)}, \tag{166}$$

where $\mathbf{u}^{(i)},\mathbf{v}^{(i)}$ are unit eigenvectors of $\mathbf{A}$ and $\mathbf{B}$, respectively. Let us choose the transformation $\mathbf{O}$ in such a way that

$$\mathbf{u}^{(i)}=\mathbf{Ov}^{(i)}. \tag{167}$$

then the spectral representations (166) yield

$$\mathbf{A}=\mathbf{OBO}^{T}. \tag{168}$$

Hence

$$\varphi\left(\mathbf{A}\right)=\varphi\left(\mathbf{OBO}^{T}\right), \tag{169}$$

and the definition of isotropy: $\varphi\left(\mathbf{OBO}^{T}\right)=\varphi\left(\mathbf{B}\right)$ yields the Theorem.

It remains to prove the representation for the tensor function $\mathbf{T}$. We prove it in two steps. First of all, let us show that any eigenvector of $\mathbf{A}$ is also an eigenvector of $\mathbf{T}\left(\mathbf{A}\right)$. Let us choose $\mathbf{O}$ to be the rotation by 180^{0} about the eigenvector $\mathbf{u}^{(1)}$ of $\mathbf{A}$. Then

$$\mathbf{Ou}^{(1)}=\mathbf{u}^{(1)},\quad \mathbf{Ou}^{(2)}=-\mathbf{u}^{(2)},\quad \mathbf{Ou}^{(3)}=-\mathbf{u}^{(3)}\quad\Longrightarrow\quad \mathbf{OAO}^{T}=\mathbf{A}. \tag{170}$$

Since $\mathbf{T}\left(\mathbf{A}\right)$ is isotropic, we have for this $\mathbf{O}$

$$\mathbf{OT}\left(\mathbf{A}\right)\mathbf{O}^{T}=\mathbf{T}\left(\mathbf{OAO}^{T}\right)\quad\Longrightarrow\quad \mathbf{OT}\left(\mathbf{A}\right)=\mathbf{T}\left(\mathbf{A}\right)\mathbf{O}. \tag{171}$$

Hence

$$\mathbf{OT}\left(\mathbf{A}\right)\mathbf{u}^{(1)}=\mathbf{T}\left(\mathbf{A}\right)\mathbf{Ou}^{(1)}=\mathbf{T}\left(\mathbf{A}\right)\mathbf{u}^{(1)}, \tag{172}$$

and, for our choice of $\mathbf{O}$ it means that $\mathbf{T}\left(\mathbf{A}\right)\mathbf{u}^{(1)}$ must be parallel to $\mathbf{u}^{(1)}$. Therefore $\mathbf{u}^{(1)}$ is the eigenvector of $\mathbf{T}$. For the remaining eigenvectors the proof is identical. Consequently, we can write the tensor $\mathbf{T}$ in the following form

$$\mathbf{T}\left(\mathbf{A}\right)=\sum_{i=1}^{3}b^{(i)}\mathbf{u}^{(i)}\otimes\mathbf{u}^{(i)}, \tag{173}$$

where $b^{(i)}$ are functions of $\mathbf{A}$.

In the second step we show that this result implies the representation for tensors. Let us first consider the case of distinct eigenvalues $a^{(i)}$ of the tensor $\mathbf{A}$. We consider the set of the following three equations for τ_0, τ_1, τ_2

$$\tau_0 + a^{(i)}\tau_1 + \left(a^{(i)}\right)^2 \tau_3 = b^{(i)}, \quad i = 1, 2, 3. \tag{174}$$

Since the determinant

$$\begin{vmatrix} 1 & a^{(1)} & \left(a^{(1)}\right)^2 \\ 1 & a^{(2)} & \left(a^{(2)}\right)^2 \\ 1 & a^{(3)} & \left(a^{(3)}\right)^2 \end{vmatrix} = \left(a^{(1)} - a^{(2)}\right)\left(a^{(2)} - a^{(3)}\right)\left(a^{(3)} - a^{(1)}\right) \tag{175}$$

does not vanish we can solve (174) with respect to τ_0, τ_1, τ_2. Substitution of (174) in (173) yields

$$\begin{aligned} \mathbf{T}(\mathbf{A}) &= \tau_0 \sum_{i=1}^{3} \mathbf{u}^{(i)} \otimes \mathbf{u}^{(i)} + \tau_1 \sum_{i=1}^{3} a^{(i)} \mathbf{u}^{(i)} \otimes \mathbf{u}^{(i)} + \tau_3 \sum_{i=1}^{3} \left(a^{(i)}\right)^2 \mathbf{u}^{(i)} \otimes \mathbf{u}^{(i)} = \\ &= \tau_0(\mathbf{A})\,\mathbf{1} + \tau_1(\mathbf{A})\,\mathbf{A} + \tau_2(\mathbf{A})\,\mathbf{A}^2. \end{aligned} \tag{176}$$

According to the *Cayley-Hamilton Theorem* for tensors generated by a three-dimensional vector space we have

$$\mathbf{A}^3 - I\mathbf{A}^2 + II\mathbf{A} - III\mathbf{1} = \mathbf{0}, \tag{177}$$

$$\begin{aligned} I &= \operatorname{tr} \sum_{i=1}^{3} a^{(i)}, \quad II = \frac{1}{2} \operatorname{tr}\left(I^2 - \operatorname{tr} \mathbf{A}^2\right) = a^{(1)}a^{(2)} + a^{(2)}a^{(3)} + a^{(1)}a^{(3)}, \\ III &= \det \mathbf{A} = a^{(1)}a^{(2)}a^{(3)}, \end{aligned} \tag{178}$$

where I, II, III are *the principal invariants* of $\mathbf{A}$. It means that the set $\left\{\mathbf{1}, \mathbf{A}, \mathbf{A}^2\right\}$ is the *basis* of three linearly independent second order tensors for the space of all symmetric second order tensors. It means that (176) is the representation of $\mathbf{T}$ in this basis. Consequently, isotropy of $\mathbf{T}$ implies the isotropy of coefficients τ_0, τ_1, τ_2. This proves the Theorem for three distinct eigenvalues.

For two distinct eigenvalues the proof is similar and it yields $\tau_2 = 0$. Finally, for three identical eigenvalues every vector is the eigenvector of $\mathbf{A}$ and, according to (173), this yields $\tau_1 = \tau_2 = 0$. This completes the proof.■

The above considerations demonstrate problems which arise in proofs of theorems on the representation of isotropic functions. We shall not go into any details of this painstaking tedious analysis (see original works of G. F. Smith, J. M. Spencer, C.-C. Wang) and present Tables 5 to 7 with final results. We skip here the problem of a maximum set of invariants needed for the representation of a given scalar-, vector- or tensor-valued function. This is related to the question of functional *independence* of invariants which we do not discuss in this course. We refer to the original literature and to the book of I-Shih Liu where some of these questions, also for anisotropic materials, are presented in details.

Let us demonstrate on a simple example how to use the Tables. Let us say that the symmetric tensor $\mathbf{T}$ is an isotropic function of two symmetric tensors $\mathbf{A}, \mathbf{B}$. Then, according to Table 6, it must have the form

$$\mathbf{T} = \alpha_0 \mathbf{1} + \alpha_1 \mathbf{A} + \alpha_2 \mathbf{A}^2 + \beta_1 \mathbf{B} + \beta_2 \mathbf{B}^2 + \gamma_1 (\mathbf{AB} + \mathbf{BA}) + \gamma_2 \mathbf{ABA} + \gamma_3 \mathbf{BAB}, \tag{179}$$

where scalar coefficients $\alpha_0, \alpha_1, \alpha_2, \beta_1, \beta_2, \gamma_1, \gamma_2, \gamma_3$ are functions of the scalar invariants

$$\begin{aligned} &\operatorname{tr}\mathbf{A}, \quad \operatorname{tr}\mathbf{A}^2, \quad \operatorname{tr}\mathbf{A}^3, \quad \operatorname{tr}\mathbf{B}, \quad \operatorname{tr}\mathbf{B}^2, \quad \operatorname{tr}\mathbf{B}^2, \\ &\operatorname{tr}\mathbf{AB}, \quad \operatorname{tr}\mathbf{AB}^2, \quad \operatorname{tr}\mathbf{A}^2\mathbf{B}, \quad \operatorname{tr}\mathbf{A}^2\mathbf{B}^2, \end{aligned} \tag{180}$$

which follow from the Table 5 (left).

Table 5: *Isotropic scalar invariants* (left) and *Isotropic vector invariants* (right)

	Invariant elements
One variable:	
$\mathbf{v}$	$\mathbf{v} \cdot \mathbf{v}$
$\mathbf{A} = \mathbf{A}^T$:	$\operatorname{tr}\mathbf{A}, \operatorname{tr}\mathbf{A}^2, \operatorname{tr}\mathbf{A}^3$
$\mathbf{W} = -\mathbf{W}^T$:	$\operatorname{tr}\mathbf{W}^2$
two variables:	
$\mathbf{v}_1, \mathbf{v}_2$:	$\mathbf{v}_1 \cdot \mathbf{v}_2$
$\mathbf{v}, \mathbf{A}$:	$\mathbf{v} \cdot \mathbf{A}\mathbf{v}, \mathbf{v} \cdot \mathbf{A}^2\mathbf{v}$
$\mathbf{v}, \mathbf{W}$:	$\mathbf{v} \cdot \mathbf{W}^2\mathbf{v}$
$\mathbf{A}_1, \mathbf{A}_2$:	$\operatorname{tr}\mathbf{A}_1\mathbf{A}_2, \operatorname{tr}\mathbf{A}_1\mathbf{A}_2^2, \operatorname{tr}\mathbf{A}_1^2\mathbf{A}_2, \operatorname{tr}\mathbf{A}_1^2\mathbf{A}_2^2,$
$\mathbf{W}_1, \mathbf{W}_2$:	$\operatorname{tr}\mathbf{W}_1\mathbf{W}_2$
three variables:	
$\mathbf{v}_1, \mathbf{v}_2, \mathbf{A}$:	$\mathbf{v}_1 \cdot \mathbf{A}\mathbf{v}_2, \mathbf{v}_1 \cdot \mathbf{A}^2\mathbf{v}_2$
$\mathbf{v}_1, \mathbf{v}_2, \mathbf{W}$:	$\mathbf{v}_1 \cdot \mathbf{W}\mathbf{v}_2, \mathbf{v}_1 \cdot \mathbf{W}^2\mathbf{v}_2$
$\mathbf{v}, \mathbf{A}_1, \mathbf{A}_2$:	$\mathbf{v} \cdot \mathbf{A}_1\mathbf{A}_2\mathbf{v}_2$
$\mathbf{v}, \mathbf{W}_1, \mathbf{W}_2$:	$\mathbf{v} \cdot \mathbf{W}_1\mathbf{W}_2\mathbf{v}, \mathbf{v} \cdot \mathbf{W}_1\mathbf{W}_2^2\mathbf{v},$ $\mathbf{v} \cdot \mathbf{W}_2\mathbf{W}_1^2\mathbf{v}$
$\mathbf{v}, \mathbf{A}, \mathbf{W}$:	$\mathbf{v} \cdot \mathbf{W}\mathbf{A}\mathbf{v}, \mathbf{v} \cdot \mathbf{W}\mathbf{A}^2\mathbf{v}, \mathbf{v} \cdot \mathbf{W}\mathbf{A}\mathbf{W}^2\mathbf{v}$
$\mathbf{A}_1, \mathbf{A}_2, \mathbf{A}_3$:	$\operatorname{tr}\mathbf{A}_1\mathbf{A}_2\mathbf{A}_3$
$\mathbf{W}_1, \mathbf{W}_2, \mathbf{W}_3$:	$\operatorname{tr}\mathbf{W}_1\mathbf{W}_2\mathbf{W}_3$
$\mathbf{A}_1, \mathbf{A}_2, \mathbf{W}$:	$\operatorname{tr}\mathbf{A}_1\mathbf{A}_2\mathbf{W}, \operatorname{tr}\mathbf{A}_1\mathbf{A}_2^2\mathbf{W},$ $\operatorname{tr}\mathbf{A}_2\mathbf{A}_1^2\mathbf{W}, \operatorname{tr}\mathbf{A}_1\mathbf{W}\mathbf{A}_2\mathbf{W}^2$
$\mathbf{A}, \mathbf{W}_1, \mathbf{W}_2$:	$\operatorname{tr}\mathbf{A}\mathbf{W}_1\mathbf{W}_2, \operatorname{tr}\mathbf{A}\mathbf{W}_1\mathbf{W}_2^2,$ $\operatorname{tr}\mathbf{A}\mathbf{W}_2\mathbf{W}_1^2$
four variables:	
$\mathbf{v}_1, \mathbf{v}_2, \mathbf{A}_1, \mathbf{A}_2$:	$\mathbf{v}_1 \cdot \mathbf{A}_1\mathbf{A}_2\mathbf{v}_2, \mathbf{v}_1 \cdot \mathbf{A}_2\mathbf{A}_1\mathbf{v}_2$
$\mathbf{v}_1, \mathbf{v}_2, \mathbf{W}_1, \mathbf{W}_2$:	$\mathbf{v}_1 \cdot \mathbf{W}_1\mathbf{W}_2\mathbf{v}_2, \mathbf{v}_1 \cdot \mathbf{W}_2\mathbf{W}_1\mathbf{v}_2$
$\mathbf{v}_1, \mathbf{v}_2, \mathbf{A}, \mathbf{W}$:	$\mathbf{v}_1 \cdot \mathbf{A}\mathbf{W}\mathbf{v}_2, \mathbf{v}_1 \cdot \mathbf{W}\mathbf{A}\mathbf{v}_2$

	Generator elements
one variable:	
$\mathbf{v}$:	$\mathbf{v}$
$\mathbf{A}$ or $\mathbf{W}$:	$\mathbf{0}$
two variables:	
$\mathbf{v}, \mathbf{A}$:	$\mathbf{A}\mathbf{v}, \mathbf{A}^2\mathbf{v}$
$\mathbf{v}, \mathbf{W}$:	$\mathbf{W}\mathbf{v}, \mathbf{W}^2\mathbf{v}$
three variables:	
$\mathbf{v}, \mathbf{A}_1, \mathbf{A}_2$:	$\mathbf{A}_1\mathbf{A}_2\mathbf{v},$ $\mathbf{A}_2\mathbf{A}_1\mathbf{v}$
$\mathbf{v}, \mathbf{W}_1, \mathbf{W}_2$:	$\mathbf{W}_1\mathbf{W}_2\mathbf{v},$ $\mathbf{W}_2\mathbf{W}_1\mathbf{v}$
$\mathbf{v}, \mathbf{A}, \mathbf{W}$:	$\mathbf{A}\mathbf{W}\mathbf{v}, \mathbf{W}\mathbf{A}\mathbf{v}$

Table 6: *Isotropic symmetric tensor invariants*

Generator elements	
no variable:	
0:	$\mathbf{1}$
one variable:	
$\mathbf{v}$:	$\mathbf{v} \otimes \mathbf{v}$
$\mathbf{A}$:	$\mathbf{A}, \mathbf{A}^2$
$\mathbf{W}$:	$\mathbf{W}^2$
two variables:	
$\mathbf{v}_1, \mathbf{v}_2$:	$\mathbf{v}_1 \otimes \mathbf{v} + \mathbf{v}_2 \otimes \mathbf{v}_1$
$\mathbf{v}, \mathbf{A}$:	$\mathbf{v} \otimes \mathbf{Av} + \mathbf{Av} \otimes \mathbf{v}, \mathbf{Av} \otimes \mathbf{Av}$
$\mathbf{v}, \mathbf{W}$:	$\mathbf{v} \otimes \mathbf{Wv} + \mathbf{Wv} \otimes \mathbf{v}, \mathbf{Wv} \otimes \mathbf{Wv},$ $\mathbf{Wv} \otimes \mathbf{W}^2\mathbf{v} + \mathbf{W}^2\mathbf{v} \otimes \mathbf{Wv}$
$\mathbf{A}_1, \mathbf{A}_2$:	$\mathbf{A}_1\mathbf{A}_2 + \mathbf{A}_2\mathbf{A}_1, \mathbf{A}_1\mathbf{A}_2\mathbf{A}_1, \mathbf{A}_2\mathbf{A}_1\mathbf{A}_2$
$\mathbf{W}_1, \mathbf{W}_2$:	$\mathbf{W}_1\mathbf{W}_2 + \mathbf{W}_2\mathbf{W}_1, \mathbf{W}_1\mathbf{W}_2^2 - \mathbf{W}_2^2\mathbf{W}_1,$ $\mathbf{W}_1^2\mathbf{W}_2 - \mathbf{W}_2\mathbf{W}_1^2$
$\mathbf{A}, \mathbf{W}$:	$\mathbf{AW} - \mathbf{WA}, \mathbf{WAW}, \mathbf{A}^2\mathbf{W} - \mathbf{WA}^2,$ $\mathbf{WAW}^2 - \mathbf{W}^2\mathbf{AW}$

Table 7: *Isotropic skew symmetric tensor invariants*

Generator elements	
one variable:	
$\mathbf{v}$ or $\mathbf{A}$:	$\mathbf{0}$
$\mathbf{W}$:	$\mathbf{W}$
two variables:	
$\mathbf{v}_1, \mathbf{v}_2$:	$\mathbf{v}_1 \otimes \mathbf{v}_2 - \mathbf{v}_2 \otimes \mathbf{v}_1$
$\mathbf{v}, \mathbf{A}$:	$\mathbf{v} \otimes \mathbf{Av} - \mathbf{Av} \otimes \mathbf{v}, \mathbf{v} \otimes \mathbf{A}^2\mathbf{v} - \mathbf{A}^2\mathbf{v} \otimes \mathbf{v},$ $\mathbf{Av} \otimes \mathbf{A}^2\mathbf{v} - \mathbf{A}^2\mathbf{v} \otimes \mathbf{Av}$
$\mathbf{v}, \mathbf{W}$:	$\mathbf{v} \otimes \mathbf{Wv} - \mathbf{Wv} \otimes \mathbf{v}, \mathbf{v} \otimes \mathbf{W}^2\mathbf{v} - \mathbf{W}^2\mathbf{v} \otimes \mathbf{v}$
$\mathbf{A}_1, \mathbf{A}_2$:	$\mathbf{A}_1\mathbf{A}_2 - \mathbf{A}_2\mathbf{A}_1, , \mathbf{A}_1\mathbf{A}_2^2 - \mathbf{A}_2^2\mathbf{A}_1, \mathbf{A}_1^2\mathbf{A}_2 - \mathbf{A}_2\mathbf{A}_1^2,$ $\mathbf{A}_1\mathbf{A}_2^2\mathbf{A}_1 - \mathbf{A}_1^2\mathbf{A}_2\mathbf{A}_1, \mathbf{A}_2\mathbf{A}_1\mathbf{A}_2^2 - \mathbf{A}_2^2\mathbf{A}_1\mathbf{A}_2$
$\mathbf{W}_1, \mathbf{W}_2$:	$\mathbf{W}_1\mathbf{W}_2 - \mathbf{W}_2\mathbf{W}_1$
$\mathbf{A}, \mathbf{W}$:	$\mathbf{AW} + \mathbf{WA}, \mathbf{AW}^2 - \mathbf{W}^2\mathbf{A}$
three variables:	
$\mathbf{v}_1, \mathbf{v}_2, \mathbf{A}$:	$\mathbf{v}_1 \otimes \mathbf{Av}_2 - \mathbf{Av}_1 \otimes \mathbf{v}_2, \mathbf{v}_2 \otimes \mathbf{Av}_1 - \mathbf{Av}_1 \otimes \mathbf{v}_2$
$\mathbf{v}_1, \mathbf{v}_2, \mathbf{W}$:	$\mathbf{v}_1 \otimes \mathbf{Wv}_2 - \mathbf{Wv}_1 \otimes \mathbf{v}_2, \mathbf{v}_2 \otimes \mathbf{Wv}_1 - \mathbf{Wv}_1 \otimes \mathbf{v}_2$
$\mathbf{v}, \mathbf{A}_1, \mathbf{A}_2$:	$\mathbf{A}_1\mathbf{v} \otimes \mathbf{A}_2\mathbf{v} - \mathbf{A}_2\mathbf{v} \otimes \mathbf{A}_1\mathbf{v}, \mathbf{A}_1\mathbf{A}_2\mathbf{v} \otimes \mathbf{v} - \mathbf{v} \otimes \mathbf{A}_1\mathbf{A}_2\mathbf{v},$ $\mathbf{A}_2\mathbf{A}_1\mathbf{v} \otimes \mathbf{v} - \mathbf{v} \otimes \mathbf{A}_2\mathbf{A}_1\mathbf{v}$
$\mathbf{A}_1, \mathbf{A}_2, \mathbf{A}_3$:	$\mathbf{A}_1\mathbf{A}_2\mathbf{A}_3 - \mathbf{A}_3\mathbf{A}_2\mathbf{A}_1, \mathbf{A}_2\mathbf{A}_3\mathbf{A}_1 - \mathbf{A}_1\mathbf{A}_3\mathbf{A}_2,$ $\mathbf{A}_3\mathbf{A}_1\mathbf{A}_2 - \mathbf{A}_2\mathbf{A}_1\mathbf{A}_3$

We can now investigate the invariance properties of the example of thermoelastic model which we have discussed in Lecture 2. The constitutive relations (73) were assumed to have the following form

$$\begin{aligned} \mathbf{P} &= \mathbf{P}(\mathbf{v},\mathbf{F},T,\mathbf{G}), \quad \varepsilon = \varepsilon(\mathbf{v},\mathbf{F},T,\mathbf{G}), \\ \mathbf{Q} &= \mathbf{Q}(\mathbf{v},\mathbf{F},T,\mathbf{G}), \quad \mathbf{G} := \operatorname{Grad} T, \end{aligned} \tag{181}$$

Quantities appearing in these relations transform under the Euclidean time dependent transformation of frames in the configuration space in the following way

$$\begin{aligned} \mathbf{P}^* &= \mathbf{OP}, \quad \varepsilon^* = \varepsilon, \quad \mathbf{Q}^* = \mathbf{Q}, \quad \mathbf{v}^* = \mathbf{Ov} + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}}, \\ \mathbf{F}^* &= \mathbf{OF}, \quad T^* = T, \quad \mathbf{G}^* = \mathbf{G}. \end{aligned} \tag{182}$$

The principle of material objectivity (frame-indifference) requires that constitutive functions in (181) remain unaffected by this transformation, i.e. in the new frame

$$\begin{aligned} \mathbf{P}^* &= \mathbf{P}(\mathbf{v}^*,\mathbf{F}^*,T^*,\mathbf{G}^*), \quad \varepsilon^* = \varepsilon(\mathbf{v}^*,\mathbf{F}^*,T^*,\mathbf{G}^*), \\ \mathbf{Q}^* &= \mathbf{Q}(\mathbf{v}^*,\mathbf{F}^*,T^*,\mathbf{G}^*), \end{aligned} \tag{183}$$

where functions $\mathbf{P}(...), \varepsilon(...), \mathbf{Q}(...)$ are the same in both frames. Consequently, the combination of these relations yields

$$\begin{aligned} \mathbf{OP}(\mathbf{v},\mathbf{F},T,\mathbf{G}) &= \mathbf{P}\left(\mathbf{Ov} + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}}, \mathbf{OF}, T, \mathbf{G}\right), \\ \varepsilon(\mathbf{v},\mathbf{F},T,\mathbf{G}) &= \varepsilon\left(\mathbf{Ov} + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}}, \mathbf{OF}, T, \mathbf{G}\right), \\ \mathbf{Q}(\mathbf{v},\mathbf{F},T,\mathbf{G}) &= \mathbf{Q}\left(\mathbf{Ov} + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}}, \mathbf{OF}, T, \mathbf{G}\right), \end{aligned} \tag{184}$$

for all orthogonal $\mathbf{O}(t)$ and for all vectors $\mathbf{c}(t)$.

Clearly, for $\mathbf{O} = \mathbf{1}$ the above relations indicate that constitutive functions cannot be dependent on the velocity $\mathbf{v}$ as we have indicated in Lecture 2.

It remains to investigate the relations

$$\begin{aligned} \mathbf{OP}(\mathbf{F},T,\mathbf{G}) &= \mathbf{P}(\mathbf{OF},T,\mathbf{G}), \quad \varepsilon(\mathbf{F},T,\mathbf{G}) = \varepsilon(\mathbf{OF},T,\mathbf{G}), \\ \mathbf{Q}(\mathbf{F},T,\mathbf{G}) &= \mathbf{Q}(\mathbf{OF},T,\mathbf{G}). \end{aligned} \tag{185}$$

The polar decomposition yields the relation $\mathbf{F} = \mathbf{RU}$, where $\mathbf{R}$ is orthogonal. Consequently, if we choose $\mathbf{O} = \mathbf{R}^T$, we obtain for the scalar function

$$\varepsilon(\mathbf{F},T,\mathbf{G}) = \varepsilon(\mathbf{U},T,\mathbf{G}), \tag{186}$$

which shows that constitutive functions cannot contain a dependence on $\mathbf{R}$ and they may be dependent only on $\mathbf{U}$ or, equivalently, on $\mathbf{C} = \mathbf{U}^2$. Hence, bearing relations (101), (102) in mind, the result of the material objectivity is as follows

$$\begin{aligned} \varepsilon &= \varepsilon(\mathbf{C},T,\mathbf{G}), \quad \psi = \psi(\mathbf{C},T,\mathbf{G}), \quad \eta = \eta(\mathbf{C},T,\mathbf{G}), \\ \mathbf{P} &= 2\rho_0 \mathbf{F} \frac{\partial \psi}{\partial \mathbf{C}}(\mathbf{C},T,\mathbf{G}), \quad \mathbf{Q} = \mathbf{Q}(\mathbf{C},T,\mathbf{G}). \end{aligned} \tag{187}$$

Hence the dependence on $\mathbf{R}$ appears in the explicit manner in the relation for Piola-Kirchhoff stress tensor and this is the result of the rule of transformation for this tensor which behaves from the left as a vector in the current configuration (Eulerian).

In general, we can formulate the principle of material objectivity as follows

> *The constitutive function of an objective quantity must be independent of the frame in the space of configurations.*

On the other hand, the orthogonal transformation of frames in the reference configuration requires

$$\begin{aligned} \mathbf{P}\left(\mathbf{C},T,\mathbf{G}\right)\mathbf{O}^T &= \mathbf{P}\left(\mathbf{OCO}^T,T,\mathbf{OG}\right), \\ \varepsilon\left(\mathbf{C},T,\mathbf{G}\right) &= \varepsilon\left(\mathbf{OCO}^T,T,\mathbf{OG}\right), \\ \mathbf{OQ}\left(\mathbf{C},T,\mathbf{G}\right) &= \mathbf{Q}\left(\mathbf{OCO}^T,T,\mathbf{OG}\right), \end{aligned} \tag{188}$$

the first transformation characteristic for three vectors $P_{kK}\mathbf{e}_K$, $k=1,2,3$, the second one for the scalar, and the last one again for the vector $Q_K\mathbf{e}_K$. These isotropic functions depend on one vector and one symmetric tensor. The dependence on the scalar T is immaterial for transformation properties. Bearing the results presented in Table 7 (left) in mind we obtain for the internal energy ε

$$\varepsilon = \varepsilon\left(T, I, II, III, \left|\mathbf{G}\right|, IV, V\right), \tag{189}$$

where the scalar invariants are defined as follows

$$\begin{aligned} I &= \operatorname{tr}\mathbf{C}, \quad II = \frac{1}{2}\left(I^2+\operatorname{tr}\mathbf{C}^2\right), \quad III = \det\mathbf{C}, \\ IV &= \mathbf{G}\cdot\mathbf{CG}, \quad V = \mathbf{G}\cdot\mathbf{CG}. \end{aligned} \tag{190}$$

This general result simplifies considerably when we account for the thermodynamical admissibility which we investigated before. Then the dependence on $\left|\mathbf{G}\right|, IV, V$ cannot appear. Simultaneously, relations between the Helmholtz free energy, internal energy and the Piola-Kirchhoff stress tensor combined together yield

$$\mathbf{P} = \mathbf{P}\left(T, I, II, III\right). \tag{191}$$

For the heat flux, we can use the result reported in Table 7 (right) and obtain

$$\mathbf{Q} = Q_1\mathbf{G} + Q_2\mathbf{CG} + Q_3\mathbf{C}^2\mathbf{G}, \tag{192}$$

where Q_1, Q_2, Q_3 are functions of $T, I, II, III, \left|\mathbf{G}\right|, IV, V$. We rest at this result the presentation of the example.

We are now in the position to formulate Theorem which enable the exploitation of some identities following from the entropy inequality.

The main Theorem proved by I-Shih Liu[9] has the following form:

Proportionaliy Theorem: Let $\mathbf{H}$ and $\mathbf{Q}$ be isotropic vector functions, and Λ be an isotropic scalar function, of an arbitrary number of vector and tensor variables. Assume that

i/ for N vector variables $\mathbf{v}^n, n=1,...,N$,

$$\left(\frac{\partial H_K}{\partial v_L^n}+\frac{\partial H_L}{\partial v_K^n}\right)-\Lambda\left(\frac{\partial Q_K}{\partial v_L^n}+\frac{\partial Q_L}{\partial v_K^n}\right)=0, \tag{193}$$

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[9] I-Shih Liu; *On entropy flux - heat flux relation in thermodynamics with Lagrange multipliers, Continuum Mech. Thermodyn.,* **8**, 247-256, 1996.

ii/ for every other vector variable $\mathbf{u}$,

$$\frac{\partial H_K}{\partial u_L} - \Lambda \frac{\partial Q_K}{\partial u_L} = 0, \tag{194}$$

iii/ for every tensor variable $\mathbf{A}$,

$$\frac{\partial H_K}{\partial A_{LM}} - \Lambda \frac{\partial Q_K}{\partial A_{LM}} = 0. \tag{195}$$

Then Λ is constant and

$$\mathbf{H} = \Lambda \mathbf{Q} \tag{196}$$

holds, for $N = 1$ and $N = 2$ with the assumption that $\mathbf{Q}$ and $\mathbf{v}^1 \times \mathbf{v}^2$ be functionally independent (i.e. $\mathbf{Q}$ does not contain contributions proportional to $\mathbf{v}^1 \times \mathbf{v}^2$).

Corollary.

The above Theorem remains valid

i/ if for any symmetric tensor variable $\mathbf{A}$, the condition (195) is replaced by

$$\left(\frac{\partial H_K}{\partial A_{LM}} + \frac{\partial H_M}{\partial A_{LK}}\right) - \Lambda \left(\frac{\partial Q_K}{\partial A_{LM}} + \frac{\partial Q_M}{\partial A_{LK}}\right) = 0; \tag{197}$$

ii/ if for any skew symmetric tensor variable $\mathbf{W}$, the condition (195) is replaced by

$$\left(\frac{\partial H_K}{\partial W_{LM}} - \frac{\partial H_M}{\partial W_{LK}}\right) - \Lambda \left(\frac{\partial Q_K}{\partial W_{LM}} - \frac{\partial Q_M}{\partial W_{LK}}\right) = 0. \tag{198}$$

These results can be generalized to cases in which the right-hand side of differential identities is different from zero.

We skip very technical proofs and use these results further in the exploitation of the entropy inequality for systems more complex than thermoelastic materials.

Lecture 5: Equilibrium thermodynamics: Gibbs equation, Maxwell relations, Legendre transformations

Classical works on thermodynamics were done primarily in relation to engineering applications. One of the first who worked on the second law of thermodynamics was Sadi Carnot [Nicolas Léonard Sadi (a name given after a medieval Persian poet and philosopher Sadi of Shiraz) Carnot, 1796-1832; he died during the cholera epidemic in Paris]. The description of his work on heat engines (Pierre R. Roberge) indicates what kind of thermodynamics was developed at this time: "Carnot devised an ideal engine in which a gas is allowed to expand to do work, absorbing heat in the process, and is expanded again without transfer of heat but with a temperature drop. The gas is then compressed, heat being given off, and finally it is returned to its original condition by another compression, accompanied by a rise of temperature. This series of operations, known as *Carnot's cycle*, shows that even under ideal conditions a heat engine cannot convert into mechanical energy all the heat energy supplied to it; some of the heat energy must be rejected."

The above description indicates that thermodynamics of these times was concerned with collections of homogeneous systems which were transferred between different equilibrium states. Neither temporal nor spatial variables were appearing in these considerations. In this Lecture, we present some basic notions which arise in such a formulation. We limit the attention to the simplest substance modelled by thermodynamics of equilibria (thermostatics) – an ideal gas.

We assume that a one-component system undergoes homogeneous and quasistatic processes which are described by changes of the *volume* V (units: $[\mathrm{m}^3]$), and of the *energy* E (units: joul $[\mathrm{J}] = [\mathrm{kg} \cdot \mathrm{m}^2/\mathrm{s}^2]$). The latter is identical with the potential energy because the kinetic energy is negligible in quasistatic processes. Each combination of these two variables (E, V) is called the *state* of the system and *processes* in this model are identified by their initial and final states and, additionally, by some quantities not belonging to the space of states.

The volume V is frequently replaced by some other equivalent variables describing the configuration of the system. One of them is the number of *moles*, n, of the substance contained in the system. One mole is defined as the mass of the system consisting of $A = 6.0237 \cdot 10^{23}$ molecules of the gas. The number A is called the *Avogadro number.* Below we quote masses corresponding to one mole of different substances. We use in these relations the notion of the relative molecular mass $M_r = \mu/\mu_0$, where μ is the molecular mass of a gas, and μ_0 is either the atomic mass of the hydrogen $\mu_H = 1.67329 \cdot 10^{-24}$ g, or, in more recent formulations, 1/12 of the atomic mass of carbon $\mu_0 = 1.66011 \cdot 10^{-24}$ g. In practical applications, the difference between these two definitions is usually ignored.

molecular hydrogen H_2	$M_r = 2$	1 mol $= A \cdot M_r \cdot \mu_H = 2.015879394$ g
molecular oxygen O_2	$M_r = 32$	1 mol $= A \cdot M_r \cdot \mu_H = 32.25407030$ g
molecular nitrogen N_2	$M_r = 28$	1 mol $= A \cdot M_r \cdot \mu_H = 28.22231152$ g
carbon C	$M_r = 12$	1 mol $= A \cdot M_r \cdot \mu_H = 12.09527636$ g
argon Ar	$M_r = 40$	1 mol $= A \cdot M_r \cdot \mu_H = 40.31758788$ g
chlor Cl	$M_r = 35$	1 mol $= A \cdot M_r \cdot \mu_H = 40.31758788$ g
natrium Na	$M_r = 23$	1 mol $= A \cdot M_r \cdot \mu_H = 23.18261303$ g

Then the following combinations of variables are frequently used

$m = n\mu = const$ [kg] – total mass of the system,
$\rho = m/V$ [kg/m^3] – mass density,
$v = 1/\rho$ [m^3/kg] – specific volume,
$\varepsilon = E/m$ [J/kg] – specific energy.

In contrast to densities which we were using before these are not fields. They are not related to the space variable $\mathbf{x}$. As systems are homogeneous they may be considered to be fields constant in space.

The number of moles is a very useful variable when we consider mixtures of many gases. Then the number of moles of a chosen component of the mixture gives a contribution of this component to the whole mixture. We discuss such mixtures in the second part of the Lecture.

Let us first consider balance equations which we have investigated in previous Lectures in the particular case of homogeneous systems.

As the motion is not considered the momentum balance equation is trivially satisfied. Only boundary conditions for the body $\mathcal{B}$ (mechanical equilibrium with the external world) must be verified.

We consider first the conservation of energy for processes without exchange of heat. Then the energy balance equation reduces to the form

$$\frac{dE}{dt} = -\oint_{\partial\mathcal{B}} p\mathbf{v}\cdot\mathbf{n}ds + \int_{\mathcal{B}} \rho\mathbf{b}\cdot\mathbf{v}, \quad \mathbf{T} = -p\mathbf{1}. \tag{199}$$

The time does not appear in classical thermostatics and, consequently, the above relations must be written in the form of increments

$$dE = d'W, \tag{200}$$

where

$$d'W = \left(\int_{\mathcal{B}} \rho\mathbf{b}\cdot\mathbf{v} - \oint_{\partial\mathcal{B}} p\mathbf{v}\cdot\mathbf{n}ds\right) dt. \tag{201}$$

This relation indicates that both approaches to thermodynamics – the field model and the model of homogeneous systems may coincide only if relaxation processes to thermodynamical equilibrium are sufficiently fast (i.e. the characteristic relaxation times are much shorter than characteristic times of macroscopic observations) and, simultaneously, sufficiently slow in order to consider them to be quasistatic.

Bearing homogeneity assumption in mind ($p = const$), according to the mass balance we obtain

$$\oint_{\partial\mathcal{B}} \mathbf{v}\cdot\mathbf{n}dS = \int_{\mathcal{B}} \operatorname{div}\mathbf{v}dV \approx \frac{dV}{dt}, \quad V = \operatorname{vol}\mathcal{B}. \tag{202}$$

Hence, when we neglect the influence of body forces,

$$dE + pdV = 0, \quad \text{where} \quad p = p\left(E, V\right). \tag{203}$$

The contribution $d'W = -pdV$ is called the *mechanical power*. The notation $d'W$ means that, in contrast to dE the mechanical power is usually not a full differential of any function.

The relation for p is the constitutive law, characteristic for the ideal gas. We transform it later to the form which is called the caloric state equation. The above form of the energy conservation law is characteristic for system in *adiabatic isolation.*

It is easy to construct examples of systems in which the volume remains constant but the energy of the system changes: $dV = 0, dE \neq 0$. In such cases, relation (200) cannot be satisfied and we have to add the contribution describing the exchange of energy with the external world which undergoes in constant volume. We denote this contribution by $d'Q$ and call it the *heat exchange.* Such systems are said to be in *diathermal isolation.* Comparison with the energy conservation which we were discussing for the field model yields

$$d'Q = \left(\int_{\mathcal{B}} \rho r dV - \oint_{\partial \mathcal{B}} \mathbf{q} \cdot \mathbf{n} dS \right) dt. \tag{204}$$

If the system is neither in adiabatic nor in diathermal isolation both changes are possible and the energy conservation law has the form

$$dE = d'W + d'Q. \tag{205}$$

In the classical thermostatics this relation is called the *first law of thermodynamics.*

Now we consider two systems $\mathcal{A}$ and $\mathcal{B}$ in the adiabatic isolation. Their states are given by (E_A, V_A) and (E_B, V_B), respectively. The corresponding pressures are $p_A = p(E_A, V_A)$ and $p_B = p(E_B, V_B)$. We create the following process. Without violating the adiabatic isolation from the external world, we bring the two systems to a contact through an diathermal wall. There appears an exchange of energy between the systems and, according to the first law of thermodynamics we have

$$dE_A = d'Q_A, \quad dE_B = d'Q_B. \tag{206}$$

As we did already in the field theory we assume that the energy is an *additive function.* Then, for the system which consists of $\mathcal{A}$ and $\mathcal{B}$

$$dE = dE_A + dE_B = 0 \quad \Longrightarrow \quad d'Q_A + d'Q_B = 0, \tag{207}$$

due to the adiabatic isolation of both systems from the external world.

The assumption on additivity implies, as before that there are no long-range interactions between systems and that the energy does not concentrate on the wall of contact between both systems. Such walls or *interfaces* are called *ideal.*

The process created in the above described manner yields new states of equilibrium $(E'_A, V_A), (E'_B, V_B)$ in which the exchange of energy between both systems ceases. As the full energy of the system does not change only one of the quantities E'_A, E'_B is independent. Consequently, for these two systems one can introduce a function θ_{AB} which determines the states of equilibrium

$$\theta_{AB}(E'_A, V_A) = \theta_{AB}(E'_B, V_B). \tag{208}$$

Properties of this function are determined by the so-called *zeroth law of thermodynamics.* It says that the equilibrium states of systems are *transitive*, i.e. for three arbitrary systems $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$, the equilibrium between two arbitrary pairs, say, ($\mathcal{A}$,$\mathcal{B}$) and ($\mathcal{A}$,$\mathcal{C}$) implies the equilibrium of the remaining pair ($\mathcal{C}$,$\mathcal{B}$). In terms of the function θ this condition has the form

$$\begin{aligned}\theta_{AB}\left(E_A,V_A\right) &= \theta_{AB}\left(E_B,V_B\right) \text{ and } \theta_{AC}\left(E_A,V_A\right)=\theta_{AC}\left(E_C,V_C\right) \quad \Longrightarrow \\ &\Longrightarrow \quad \theta_{BC}\left(E_B,V_B\right)=\theta_{BC}\left(E_C,V_C\right).\end{aligned} \tag{209}$$

It means that there exists a function $\theta\left(E,V\right)$ which determines whether two systems in contact through a diathermal wall are in equilibrium or not. This function is called the *empirical temperature.*

We assume additionally that the empirical temperature is invertible with respect to the first argument, i.e. we can write $E\left(\theta,V\right)$ and the state of the system is described by the pair (θ,V).

We proceed to formulate the second law of thermodynamics for homogeneous systems considered in this Lecture. It consists of two parts. First of all, let us consider a state (θ,V) and some vicinity of this state. Some of the states of this vicinity are attainable from (θ,V) by purely mechanical (adiabatic) processes, some other not. For latter, some heat must be exchanged with the external world. This *assumption* has been already made by Sadi Carnot in his work on efficiency of heat engines. As a mathematical statement it has been introduced to thermodynamics by C. Carathéodory in 1909: *in any neighborhood of an arbitrary state there exist states which are not attainable on an adiabatic path (a process in which* $d'Q=0$*).*

In the simple case which we consider in this Lecture it means that, for such states $dE-d'W\neq 0$. Carathéodory proved that his assumption yields the *integrability* of this 1-form, i.e. the existence of functions S and Λ such that

$$dS=\Lambda\left(dE-d'W\right). \tag{210}$$

This statement is trivial in the case of two variables θ,V – the 1-form of two variables is always integrable. However the statement is not trivial in cases of systems described by more variables. We consider some of them further in this Lecture.

The state function S is called the *entropy* of the system. We proceed to prove some properties of this function. However, it should be stressed that, in contrast to claims in some books on the classical thermostatics, the above relation is only a part of the second law. We return later to this point.

Let us begin with the investigation of the multiplier Λ. We consider two systems $\mathcal{A}$, $\mathcal{B}$ in thermodynamical equilibrium and possessing states $\left(\theta,V_A\right),\left(\theta,V_B\right)$. Bearing (210) in mind we have

$$dS_A=\Lambda_A\left(dE_A+p_AdV_A\right),\quad dS_B=\Lambda_B\left(dE_B+p_BdV_B\right), \tag{211}$$

for an infinitesimal change of these states. Simultaneously, the state of the system which consists of $\mathcal{A}$ and $\mathcal{B}$ in the diathermal contact is described by the parameters (θ,V_A,V_B) and its changes of energy E and entropy S are as follows

$$\begin{aligned}dE &= dE_A+dE_B=-\left(p_AdV_A+p_BdV_B\right) \quad \Rightarrow \\ &\Rightarrow \quad dS=\Lambda\left(dE_A+dE_B+p_AdV_A+p_BdV_B\right).\end{aligned} \tag{212}$$

where the additivity of the energy was used.

Let us transform the variables

$$(\theta, V_A) \to (\theta, S_A)\,, \quad (\theta, V_B) \to (\theta, S_B)\,. \tag{213}$$

Bearing (211) in mind we obtain

$$dS = \frac{\partial S}{\partial \theta} d\theta + \frac{\partial S}{\partial S_A} dS_A + \frac{\partial S}{\partial S_B} dS_B = \Lambda \left(\frac{dS_A}{\Lambda_A} + \frac{dS_B}{\Lambda_B} \right).$$

Hence

$$\frac{\partial S}{\partial \theta} = 0, \quad \frac{\partial S}{\partial S_A} = \frac{\Lambda}{\Lambda_A}, \quad \frac{\partial S}{\partial S_B} = \frac{\Lambda}{\Lambda_B}. \tag{214}$$

These relations imply the following *integrability conditions*

$$\begin{aligned} \frac{\partial^2 S}{\partial \theta \partial S_A} &= \frac{\partial^2 S}{\partial S_A \partial \theta} &\Rightarrow \quad \frac{\partial}{\partial \theta}\left(\frac{\Lambda}{\Lambda_A} \right) = 0, \\ \frac{\partial^2 S}{\partial \theta \partial S_B} &= \frac{\partial^2 S}{\partial S_B \partial \theta} &\Rightarrow \quad \frac{\partial}{\partial \theta}\left(\frac{\Lambda}{\Lambda_B} \right) = 0. \end{aligned} \tag{215}$$

They can be written in the form

$$\frac{1}{\Lambda}\frac{\partial \Lambda}{\partial \theta} = \frac{1}{\Lambda_A}\frac{\partial \Lambda_A}{\partial \theta} = \frac{1}{\Lambda_B}\frac{\partial \Lambda_B}{\partial \theta} = \mu(\theta)\,, \tag{216}$$

where $\mu(\theta)$ is an arbitrary function of the empirical temperature θ. Integration of these relations yields the following *multiplicative* representation of multipliers

$$\begin{aligned} \Lambda_A(\theta, S_A) &= \nu(S_A) \exp\left(\int \mu(\theta)\, d\theta \right), \\ \Lambda_B(\theta, S_B) &= \nu(S_B) \exp\left(\int \mu(\theta)\, d\theta \right), \\ \Lambda(\theta, S_A, S_B) &= \nu(S_A, S_B) \exp\left(\int \mu(\theta)\, d\theta \right). \end{aligned} \tag{217}$$

Let us introduce the notation

$$T(\theta) = \left[C \exp\left(\int \mu(\theta)\, d\theta \right) \right]^{-1}, \tag{218}$$

where C is an arbitrary positive constant. The quantity T is called the *absolute temperature*. It is clear from the above construction that it is a *universal* function, i.e. it is the same for all systems described by the above model.

Substitution of results (217), (218) in (211) yields

$$dS'_A = \frac{1}{T(\theta)}(dE_A + p_A dV_A)\,, \quad S'_A = \frac{1}{C}\int \frac{dS_A}{\nu_A} + \text{const.} \tag{219}$$

This new function S' is also called the entropy. The above relation is quite general and we use it in the form

$$dS = \frac{1}{T}(dE - d'W)\,. \tag{220}$$

It is called the *Gibbs equation*.

Gibbs equation describes only reversible changes of the entropy. We have seen that the second law of thermodynamics in the field approach defines as well the so-called *dissipation function*. In order to introduce a similar notion within the frame of thermostatics, we have to make a rather artificial extension of the notion of changes of entropy. Namely, we have to assume that the increment of entropy $d'S$ consists of two contributions: a reversible part which appears in the Gibbs equation and is related to the heat exchange $dS_{rev} = d'Q/T$ and from the irreversible part $d'S_{irr}$ which is nonnegative[10]. For changes of the total entropy we have then $d'S = dS_{rev} + d'S_{irr} = d'S_{irr} + \frac{d'Q}{T}$ and the following inequality is assumed to hold

$$d'S - \frac{d'Q}{T} \equiv d'S - \frac{1}{T}\left(dE + pdV\right) \geq 0, \tag{221}$$

where we have used the first law of thermodynamics. Gibbs equation and the above inequality form together the second law of thermodynamics in the form presented in this Lecture.

The above inequality can be written in the form

$$d\left(E - TS\right) \leq -SdT - pdV, \tag{222}$$

provided we assume the existence of the entropy function beyond reversible processes. This inequality forms the basis for analysis of stability of equilibrium states. It says that the *Helmholtz free energy* $\Psi = E - TS$ possesses a *minimum* in the state of equilibrium reached on the isothermal ($dT = 0$) and isochoric ($dV = 0$) ways. Further we show such an analysis for systems in adiabatic isolation.

Now we present a few simple conclusions from Gibbs equation. Let us assume that states are described by variables: absolute temperature T and volume V. Then we have

$$dS = \frac{\partial S}{\partial T}dT + \frac{\partial S}{\partial V}dV = \frac{1}{T}\left(\frac{\partial E}{\partial T}dT + \left(\frac{\partial E}{\partial V} + p\right)dV\right). \tag{223}$$

Since dT and dV are arbitrary it follows immediately

$$\frac{\partial E}{\partial T} = T\frac{\partial S}{\partial T}, \quad p = -\left(\frac{\partial E}{\partial V} - T\frac{\partial S}{\partial V}\right). \tag{224}$$

These important relations couple *constitutive relations* for E, S and p. They can be written in a simpler form by means of the *Helmholtz free energy*, Ψ,

$$\begin{aligned} \Psi &= E - TS = \Psi\left(T, V\right) \quad \Rightarrow \\ &\Rightarrow \quad S = -\frac{\partial \Psi}{\partial T}, \quad E = \Psi - T\frac{\partial \Psi}{\partial T}, \quad p = -\frac{\partial \Psi}{\partial V}. \end{aligned} \tag{225}$$

Hence, it follows from the Gibbs equation that we have to know only one constitutive function for the Helmholtz free energy, the remaining relations for internal energy, entropy and pressure following by differentiation. We say that the Helmholtz free energy is a *thermodynamical potential* for this choice of state variables.

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[10] In the general case, one cannot even assume that $d'S_{irr}$, and consequently $d'S$, are full differentials of some functions. In this sense, the nonequilibrium entropy S_{irr} and the total entropy S may not exist within this approach.

Let us transform the state variables in the following way

$$(T, V) \rightarrow (T, p) . \tag{226}$$

Then the Gibbs equation can be written in the form

$$dG = -SdT + Vdp, \quad G = E - TS + pV = G(T, p) . \tag{227}$$

Similarly as before we obtain by differentiation

$$S = -\frac{\partial G}{\partial T}, \quad V = \frac{\partial G}{\partial p}, \quad E = G - T\frac{\partial G}{\partial T} - p\frac{\partial G}{\partial p}. \tag{228}$$

Therefore for this choice of state variables the function G is the thermodynamical potential. It is called the *Gibbs free energy.*

Finally for the transformation of variables

$$(T, V) \rightarrow (S.p) , \tag{229}$$

we have

$$dH = TdS + Vdp, \quad H = E + pV = H(S, p) , \tag{230}$$

and

$$T = \frac{\partial H}{\partial S}, \quad V = \frac{\partial H}{\partial p}, \quad E = H - p\frac{\partial H}{\partial p}. \tag{231}$$

The potential H is called the *enthalpy.*

state variables	**thermodynamical potential**
(E, V)	– entropy S
(T, V)	– Helmholtz free energy $\Psi = E - TS$
(T, p)	– Gibbs free energy (free enthalpy) $G = E - TS + pV$
(S, p)	– enthalpy $H = E + pV$

The above presented transformations of variables illustrate the so-called *Legendre transformation*, in which the transformation of variables yields a corresponding transformation of the potential. A particular choice of variables depends only on a particular application of the model especially related to possibilities of control of variables in experiments. For instance, in a simple mechanical experiment of extension of the rod we can control either the force applied to the rod (*soft loading device*), or its extension (*hard loading device*). In thermodynamics it is sometimes easier to control the temperature and sometimes (e.g. for shock waves) the entropy.

Apart from the above direct consequences of the Gibbs equation constitutive relations lead to the so-called integrability conditions. We show here only one example.

Relation (223) contains on the left hand side the full differential. This yields the symmetry of the second mixed derivative with respect to T, V. Hence, we have

$$\frac{\partial}{\partial V}\left(\frac{1}{T}\frac{\partial E}{\partial T}\right) = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial E}{\partial V} + p\right)\right] , \tag{232}$$

or, after simplifications,

$$\frac{\partial E}{\partial V} = T\frac{\partial p}{\partial T} - p. \tag{233}$$

This is an example of the *Maxwell relation.* The above relation is called *Clausius-Clapeyron equation.* Such relations appear in thermodynamics of more complex systems and form the basis of chemical thermodynamics. They play, for example, a very important role in experimental verification of thermodynamical potentials. Relation (233) means that the derivative of internal energy does not have to be estimated from difficult calorimetric experiments but it follows from the so-called *thermal state equation*

$$p = p\left(T, V\right). \tag{234}$$

However, some calorimetric experiment are necessary for the estimation of internal energy. Namely, from the first law of thermodynamics we have

$$d'Q = mc_v dT + \left(\frac{\partial E}{\partial V} + p\right) dV, \quad c_v = \frac{1}{m}\frac{\partial E}{\partial T}, \tag{235}$$

where c_v is *specific heat under constant volume.* Bearing (233) in mind, we obtain

$$m\frac{\partial c_v}{\partial V} = T\frac{\partial^2 p}{\partial T^2} \quad \Rightarrow \quad mc_v = mc_v^0 + T\frac{\partial^2}{\partial T^2}\int\limits_{V_0}^{V} pdV. \tag{236}$$

This relation shows that the specific heat follows from the thermal state equation (234) up to a function of temperature $c_v^0\left(T\right)$. This function must be found in a single calorimetric experiment for which $V = V_0$.

Relations (233) and (236) determine both derivatives of the energy and their integration yields up to a constant the following *caloric state equation*

$$E = E\left(T, V\right). \tag{237}$$

In many cases it is more convenient to control pressure rather than volume. From the first law of thermodynamics it follows for the state variables (T, p)

$$d'Q = d\left(E + pV\right) - Vdp = \frac{\partial\left(E + pV\right)}{\partial T}dT + \left[\frac{\partial\left(E + pV\right)}{\partial T} - V\right] dp. \tag{238}$$

It should be stresses that $E + pV$ is here not the enthalpy H which is the potential for variables (S, p). The quantity

$$c_p = \frac{1}{m}\frac{\partial\left(E + pV\right)}{\partial T}, \quad E = E\left(T, p\right), \quad V = V\left(T, p\right),$$

is called the *specific heat under constant pressure.*

The above transformation of variables leads also to the following relation

$$c_p - c_v = \frac{1}{m}\left(\frac{\partial E}{\partial V} + p\right)\frac{\partial V}{\partial T}, \tag{239}$$

i.e.

$$\gamma = \frac{c_p}{c_v} = 1 + \left[\left(\frac{\partial E}{\partial V} \right) \bigg|_{T=const.} + p \right] \frac{\partial V}{\partial T} \left(\frac{\partial E}{\partial T} \right) \bigg|_{V=const}^{-1}, \tag{240}$$

where the coefficient γ is the so-called *adiabatic exponent* frequently appearing in gas dynamics.

Apart from the above discussed laws (principles) of thermodynamics it is assumed that the state of thermodynamical equilibrium is *stable.* Let us investigate this assumption. The condition of stability for systems in adiabatic isolation (i.e. for $d'Q = 0, dS = 0$) requires that entropy should have a maximum in this state. In some practical applications this condition may not be satisfied. It concerns, in particular, the so-called metastable equilibrium states which appear in the description of phase transformations. They are sometimes called *frozen equilibria* because systems may appear in these states only for a finite time duration. We shall not discuss such problems in this course.

Let us consider two identical thermodynamical systems each of them having the energy E and the volume V. We connect these systems and assume that the joined system is in adiabatic isolation. Let us assume that the initial equilibrium state has been disturbed in such a way that the initial state of the first system becomes $(E + \delta E, V + \delta V)$ while the initial state of the second system becomes $(E - \delta E, V - \delta V)$. The system develops to a new equilibrium state in which the entropy reaches its maximum. As the entropy is an additive function we have

$$S(2E, 2V) > S(E + \delta E, V + \delta V) + S(E - \delta E, V - \delta V). \tag{241}$$

Let us expand this relation into the Taylor series. We obtain ($\frac{\partial S}{\partial E} = 0, \frac{\partial S}{\partial V} = 0$)

$$\frac{\partial^2 S}{\partial E^2} (\delta E)^2 + 2 \frac{\partial^2 S}{\partial E \partial V} \delta E \delta V + \frac{\partial^2 S}{\partial V^2} (\delta V)^2 < 0. \tag{242}$$

It means that Hessian (the matrix of second derivatives) has to be negative definite. For chosen variables Gibbs equation indicates as well

$$\frac{\partial S}{\partial E} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} = \frac{p}{T}. \tag{243}$$

Changing the variables $(E, V) \rightarrow (T, V)$ we obtain immediately

$$\frac{mc_v}{T^2} (\delta T)^2 - \frac{1}{T} \frac{\partial p}{\partial V} (\delta V)^2 > 0. \tag{244}$$

This inequality indicates the following *stability conditions* of the thermodynamical equilibrium

$$c_v > 0, \quad \kappa_T > 0, \quad \kappa_T = -V \frac{\partial p}{\partial V}, \tag{245}$$

where the coefficient κ_T is called *isothermal compressibility modulus.*

We complete this review of classical thermostatics of single component systems with the presentation of the simplest example of the thermodynamical model of ideal gases.

Real gases of small densities behave in high temperatures almost like ideal gases, i.e. substances whose thermal state equation $p = p(\rho, T)$ has the form

$$p = \rho \frac{R}{M_r} T \quad \text{where} \quad R = 8.3153 \cdot 10^3 \, \frac{\mathrm{J}}{\mathrm{kg} \cdot \mathrm{K}}, \quad M_r = \frac{\mu}{\mu_0}. \tag{246}$$

Depending on applications the thermal state equation is written in different forms. Most frequently used relations are collected below.

$$\begin{aligned} pV &= m \frac{R}{M_r} T, \\ p\nu &= \frac{R}{M_r} T \quad \text{where} \quad \nu = \frac{1}{\rho} = \frac{V}{m}, \quad \text{or applying} \quad m = N\mu, \quad M_r = \frac{\mu}{\mu_0} \\ pV &= NkT \quad \text{where} \quad k = R\mu_0 = 1.38044 \cdot 10^{-23} \tfrac{\mathrm{J}}{\mathrm{K}} \text{ – Boltzmann constant}, \\ p &= \frac{kT}{v\mu} = \frac{\rho kT}{\mu}. \end{aligned} \tag{247}$$

R is the *universal gas constant.* Thermal state equation implies for normal conditions: $p = 1$ atm., $T = 273.15$ K (0^0 C), $N = A$ (Avogadro number)

$$V_{mol} = \frac{NkT}{p} = 22.4207 \text{ liter}.$$

The air is the mixture of gases

78.08% nitrogen N_2, 20.95% oxygen O_2, 0.94% argon Ar, 0.03% carbon dioxide CO_2.

Hence the molecular mass of the air is as follows

$$\begin{aligned} \mu_{air} &= 0.7808\mu_{N_2} + 0.2095\mu_{O_2} + 0.009\mu_{Ar} + 0.0003\mu_{CO_2} \quad \Longrightarrow \\ &\Rightarrow \quad M_r^{air} = \frac{\mu_L}{\mu_0} = 28.96. \end{aligned}$$

In contrast to the thermal state equation, specifying the constitutive relation for pressure, *caloric state equation* specifies the *constitutive relation* for the specific *internal energy* $\varepsilon(\rho, T)$. For ideal gases

$$\varepsilon = z \frac{R}{M_r} T + \alpha, \tag{248}$$

where z is a constant:

$$z = \begin{cases} \frac{3}{2} \text{ for monatomic gases,} \\ \frac{5}{2} \text{ for two-atomic gases,} \\ 3 \text{ dla poliatomic gases.} \end{cases} \tag{249}$$

The constant α is different for different gases and it has a bearing in description of chemical reactions. It is important to notice that the internal energy of ideal gases is independent of pressure.

We proceed to present some elements of the thermostatic mixture theory. We consider a thermodynamical system which is the homogeneous mixture of A distinguishable components. In thermostatics we are not interested in a relative motion of these components (diffusion processes). This will be the subject of further Lectures. Thermostatics of homogeneous multicomponent systems (mixtures) was constructed by Gibbs.

The following notions are characteristic for a mixture of A components

m_a	– mass of the component a, $a = 1, ..., A$
$\rho_a = m_a/V$	– partial mass density of the component a
$v_a = V/m_a$	– partial specific volume (V - volume under pressure p and temperature T)
$c_a = m_a/m$	– concentration of the component a ($m = \sum_{b=1}^{A} m_a$ - total mass)
N_a	– particle number of the component a
$\nu_a = N_a/A$	– mol number (A – Avogadro number: $6.0221367 \times 10^{23}\,\mathrm{mol}^{-1}$)
$n_a = N_a/V$	– particle density
$X_a = \nu_a/\nu$	– mol fraction ($\nu = \sum_{a=1}^{A} \nu_a$ – total number of moles)
V_a/V	– volume fraction (V_a – volume of the pure substance a under p and T)
p_a/p	– pressure fracture

where p_a is the so-called partial pressure, and the total (bulk) pressure p, the total mass density ρ, the total (bulk) specific internal energy ε and the total (bulk) specific entropy η are given by the relations

$$p = \sum_{a=1}^{A} p_a, \quad \rho = \sum_{a=1}^{A} \rho_a, \quad \rho\varepsilon = \sum_{a=1}^{A} \rho_a \varepsilon_a, \quad \rho\eta = \sum_{a=1}^{A} \rho_a \eta_a. \tag{250}$$

As the system is homogeneous the total energy, entropy, etc. follow by the multiplication with the total mass m, e.g. $E = m\varepsilon, S = m\eta$, etc.

The most important thermodynamical potential for an arbitrary component a of the mixture is the so-called *chemical potential* μ_a. Its importance follows from the fact that, in contrast to the partial pressure, p_a, it is continuous across semipermeable membranes. *Semipermeable membranes* are walls (interfaces) between systems which are permeable only for some components of these systems. We proceed to present some details.

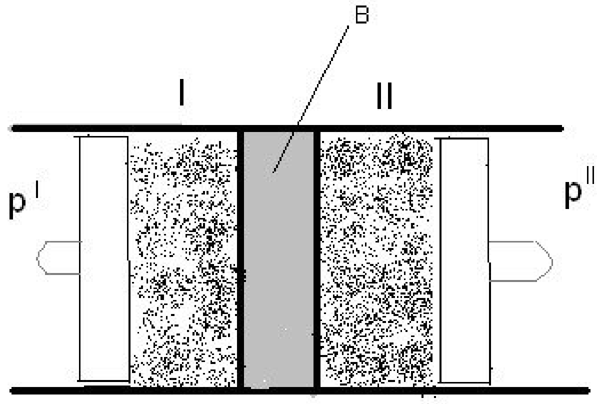

Fig. 8: *Semipermeable membrane* B *between two mixtures containing the component* a.

Let us consider a system at a given constant temperature T schematically shown in Fig. 8. On both sides of the membrane B permeable for the component a (i.e. the membrane is material with respect to all components except of a which may flow through the membrane) there is a mixture in which the schematically indicated pistons sustain constant total pressures p^I and p^{II}. According to the stability condition (222) we have for this system

$$\begin{aligned} d(E-TS) &\leq -SdT - p^I dV^I - p^{II} dV^{II} \quad \Rightarrow \\ d\left(E - TS + p^I V^I + p^{II} V^{II}\right) &\leq -SdT + V^I dp^I + V^{II} dp^{II} = 0. \end{aligned} \tag{251}$$

Hence the quantity $G = \left(E^I - TS^I + p^I V^I\right) + \left(E^{II} - TS^{II} + p^{II} V^{II}\right)$ reaches minimum in the equilibrium state (in an arbitrary process approaching equilibrium it must decay). This quantity is called the *free enthalpy* of the whole system and it is the sum of free enthalpies of both subsystems. Due to the fact that mixtures on both sides of the membrane may be different these free enthalpies may be functions of different variables. Of course, they must be functions of temperature and total pressure but they may depend on mass contributions of components as well. For the total free enthalpy G, we have then

$$G = G^I\left(T, p^I, m_1^I, ..., m_a^I, ..., m_{A^I}^I\right) + G^{II}\left(T, p^{II}, m_1^{II}, ..., m_a^{II}, ..., m_{A^{II}}^{II}\right). \tag{252}$$

Due to the fact that the membrane B is permeable only for the component a, all variables except of m_a^I, m_a^{II} are in this relation constant and, additionally, the sum $m_a = m_a^I + m_a^{II}$ must be constant as well. Consequently, the minimum condition has the form

$$\frac{\partial G}{\partial m_a^I} = 0 \quad \Rightarrow \quad \frac{\partial G^I}{\partial m_a^I} = \frac{\partial G^{II}}{\partial m_a^{II}}. \tag{253}$$

It means that the derivative of the free enthalpy with respect to the mass contribution of the component a is continuous across the semipermeable membrane. For this reason, we define the *chemical potential* in the following way

$$\mu_a = \frac{\partial G}{\partial m_a}. \tag{254}$$

Then the equilibrium condition has the form

$$\mu_a^I\left(T, p^I, m_1^I, ..., m_{A^I}^I\right) = \mu_a^{II}\left(T, p^{II}, m_1^{II}, ..., m_{A^{II}}^{II}\right). \tag{255}$$

Definition (254) yields immediately the following integrability condition

$$\frac{\partial \mu_a}{\partial m_b} = \frac{\partial \mu_b}{\partial m_a}. \tag{256}$$

Additionally, additivity of the free enthalpy G leads to the relation

$$G = \sum_{a=1}^{A} \mu_a m_a. \tag{257}$$

Namely, let us consider a z-tuple enlargement of the system. We have then

$$G\left(T, p, zm_1, ..., zm_A\right) = zG\left(T, p, m_1, ..., m_A\right).$$

Differentiating with respect to z we obtain

$$\sum_{a=1}^{A} \frac{\partial G\left(T, p, zm_1, ..., zm_A\right)}{\partial\left(zm_a\right)} m_a = \sum_{a=1}^{A} \frac{\partial G\left(T, p, m_1, ..., m_A\right)}{\partial m_a} m_a = G\left(T, p, m_1, ..., m_A\right).$$

Bearing (254) in mind we obtain (257).

This means as well that additivity of G yields the invariance of the chemical potential with respect to the enlargement of the system, i.e.

$$\mu_a\left(T,p,zm_1,...,zm_A\right)=\mu_a\left(T,p,m_1,...,m_A\right).$$

This is possible only if the chemical potential μ_a does not depend directly on the mass of components but on their fractions such as concentrations c_b, or mol fractions X_b, $b=1,...,A-1$ ($X_A=-\sum_{a=1}^{A-1}X_a!$),

$$\mu_a=\mu_a\left(T,p,X_1,...,X_{A-1}\right). \tag{258}$$

This property of the chemical potential shows that for a one-component system the chemical potential and the density of the free enthalpy $g=G/m$ are identical.

Differentiation of the relation (257) with respect to m_b yields

$$\frac{\partial G}{\partial m_b}=\mu_b+\sum_{a=1}^{A}\frac{\partial\mu_a}{\partial m_b}m_a \quad\Rightarrow\quad \sum_{a=1}^{A}\frac{\partial\mu_a}{\partial m_b}m_a=0,$$

and, accounting for the integrability condition (256),

$$\sum_{a=1}^{A}\frac{\partial\mu_b}{\partial m_a}m_a=0. \tag{259}$$

This relation is called the *Gibbs-Duhem relation.*

It remains to formulate the Gibbs equation for mixtures. According to the definition of the chemical potential (254) we obtain

$$dG=-SdT+Vdp+\sum_{a=1}^{A}\mu_a dm_a. \tag{260}$$

The following *Maxwell relations* (integrability conditions) result from this Gibbs equation

$$\frac{\partial S}{\partial m_a}=-\frac{\partial\mu_a}{\partial T}\quad\text{and}\quad\frac{\partial V}{\partial m_a}=\frac{\partial\mu_a}{\partial p}. \tag{261}$$

This completes the review of thermostatics.

Lecture 6: Extended thermodynamics: introduction, kinetic theory of rarified gases

Apart from the experience with macroscopic systems which yields the phenomenological formulation of macroscopic continuum thermodynamical models it is advisable to justify such models by their derivation from more fundamental microscopic models. It is rather unfortunate that only one such derivation could be successfully constructed and it is based on the *kinetic theory of ideal monatomic gases.* Attempts to proceed in a similar way in cases of nonideal gases in which particles interact with each other or in cases of granular and molecular substances (e.g. solutions of high polymers) have been not fully successful and only partial results are available. In this lecture, we present the transition from the kinetic theory of ideal rarified gases to the macroscopic description. This transition motivates a macroscopic thermodynamical strategy of constructing models which is called the *extended thermodynamics.*

The exact microscopic description of the system of N material points of equal mass m is based on the set of Newton equations

$$m\ddot{\mathbf{x}}_\alpha = \mathbf{F}_\alpha\left(\mathbf{x}_\beta, \dot{\mathbf{x}}_\beta\right), \quad \alpha, \beta = 1, ..., N, \tag{262}$$

with the corresponding initial conditions $\mathbf{x}_\alpha\left(t = t_0\right) = \mathbf{x}_\alpha^0, \quad \dot{\mathbf{x}}_\alpha = \dot{\mathbf{x}}_\alpha^0$. As usual, the dot denotes the time derivative. As exact solutions for many interacting material points (particles) cannot be constructed and do not have any practical bearing anyway one replaces this problem with the problem of construction of the *distribution function* $f_N\left(t, \boldsymbol{\xi}_1, ..., \boldsymbol{\xi}_N, \varsigma_1, ..., \varsigma_N\right)$ which determines, when normalized, the *probability* that at the instant of time t the points shall occupy a given set of positions $\boldsymbol{\xi}_1, ..., \boldsymbol{\xi}_N$ and possess a set of velocities $\varsigma_1, ..., \varsigma_N$. Such a function satisfies the exact Liouville equation which follows from Newton's equations

$$\frac{\partial f_N}{\partial t} + \sum_{\alpha=1}^{N}\left(\frac{\partial f_N}{\partial \boldsymbol{\xi}_\alpha} \cdot \varsigma_\alpha + \frac{1}{m}\frac{\partial f_N}{\partial \varsigma_\alpha} \cdot \mathbf{F}_\alpha\right) = 0, \tag{263}$$

and expresses the measure conservation of the phase space constructed of points $\left\{\boldsymbol{\xi}_1, ..., \boldsymbol{\xi}_N, \varsigma_1, ..., \varsigma_N\right\}$. Its formal solution is of the form

$$f_N = \frac{1}{N}\sum_{\alpha=1}^{N}\delta\left(\mathbf{x}_\alpha\left(t\right) - \boldsymbol{\xi}_\alpha\right)\delta\left(\dot{\mathbf{x}}_\alpha\left(t\right) - \varsigma_\alpha\right), \tag{264}$$

where δ is the Dirac delta. This is still not a simplification of the original problem. However, the n-tuple integrations of the Liouville equation with respect to variables $\boldsymbol{\xi}_\alpha$ and ς_α yield a hierarchy of equations for functions $f_1\left(t, \boldsymbol{\xi}, \varsigma\right), f_2\left(t, \boldsymbol{\xi}_1, \varsigma_1, \boldsymbol{\xi}_2, \varsigma_2\right), ...,$ etc., which specify the *reduced probabilities* for one, two,..., etc. material points. This is the so-called BBGKY-*hierarchy* which gives rise to various simplified microscopic models. Simplifications following from this hierarchy are justified by the existence of a natural small parameter in the model – the so-called *synchronization time.* The most elementary simplification of this art appears in the case of description by a single function $f_1\left(t, \boldsymbol{\xi}, \varsigma\right)$ which, when not normalized, is called the *phase density.* The equation for this function which is the first equation in the BBGKY-hierarchy still contains the function

$f_2(t, \boldsymbol{\xi}_1, \boldsymbol{\varsigma}_1, \boldsymbol{\xi}_2, \boldsymbol{\varsigma}_2)$. However, under the additional assumption that this function factorizes $f_2(t, \boldsymbol{\xi}_1, \boldsymbol{\varsigma}_1, \boldsymbol{\xi}_2, \boldsymbol{\varsigma}_2) = f_1(t, \boldsymbol{\xi}_1, \boldsymbol{\varsigma}_1) f_1(t, \boldsymbol{\xi}_2, \boldsymbol{\varsigma}_2)$ (i.e. the probabilities for various points become independent from each other) we obtain the *closure* of the equation. This is the so-called *molecular chaos* assumption and it has been introduced by L. Boltzmann in 1868. If, in addition, interactions of points are included only through their direct elastic encounters (elastic collisions in which mass, momentum and energy are conserved), one obtains the following Boltzmann equation

$$\frac{\partial f}{\partial t} + \boldsymbol{\varsigma} \cdot \frac{\partial f}{\partial \boldsymbol{\xi}} + (\mathbf{b} + \mathbf{i}) \cdot \frac{\partial f}{\partial \boldsymbol{\varsigma}} = \mathcal{C}[f, f], \tag{265}$$

where $\mathbf{b}$ is the external body force independent of $\boldsymbol{\xi}$ and $\boldsymbol{\varsigma}$ and

$$\mathbf{i} = 2\boldsymbol{\Omega}(\boldsymbol{\varsigma} - \dot{\mathbf{c}}) - \boldsymbol{\Omega}^2(\boldsymbol{\xi} - \mathbf{c}) + \dot{\boldsymbol{\Omega}}(\boldsymbol{\xi} - \mathbf{c}) + \ddot{\mathbf{c}}, \tag{266}$$

is the inertial acceleration following from the relative motion of the frame with respect to the inertial frame (comp. relation (26) in Lecture 1). The noninertial reference frame was chosen because it demonstrates in the explicit manner the influence of Euclidean transformation on the distribution function. This has the paramount importance for the material objectivity of macroscopic quantities derived from the kinetic theory. We discuss this problem further in this Lecture. In equation (265), we have skipped for simplicity the index by the phase density f. This function specifies the number density of atoms. Namely, $f(t, \boldsymbol{\xi}, \boldsymbol{\varsigma})\, d\boldsymbol{\varsigma}$ is the number of particles per unit volume at the point $\boldsymbol{\xi}$ and at time t such that their velocities lie between $\boldsymbol{\varsigma}$ and $\boldsymbol{\varsigma}+d\boldsymbol{\varsigma}$, i.e. velocities whose endpoints lie in the sphere with the centre $\boldsymbol{\varsigma}$ and the radius $|d\boldsymbol{\varsigma}|$. $\mathcal{C}[f, f]$ is the so-called *collision operator*. Its structure follows from the assumption on interactions of particles and from the factorization of two-point distribution functions. Boltzmann's assumptions can be satisfied only for *rarified gases*. This yields a structure of the collision operator which contains the so-called Knutsen number

$$\mathrm{Kn} = \frac{\text{mean time of free flight}}{\text{observation time scale}} = \frac{\text{mean free path}}{\text{observation length scale}}. \tag{267}$$

This number forms the foundation for approximate solutions of Boltzmann's equation.

The Boltzmann equation follows from the BBGKY-hierarchy cut at the first equation containing only two-point distribution functions. Consequently, only binary collisions are accounted for in this model. Two colliding particles have the velocities $\boldsymbol{\varsigma}, \boldsymbol{\varsigma}^1$ before the collision and $\boldsymbol{\varsigma}', \boldsymbol{\varsigma}^{1\prime}$ after the collision. If they have the equal radius r then in the explicit form the collision operator is as follows

$$\mathcal{C}[f, f] = \int \left(f' f^{1\prime} - f f'\right) r g \sin\theta d\theta d\epsilon d\boldsymbol{\varsigma}^1, \tag{268}$$

where θ, ϵ are angles characterizing the encounter, $rg \sin\theta d\theta d\epsilon$ is the volume element in the three-dimensional space of positions $\boldsymbol{\xi}_1$ (see: Fig: 9). We need further only some invariance properties of this operator.

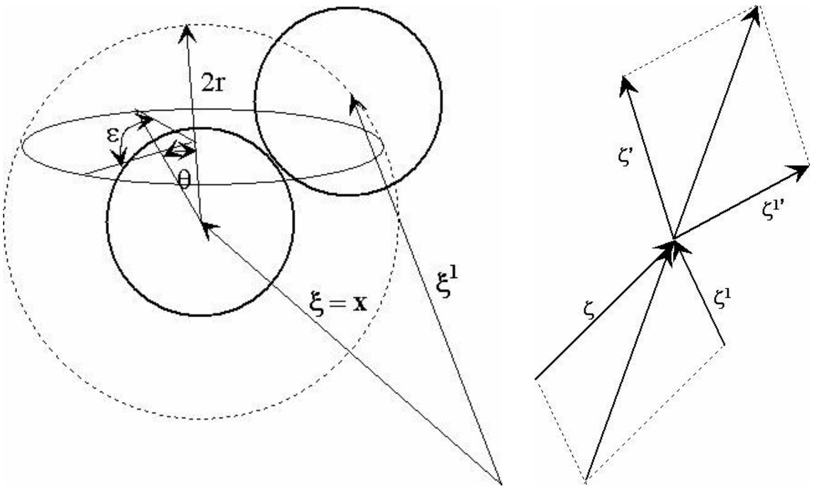

Fig. 9: *Geometry and kinematics of the encounter – constuction of the collision operator*

On the basis of the kinetic theory described by the Boltzmann equation we construct a series of macroscopic models which are supposed to yield *approximate solutions* for the phase density f. To this aim, we construct macroscopic fields and macroscopic field equations and this construction is based on expansions using the Knudsen number as a small parameter.

Most macroscopic thermodynamic fields are formed by taking *moments* of the phase density. The generic moment has the form

$$F_{i_1 i_2 \ldots i_N} = \int m \varsigma_{i_1} \varsigma_{i_1} \ldots \varsigma_{i_N} f d\boldsymbol{\varsigma}, \tag{269}$$

where $\varsigma_{i_\alpha}, i_\alpha = 1, 2, 3$ are Cartesian coordinates of the velocity vector $\boldsymbol{\varsigma}$. Thus we have in particular

$$\begin{aligned} \text{mass density} \qquad F &= \int m f d\boldsymbol{\varsigma} = \rho, \\ \text{momentum density} \quad F_i &= \int m \varsigma_i f d\boldsymbol{\varsigma} = \rho v_i. \end{aligned} \tag{270}$$

It is convenient to use in definitions of moments the so-called *peculiar velocity* $\mathbf{C} = \boldsymbol{\varsigma} - \mathbf{v}$ for which

$$\int m C_i f d\boldsymbol{\varsigma} = 0.$$

We use as well the following *internal moments*

$$\rho_{i_1 i_2 \ldots i_N} = \int m C_{i_1} C_{i_2} \ldots C_{i_N} f d\boldsymbol{\varsigma}. \tag{271}$$

The first few moments and internal moments have their canonical notation and names that suggest their interpretation:

$\frac{1}{2}F_{ii} = \rho\left(\varepsilon + \frac{1}{2}v^2\right)$	- energy density	$\frac{1}{2}\rho_{ii} = \rho\varepsilon$	- internal energy density
F_{ij}	- momentum flux	$-\rho_{ij} = t_{ij}$	- Cauchy stress tensor
$\frac{1}{2}F_{ijj}$	- energy flux	$\frac{1}{2}\rho_{ijj} = q_i$	- heat flux.

The definition of the peculiar velocity yields simple relations between the moments and the internal moments

$$\begin{aligned}
F &= \rho, \\
F_i &= \rho v_i, \\
F_{ij} &= \rho_{ij} + \rho v_i v_j, \\
F_{ijk} &= \rho_{ijk} + 3\rho_{(ij}v_{k)} + \rho v_i v_j v_k, \\
F_{ijkl} &= \rho_{ijkl} + 4\rho_{(ijk}v_{l)} + 6\rho_{(ij}v_k v_{l)} + \rho v_i v_j v_k v_l,
\end{aligned} \tag{272}$$

Round brackets indicate symmetrization, i.e. the sum of the permutations of all N indices divided by $N!$. It is clearly seen that fluxes in the above relations have the same structure as fluxes in phenomenological local balance equations

$$\begin{aligned}
F_{ij} &= \rho v_i v_j - t_{ij}, \\
\tfrac{1}{2}F_{ijj} &= \rho\left(\varepsilon + \tfrac{1}{2}v^2\right)v_i + q_i - t_{ij}v_j.
\end{aligned} \tag{273}$$

In a monatomic ideal gas $t_{ii} = -3p$ and, consequently,

$$p = \frac{2}{3}\rho\varepsilon. \tag{274}$$

This is the relation between the thermal and caloric equations of state in a monatomic gas which we were discussing in the previous Lecture. In monatomic ideal gases we have as well the following thermal state equation $\varepsilon = \frac{3}{2}\frac{k}{m}T$, and this yields

$$\frac{3}{2}\frac{kT}{m} = \frac{1}{\rho}\int \frac{m}{2}C^2 f d\mathbf{c}. \tag{275}$$

This relation may be used as the definition of the temperature in the kinetic theory of ideal monatomic gases.

Multiplication of the Boltzmann equation by a generic function $\psi(t, \mathbf{x}, \boldsymbol{\varsigma})$ and integration over all microscopic velocities $\boldsymbol{\varsigma}$ yields the balance equation for the mean value $\bar{\psi}(t, \mathbf{x})$ defined by the relation

$$\rho\bar{\psi}(t, \mathbf{x}) = \int \psi(t, \mathbf{x}, \boldsymbol{\varsigma})\, f(t, \mathbf{x}, \boldsymbol{\varsigma})\, d\boldsymbol{\varsigma}. \tag{276}$$

The balance equation for $\bar{\psi}$ is derived under the assumption that the phase density $f(t, \mathbf{x}, \boldsymbol{\varsigma})$ falls rapidly for large values of $|\boldsymbol{\varsigma}|$ which means that the probability of appearance of particles with large velocities decays sufficiently rapidly as $|\boldsymbol{\varsigma}| \to \infty$. Then we obtain

$$\begin{aligned}
&\frac{\partial\rho\bar{\psi}}{\partial t} + \frac{\partial\rho\overline{(\psi\varsigma_i)}}{\partial x_i} - \overline{\rho(b_i + i_i)\frac{\partial\psi}{\partial\varsigma_i}} = \\
&= \overline{\rho\left(\frac{\partial\psi}{\partial t} + \varsigma_i\frac{\partial\psi}{\partial x_i}\right)} + \frac{1}{4}\int\left(\psi + \psi^1 - \psi' - \psi^{1'}\right)\left(f'f^{1'} - ff^1\right) rg\sin\theta d\theta d\boldsymbol{\varsigma}^1 d\boldsymbol{\varsigma}.
\end{aligned} \tag{277}$$

Of course, the third term represents the supply due to external and inertial forces, while the right-hand side is the production (source).

In derivation of macroscopic equations for ideal gases we need balance equations of moments of microscopic velocities. We set

$$\psi = m\varsigma_{i_1}\varsigma_{i_2}...\varsigma_{i_N}. \tag{278}$$

It follows

$$\frac{\partial F_{i_1...i_N}}{\partial t}+\frac{\partial F_{i_1...i_N j}}{\partial x_j}-NF_{(i_1...i_{N-1}}\left(f_{i_N)}+i^0_{i_N)}\right)-NF_{k(i_1...i_{N-1}}2\Omega_{i_N)k}=S_{i_1...i_N}, \tag{279}$$

where i^0_j is the part of the inertial acceleration i_j that is independent of the velocity $\boldsymbol{\varsigma}$. The right-hand side follows from the production by collisions. The symmetry of the collision operator clearly seen in (277) yields

$$S=0, \quad S_i=0, \quad S_{ii}=0. \tag{280}$$

These are, of course, consequences of the mass, momentum and energy conservations during the collision.

We write the equations (279) in the explicit form for the first thirteen moments: $F=\rho$, $F_i=\rho v_i$, F_{ij} and F_{ijj}. We have

$$\begin{aligned}
&\frac{\partial \rho}{\partial t}+\frac{\partial\left(\rho v_i\right)}{\partial x_i}=0,\\
&\frac{\partial\left(\rho v_i\right)}{\partial t}+\frac{\partial F_{ij}}{\partial x_j}-\rho\left(b_i+i^0_i\right)-2\rho v_k\Omega_{ik}=0,\\
&\frac{\partial F_{ij}}{\partial t}+\frac{\partial F_{ijk}}{\partial x_k}-2\rho v_{(i}\left(b_{j)}+i^0_{j)}\right)-4F_{k(i}\Omega_{j)k}=S_{\langle ij\rangle},\\
&\frac{\partial F_{ijj}}{\partial t}+\frac{\partial F_{ijjk}}{\partial x_k}-3F_{(ij}\left(b_{j)}+i^0_{j)}\right)-6F_{k(ij}\Omega_{j)k}=S_{ijj},
\end{aligned} \tag{281}$$

where the traceless (deviatoric) part of the symmetric tensor S_{ij} is defined as follows

$$S_{\langle ij\rangle}=S_{ij}-\frac{1}{3}S_{kk}\delta_{ij}. \tag{282}$$

In this explicit form, it becomes clear that the first two equations and the trace of the third equation represent the macroscopic conservation laws of mass, momentum and energy. Contributions of inertial forces have the familiar form known in continuum thermodynamics.

The remaining equations are balance laws for the traceless (deviatoric) part of the momentum flux F_{ij} and the energy flux F_{ijj}. These equations are not conservation laws because they contain productions due to collisions. Simultaneously, they contain explicit contributions of inertial forces. This is a very important property because it yields the answer to the question if the requirement of material objectivity follows from the above construction of the macroscopic thermodynamical model.

The set (281) forms the foundation of the model based on the fields $\rho, v_i, F_{ij}, F_{ijj}$. However, it is not yet the set of field equations as the fluxes $F_{\langle ijk\rangle}$ and F_{ijjk} as well as productions $S_{\langle ij\rangle}, S_{ijj}$ are not specified. Even in the simplest case of a linear isotropic representation for productions

$$\begin{aligned} S_{\langle ij\rangle} &= -\frac{1}{\tau}t_{\langle ij\rangle} = -\frac{1}{\tau}\left(F_{\langle ij\rangle} - \rho v_{\langle i}v_{j\rangle}\right), \\ S_{ijj} &= -\frac{4}{3\tau}q_i = -\frac{2}{3\tau}\left(F_{ijj} - 3F_{(ij}v_{j)} - \rho v_i v^2\right), \end{aligned} \tag{283}$$

which appears for the simplest case of the so-called Maxwellian molecules, we have to define constitutive relations for the above mentioned fluxes. τ in the above relations denotes the mean time of the free flight and it is the same characteristic time which appears in the definition of Knudsen number. This constitutes the *closure* problem of the kinetic theory which we proceed to discuss.

Let us begin with a definition proposed by L. Boltzmann for the entropy and the entropy flux. If we insert[11]

$$\psi = -k\left(\ln\frac{f}{y} - 1\right), \tag{284}$$

into the general balance equation (277), we obtain

$$\begin{aligned} &\frac{\partial\left(-k\int f\ln f d\boldsymbol{\varsigma}\right)}{\partial t} + \frac{\partial\left(-k\int \varsigma_i f\ln f d\boldsymbol{\varsigma}\right)}{\partial x_i} = \\ &= \frac{m}{4}\int \ln\frac{f' f^{1\prime}}{f f^1}\left(f' f^{1\prime} - f f^1\right) rg\sin\theta d\theta d\varepsilon d\boldsymbol{\varsigma}^1 d\boldsymbol{\varsigma}. \end{aligned} \tag{285}$$

It is easy to observe that the right-hand side in the above equation is always nonnegative. This property of the collision operator is called the *H-Theorem* of L. Boltzmann and it motivates the second law of thermodynamics. We have already mentioned that this Theorem was vehemently criticized by many physicists contemporary to Boltzmann as contradicting Poincare's recurrence Theorem (see: Lecture 3). It is now clear that this property is the consequence of the probabilistic element of Boltzmann's derivation which appears in the assumption on the molecular chaos.

Bearing the above property in mind, we can introduce the following definitions

$\eta = -\frac{k}{\rho}\int f\left(\ln\frac{f}{y} - 1\right) d\boldsymbol{\varsigma}$ – as the specific entropy,
$\varphi_i = -k\int \varsigma_i f\left(\ln\frac{f}{y} - 1\right) d\boldsymbol{\varsigma}$ – as the entropy flux,
$\hat{\eta} = \frac{k}{4}\int \ln\frac{f' f^{1\prime}}{f f^1}\left(f' f^{1\prime} - f f^1\right) rg\sin\theta d\theta d\varepsilon d\boldsymbol{\varsigma}^1 d\boldsymbol{\varsigma}$ – as the entropy production.

(286)

---

[11] The constant $1/y$ is introduced to eliminate the so-called Gibbs paradox of classical statistical mechanics. It has the interpretation of the smallest element in $(\mathbf{x}, \boldsymbol{\varsigma})$ - space that can accomodate a position $\mathbf{x}$ and a velocity $\boldsymbol{\varsigma}$. It is equal to $h^3/m^3/(2s+1)$, where h is Planck's constant and $sh/2\pi$ is the spin of an atom. The occurence of y and of the other constant in the definition (284) is unimportant for our considerations and it plays a role only in problems where the entropy constant is material (e.g. chemical reactions). For relations discussed in this Lecture one could use as well the definition $\psi = -k\ln f$.

The flux contains in this formulation both a convective part with an explicit dependence on the velocity as well as the intrinsic velocity-independent part. This is characteristic for the Eulerian description which follows from the derivation of macroscopic equations by means of the kinetic theory of gases. The entropy inequality follows from (285) in the form: *for all processes*

$$\frac{\partial \rho \eta}{\partial t} + \frac{\partial \varphi_i}{\partial x_i} \geq 0. \tag{287}$$

The separation of convective and nonconvective parts follows from the transformation to peculiar velocities which we present further.

The above inequality suggests the definition of the *thermodynamical equilibrium* in the kinetic approach (compare $(286)_3$)

$$\ln f_E + \ln f_E^1 = \ln f_E' + \ln f_E^{1\prime}. \tag{288}$$

for which the entropy production vanishes identically. Hence it is the *summation invariant* of the collision operator. However, we know already that there are only five such independent invariants: the atomic mass, momenta and energy. Therefore $\ln f_E$ must be their linear combination

$$\ln f_E = \alpha + \beta_i \varsigma_i + \gamma \varsigma^2, \tag{289}$$

where the coefficients α, β_i, γ must be determined from the conditions

$$\rho = \int m f_E d\boldsymbol{\varsigma}, \quad \rho v_i = \int m \varsigma_i f_E d\boldsymbol{\varsigma}, \quad \rho \frac{3}{2}\frac{kT}{m} = \int \frac{m}{2} C^2 f_E d\boldsymbol{\varsigma}. \tag{290}$$

After simple calculations we obtain

$$f_E = \frac{\rho}{m} \sqrt[3]{\frac{m}{2\pi kT}} e^{-\frac{m(\boldsymbol{\varsigma}-\mathbf{v})^2}{2kT}}. \tag{291}$$

This is the so-called *Maxwell distribution.*

The Maxwell distribution yields the vanishing entropy production for a large variety of fields $\rho(t,\mathbf{x}), v_i(t,\mathbf{x}), T(t,\mathbf{x})$. However, in order to satisfy the Boltzmann equation they must additionally satisfy the following field equations

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \frac{\partial \rho v_i}{\partial x_i} &= 0, \\ \rho\left(\frac{\partial v_i}{\partial t} + v_j \frac{\partial v_i}{\partial x_j}\right) + \frac{\partial \rho \frac{k}{m} T}{\partial x_i} &= \rho(b_i + i_i), \quad i_i = i_i^0 + 2\Omega_{ik} v_k, \\ \frac{\partial T}{\partial t}\delta_{ij} + 2T \frac{\partial v_{(i}}{\partial x_{j)}} &= 0, \\ \frac{\partial T}{\partial x_i} &= 0. \end{aligned} \tag{292}$$

Hence, in a monatomic gas equilibrium processes contain rigid rotations, isotropic expansions, a variety of density gradients, and a time dependent temperature whose gradient vanishes.

The extension of this equilibrium distribution to nonequilibrium situation of the thirteen moments: $F = \rho$, $F_i = \rho v_i$, F_{ij} and F_{ijj} has been proposed by H. Grad in 1949. He proposed to use the following expansion for the phase density f

$$f = \left(a + a_i \frac{\partial}{\partial \varsigma_i} + a_{ij} \frac{\partial^2}{\partial \varsigma_i \partial \varsigma_j} + a_{ijk} \frac{\partial^3}{\partial \varsigma_i \partial \varsigma_j \partial \varsigma_k} + ... \right) f_E. \tag{293}$$

Bearing relation (291) in mind, we obtain immediately

$$\begin{aligned} f = f_E & \left(a - a_i \frac{m}{kT} C_i + a_{ij} \left(\frac{m}{kT} \right)^2 \left(C_i C_j - \frac{kT}{m} \delta_{ij} \right) - \right. \\ & \left. - a_{ijk} \left(\frac{m}{kT} \right)^3 \left(C_i C_j C_k - \frac{kT}{m} \left(\delta_{ij} C_k + \delta_{kj} C_i + \delta_{ik} C_j \right) \right) + ... \right). \end{aligned} \tag{294}$$

This is the expansion of f in terms of Hermite polynomials. Its coefficients $a, a_i, a_{ij}, a_{ijk}, ...$ follow by insertion in (269). For thirteen moments, this yields the so-called *Grad distribution function*

$$f_G = f_E \left(1 - \frac{1}{2p} t_{\langle ij \rangle} \left(\frac{m}{kT} C_i C_j - \delta_{ij} \right) - \frac{1}{p} \frac{m}{kT} q_i C_i \left(1 - \frac{1}{5} \frac{m}{kT} C^2 \right) \right). \tag{295}$$

Substitution of this function in relations (286) yields

$$\begin{aligned} \eta &= \frac{k}{m} \ln \frac{T^{3/2}}{\rho} - \underline{\frac{t_{\langle ij \rangle} t_{\langle ij \rangle}}{4 p \rho T}} - \underline{\frac{q_i q_i}{5 p^2 T}}, \\ \varphi_i &= \rho \eta v_i + h_i, \quad h_i = \frac{q_i}{T} + \underline{\frac{2}{5pT} t_{\langle ij \rangle} q_j}. \end{aligned} \tag{296}$$

Hence both the entropy and the entropy flux contain a dependence on $t_{\langle ij \rangle}$ and q_i which measure the deviation from the thermodynamical equilibrium. In addition, the nonconvective entropy flux h_i is not proportional to q_i/T but it contains a term proportional to $t_{\langle ij \rangle} q_j$ as well. This is the challenge to the phenomenological thermodynamics and it is resolved, as we see in the next Lecture, by the *extended thermodynamics* which we present in the next Lecture.

We complete the presentation of the construction of the macroscopic thirteen fields model based on the kinetic theory by the derivation of constitutive relations. As already mentioned, we need them in order to transform equation (281) into field equations for the following thirteen fields $\rho \equiv F$, $v_i \equiv \frac{1}{\rho} F_i$, $T \equiv \frac{m}{3 \rho k} \left(F_{ii} - \rho v^2 \right)$, $t_{\langle ij \rangle} \equiv - \left(F_{\langle ij \rangle} - \rho v_{\langle i} v_{j \rangle} \right)$, $q_i \equiv \frac{1}{2} \left(F_{ijj} - 3 F_{ij} v_j + 2 v_i v^2 \right)$. We accept relations (283) as constitutive relations for productions, i.e.

$$S_{\langle ij \rangle} = - \frac{1}{\tau} t_{\langle ij \rangle}, \quad S_{ijj} = - \frac{4}{3\tau} q_i. \tag{297}$$

Consequently, we have to add relations for $\rho_{\langle ij \rangle k} \equiv F_{\langle ij \rangle k} - 3 \rho_{(\langle ij \rangle} v_{k)} - \rho v_{\langle i} v_{j \rangle} v_k$ and $\rho_{ijjk} \equiv F_{ijjk} - 4 \rho_{(ijj} v_{k)} - 6 \rho_{(ij} v_j v_{k)} - \rho v_i v_k v^2$. In terms of peculiar velocities they have the following form

$$\rho_{\langle ij \rangle k} = \int m C_{\langle i} C_{j \rangle} C_k f d\boldsymbol{\varsigma}, \quad \rho_{ijjk} = \int m C_i C^2 C_k f d\boldsymbol{\varsigma}. \tag{298}$$

We substitute now the Grad distribution (295) in these relations. It follows

$$\begin{aligned}
\rho_{\langle ij\rangle k} &= \frac{2}{5}\left(q_i\delta_{jk} + q_j\delta_{ik} - \frac{2}{3}q_k\delta_{ij}\right), \\
\rho_{ijjk} &= 5p\frac{kT}{m}\delta_{ij} - \frac{7}{2}t_{\langle pq\rangle}\frac{kT}{m}\left(\delta_{ip}\delta_{jq} + \delta_{iq}\delta_{jp}\right).
\end{aligned} \tag{299}$$

Substitution of these relations in $(281)_{3,4}$ yields for the deviatoric part of stresses

$$\begin{aligned}
t_{\langle ij\rangle} = {} & 2p\tau\left(\underline{\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}} + \frac{2}{5p}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}}\right) - \\
& -\tau\left(\underbrace{\dot{t}_{\langle ij\rangle} + 2t_{\langle n\,\langle i\rangle}\frac{\partial v_{j\rangle}}{\partial x_n} - 4t_{\langle n\,\langle i\rangle}\Omega_{j\rangle n}}\right) - \boxed{\tau t_{\langle ij\rangle}\tfrac{\partial v_n}{\partial x_n}},
\end{aligned} \tag{300}$$

and for the heat flux

$$\begin{aligned}
q_i = {} & -\frac{15}{4}\frac{kp\tau}{m}\left(\underline{\frac{\partial T}{\partial x_i}} + \frac{2}{5}\frac{T}{p}\frac{\partial t_{\langle in\rangle}}{\partial x_n}\right) - \\
& -\frac{3}{2}\tau\left(\underbrace{\dot{q}_i + q_n\frac{\partial v_i}{\partial x_n} - 2q_n\Omega_{in}}\right) - \\
& -\boxed{\tfrac{3}{2}\tau\left(\tfrac{7}{5}q_i\tfrac{\partial v_n}{\partial x_n} + \tfrac{4}{5}q_n\tfrac{\partial v_{(i}}{\partial x_{n)}} - \tfrac{7}{2}\tfrac{k}{m}t_{\langle in\rangle}\tfrac{\partial T}{\partial x_n} - \tfrac{1}{\rho}t_{\langle ik\rangle}\tfrac{\partial t_{\langle kn\rangle}}{\partial x_n} + \tfrac{1}{\rho}t_{\langle in\rangle}\tfrac{\partial p}{\partial x_n}\right)}.
\end{aligned} \tag{301}$$

First of all, the terms in boxes are nonlinear. As we neglected already nonlinear contributions to productions their contribution to field equations is not reliable. Therefore, we neglect them as well.

Secondly, the braced terms contain the combinations of terms which are altogether objective provided we tolerate some nonlinear contributions. However, they are different from those which would follow if we were using Lie derivatives discussed in Lecture 1:

$$\mathcal{L}_{\mathrm{v}}t_{\langle ij\rangle} = \dot{t}_{\langle ij\rangle} - 2t_{\langle n\,\langle i\rangle}\frac{\partial v_{j\rangle}}{\partial x_n}, \mathcal{L}_{\mathrm{v}}q_i = \dot{q}_i - q_n\frac{\partial v_i}{\partial x_n}. \tag{302}$$

Combinations $4t_{\langle n\,\langle i\rangle}\left(\frac{\partial v_{j\rangle}}{\partial x_n} - \Omega_{j\rangle n}\right)$, $2q_n\left(\frac{\partial v_i}{\partial x_n} - \Omega_{in}\right)$ are objective (compare (25)), but the form of constitutive relations following from the kinetic theory is different from this which we would obtain extending phenomenological equations by addition of evolutionary contributions. This makes the extensions proposed, for example, by Cattaneo for the heat flux equation not compatible with the kinetic theory. We return to this problem in the next Lecture.

If we introduce the notation

$$\mu = p\tau \equiv \rho\frac{kT}{m}\tau, \quad K = \frac{15}{4}\frac{k}{m}p\tau \equiv \frac{15}{4}\frac{k}{m}\left(\rho\frac{kT}{m}\tau\right), \tag{303}$$

then (300) and (301) lead to the following constitutive relations

$$
\begin{aligned}
t_{\langle ij\rangle} &= 2\mu\left(\underline{\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}}+\frac{2}{5p}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}}\right)-\tau\left(\mathcal{L}_{\mathrm{v}}t_{\langle ij\rangle}+4t_{\langle n\langle i\rangle}\left(\frac{\partial v_{j\rangle}}{\partial x_n}-\Omega_{j\rangle n}\right)\right), \qquad (304)\\
q_i &= K\left(\underline{\frac{\partial T}{\partial x_i}}+\frac{2}{5}\frac{T}{p}\frac{\partial t_{\langle in\rangle}}{\partial x_n}\right)-\frac{3}{2}\tau\left(\mathcal{L}_{\mathrm{v}}q_i+2q_n\left(\frac{\partial v_i}{\partial x_n}-\Omega_{in}\right)\right).
\end{aligned}
$$

Clearly, if we make the assumption that both μ and K remain finite in the limit $\tau\rightarrow 0$, the above constitutive relations are identical with the classical Navier-Stokes and Fourier laws if we leave out couplings not underlined in the first terms on the right-hand sides. Otherwise, we have to deal with evolution equations for deviatoric stresses $t_{\langle ij\rangle}$ and for heat flux q_i. In the first case the speeds of shear and thermal pulses propagate with an infinite speed, while in the evolutionary case both speeds are finite. This will be also the subject of discussion of the next Lecture.

Summing up, let us note that the kinetic theory of rarified gases yields, by means of the Grad distribution function and in the simplest linear approximation, the first order field equations for thirteen fields ρ, v_i, ε, $t_{\langle ij\rangle}$, q_i. In addition, it produces the entropy inequality with the entropy density η and the entropy flux h_i dependent on these fields. Macroscopic equations obtained in this way coincide with phenomenological equations of the Navier-Stokes-Fourier viscous fluid and, simultaneously, provide an additional physical insight by revealing the structure of the nonequilibrium entropy. The structure of this kinetic model motivates a phenomenological construction of the so-called *extended thermodynamics of ideal gases* which is the subject of the next Lecture.

For the further use we collect the results of the kinetic theory of thirteen moments:

1. Balance equations

$$
\begin{aligned}
&\frac{\partial\rho}{\partial t}+\frac{\partial\left(\rho v_i\right)}{\partial x_i}=0,\\
&\frac{\partial}{\partial t}\left(\rho v_i\right)+\frac{\partial}{\partial x_j}\left(\rho v_i v_j+\rho_{ij}\right)-\rho\left(b_i+i_i^0\right)-2\rho v_k\Omega_{ik}=0,\\
&\frac{\partial}{\partial t}\left(\rho v_i v_j+\rho_{ij}\right)+\frac{\partial}{\partial x_k}\left(3\rho_{(ij}v_{k)}+\rho v_i v_j v_k+\rho_{ijk}\right)- \qquad (305)\\
&-2\rho v_{(i}\left(b_{j)}+i_{j)}^0\right)-4F_{k(i}\Omega_{j)k}=S_{\langle ij\rangle},\\
&\frac{\partial}{\partial t}\left(\rho v_i v^2+3\rho_{ij}v_j+\rho_{ijj}\right)+\frac{\partial}{\partial x_k}\left(\rho v_i v_k v^2+6\rho_{ij}v_j v_k+4\rho_{ijj}v_k+\rho_{ijjk}\right)\\
&-3F_{(ij}\left(b_{j)}+i_{j)}^0\right)-6F_{k(ij}\Omega_{j)k}=S_{ijj},
\end{aligned}
$$

where ρ, v_i, $\frac{1}{3}\rho_{ii}=p$, $\rho_{\langle ij\rangle}=-t_{\langle ij\rangle}$, $\frac{1}{2}\rho_{jji}=q_i$ are **thirteen fields**, and $\rho_{\langle ij\rangle k}$, ρ_{ijjk}, $S_{\langle ij\rangle}$, S_{ijj} are constitutive functions.

2. Grad distribution function

$$f_G = f_E \left(1 - \frac{1}{2p} t_{\langle ij \rangle} \left(\frac{m}{kT} C_i C_j - \delta_{ij} \right) - \frac{1}{p} \frac{m}{kT} q_i C_i \left(1 - \frac{1}{5} \frac{m}{kT} C^2 \right) \right), \tag{306}$$

where the Maxwell distribution f_E is given by the relation

$$f_E = \frac{\rho}{m} \sqrt[3]{\frac{m}{2\pi kT}} e^{-\frac{m(\boldsymbol{\varsigma} - \mathbf{v})^2}{2kT}}. \tag{307}$$

2. Constitutive relations for fluxes $\rho_{\langle ij \rangle k}, \rho_{ijjk}$

$$\begin{aligned} \rho_{\langle ij \rangle k} &= \frac{2}{5} \left(q_i \delta_{jk} + q_j \delta_{ik} - \frac{2}{3} q_k \delta_{ij} \right), \\ \rho_{ijjk} &= 5p \frac{kT}{m} \delta_{ij} - \frac{7}{2} t_{\langle pq \rangle} \frac{kT}{m} \left(\delta_{ip} \delta_{jq} + \delta_{iq} \delta_{jp} \right). \end{aligned} \tag{308}$$

3. Constitutive relations for sources (productions)

$$S_{\langle ij \rangle} = \frac{1}{\tau} \rho_{\langle ij \rangle} \equiv -\frac{1}{\tau} t_{\langle ij \rangle}, \quad S_{ijj} = -\frac{2}{3\tau} \rho_{jji} \equiv -\frac{4}{3\tau} q_i. \tag{309}$$

4. Entropy inequality and its constitutive relations for the entropy and the entropy flux

$$\frac{\partial \rho \eta}{\partial t} + \frac{\partial \varphi_i}{\partial x_i} \geq 0, \quad \eta = \frac{k}{m} \ln \frac{T^{3/2}}{\rho} - \frac{t_{\langle ij \rangle} t_{\langle ij \rangle}}{4p\rho T} - \frac{q_i q_i}{5p^2 T}, \tag{310}$$

$$\varphi_i = \rho \eta v_i + h_i, \quad h_i = \frac{q_i}{T} + \frac{2}{5pT} t_{\langle ij \rangle} q_j.$$

It should be mentioned as well that neither the model of thirteen moments nor Grad's method of construction of the nonequilibrium phase density f_G exhaust the results based on the Boltzmann equation. There exist numerous attempts to extend the hierarchy of equations to higher moments on the basis of the assumption that such an extension improves the approximation of a true solution f of the Boltzmann equation. Some of these extensions seem to be physically meaningful and confirmed by, for instance, light scattering experiments. However, there exists no proof of convergence of such a hierarchy. Even worse, some of such models, for instance the so-called Burnett model, corresponding to the Chapman-Enskog expansion of the Boltzmann equation with respect to the Knudsen number, Kn, as a small parameter (to the order $(Kn)^2$), possess instabilities which do not correspond to any real phenomena.

Lecture 7: Extended thermodynamics: general structure, thermodynamics of ideal gases

As indicated in the previous Lecture, we intend to construct a continuum thermodynamical model of a system whose set of fields goes beyond this of ordinary continuum thermodynamics i.e. beyond the set of densities of mass, momentum and energy. The purpose of these additional fields is to describe deviations from the local thermodynamical equilibrium. We have demonstrated an example of such a model arising from the kinetic theory of ideal gases and this example shows that typical extensions would be fluxes of momentum and energy.

Thermodynamical modeling for an extended set of fields should possess the following essential ingredients

- fundamental equations are of balance type; this yields mathematically a possibility of weak solutions and shock waves,
- constitutive relations (closure problem for balance equations) are local in space and time which yields sets of quasilinear field equations of the first order,
- second law of thermodynamics consists of the entropy inequality and conditions on ideal walls in which the entropy density is concave and this, in turn, yields symmetric hyperbolic field equations (well-posed Cauchy initial value problems).

In this Lecture we first demonstrate a general structure of such a modeling procedure and then we illustrate this procedure with an example of ideal gas model. This model motivates the general procedure and it can be easily compared with results of the kinetic theory.

Let us begin with an analysis of a thermodynamical model which describes n-dimensional vector field $\mathbf{w} \in \mathcal{V}^n$ as a function of spatial and temporal variables $(\mathbf{x}, t)$. This field is assumed to satisfy balance equations

$$\frac{\partial \mathbf{F}_0}{\partial t} + \frac{\partial \mathbf{F}_k}{\partial x_k} = \hat{\mathbf{f}}, \quad \mathbf{F}_0, \mathbf{F}_1, \mathbf{F}_2, \mathbf{F}_3, \hat{\mathbf{f}} \in \mathcal{V}^n, \tag{311}$$

where *densities* $\mathbf{F}_0$, *fluxes* $\mathbf{F}_k, k = 1, 2, 3$, and *productions* $\hat{\mathbf{f}}$ are assumed to be only functions of fields $\mathbf{w}$. This is a particular case of the structure investigated in Lecture 3, where constitutive variables $\mathfrak{w} \in \mathcal{V}^N$ were assumed to contain not only fields $\mathbf{w}$ but also some derivatives of fields. The constitutive dependence on fields alone is the first characteristic feature of the extended thermodynamics and this feature was already discovered in kinetic models which we discussed in the previous Lecture. Hence, *field equations of extended thermodynamics* are provided by constitutive relations of the form

$$\mathbf{F}_0 = \mathbf{F}_0(\mathbf{w}), \quad \mathbf{F}_k = \mathbf{F}_k(\mathbf{w}), \quad k = 1, 2, 3, \quad \hat{\mathbf{f}} = \hat{\mathbf{f}}(\mathbf{w}). \tag{312}$$

For this reason, we say that constitutive relations of extended thermodynamics are *local* in space and time: they depend on fields in the same space-time point as the constitutive quantities without any constitutive influence of gradients or time derivatives of fields.

All solutions of field equations which follow by the above *closure* are called *thermodynamical processes.*

According to procedures which we were already discussing in this course there are some principles which restrict the class of thermodynamical processes. The main of them are as follows

- the entropy inequality,
- the convexity,
- the principle of relativity.

The combination of the first two principle is called the *entropy principle* and it is the most essential part of the *second law of thermodynamics.*

As we know already thermodynamical processes are *admissible* if the following inequality is fulfilled

$$\frac{\partial \rho\eta}{\partial t}+\frac{\partial \varphi_k}{\partial x_k}\geq 0, \quad \rho\eta=\rho\eta\left(\mathbf{w}\right), \quad \varphi_k=\varphi_k\left(\mathbf{w}\right). \tag{313}$$

The principle of convexity has then the form

$$\forall \mathbf{z}\in\mathcal{V}^n:\mathbf{z}\cdot\frac{\partial^2\rho\eta}{\partial\mathbf{w}\partial\mathbf{w}}\mathbf{z}<0. \tag{314}$$

Finally, the principle of relativity within the frame of nonrelativistic models means that field equations and the entropy inequality have the same form in all Galilean frames.

Let us investigate the condition of thermodynamical admissibility. According to Liu's Theorem we can introduce the Lagrange multipliers $\mathbf{\Lambda}\left(\mathbf{w}\right)\in\mathcal{V}^n$ such that the inequality

$$\frac{\partial \rho\eta}{\partial t}+\frac{\partial \varphi_k}{\partial x_k}-\mathbf{\Lambda}\cdot\left(\frac{\partial \mathbf{F}_0}{\partial t}+\frac{\partial \mathbf{F}_k}{\partial x_k}-\hat{\mathbf{f}}\right)\geq 0, \tag{315}$$

holds for all fields and not only for solutions of field equations. The solution of this inequality is as follows

$$\frac{\partial \rho\eta}{\partial \mathbf{w}}=\left(\frac{\partial \mathbf{F}_0}{\partial \mathbf{w}}\right)^T\mathbf{\Lambda}, \quad \frac{\partial \varphi_k}{\partial \mathbf{w}}=\left(\frac{\partial \mathbf{F}_k}{\partial \mathbf{w}}\right)^T\mathbf{\Lambda}, \quad \mathbf{\Lambda}\cdot\hat{\mathbf{f}}\geq 0. \tag{316}$$

The first two conditions can be also written in the form

$$d\left(\rho\eta\right)=\mathbf{\Lambda}\cdot d\mathbf{F}_0, \quad d\varphi_k=\mathbf{\Lambda}\cdot d\mathbf{F}_k. \tag{317}$$

Hence the multipliers are independent of the choice of the fields $\mathbf{w}$. In particular, assuming that $\mathbf{F}_0$ is not degenerate we can choose

$$\mathbf{w}=\mathbf{F}_0\Longrightarrow\frac{\partial\rho\eta}{\partial\mathbf{w}}=\mathbf{\Lambda}\quad\Longrightarrow\quad\frac{\partial\mathbf{\Lambda}}{\partial\mathbf{w}}=\frac{\partial^2\rho\eta}{\partial\mathbf{w}\partial\mathbf{w}}. \tag{318}$$

Consequently, the derivatives $\frac{\partial\mathbf{\Lambda}}{\partial\mathbf{w}}$ form the symmetric and negative definite (principle of convexity!) matrix. This means that the map $\mathbf{w}\rightarrow\mathbf{\Lambda}$ is globally invertible. By doing such a change of variables we obtain the following transformed constitutive relations

$$\begin{aligned}\mathbf{F}_0&=\mathbf{F}_0\left(\mathbf{\Lambda}\right), \quad \mathbf{F}_k=\mathbf{F}_k\left(\mathbf{\Lambda}\right), \quad k=1,2,3, \quad \hat{\mathbf{f}}=\hat{\mathbf{f}}\left(\mathbf{\Lambda}\right). \\ \rho\eta&=\rho\eta\left(\mathbf{\Lambda}\right), \quad \varphi_k=\varphi_k\left(\mathbf{\Lambda}\right).\end{aligned} \tag{319}$$

Then relations (317) can be written in the following form

$$d\left(\rho\eta - \mathbf{\Lambda}\cdot\mathbf{F}_0\right) = -\mathbf{F}_0\cdot d\mathbf{\Lambda},\quad d\left(\varphi_k - \mathbf{\Lambda}\cdot\mathbf{F}_k\right) = -\mathbf{F}_k\cdot d\mathbf{\Lambda}. \tag{320}$$

Hence, one can introduce the *four-potential*

$$\mathbf{h}'\left(\mathbf{\Lambda}\right) \equiv \left\{h'_0, h'_k\right\} := \left\{\rho\eta - \mathbf{\Lambda}\cdot\mathbf{F}_0, \varphi_k - \mathbf{\Lambda}\cdot\mathbf{F}_k\right\}, \tag{321}$$

which specifies the constitutive relations of contributions to the left-hand side of field equations

$$\mathbf{F}_0 = -\frac{\partial h'_0}{\partial\mathbf{\Lambda}},\quad \mathbf{F}_k = -\frac{\partial h'_k}{\partial\mathbf{\Lambda}}. \tag{322}$$

Simultaneously

$$\rho\eta\left(\mathbf{\Lambda}\right) = h'_0 - \mathbf{\Lambda}\cdot\frac{\partial h'_0}{\partial\mathbf{\Lambda}},\quad \varphi_k\left(\mathbf{\Lambda}\right) = h'_k - \mathbf{\Lambda}\cdot\frac{\partial h'_k}{\partial\mathbf{\Lambda}}. \tag{323}$$

The residual inequality has the form

$$\mathbf{\Lambda}\cdot\hat{\mathbf{f}}\left(\mathbf{\Lambda}\right) \geq 0. \tag{324}$$

The existence of the four-potential (321), (322) whose components are also known as *generators* and the residual inequality (324) exhaust the consequences of the entropy inequality.

Integrability conditions for $\mathbf{h}'\left(\mathbf{\Lambda}\right)$ yield the symmetry of the matrices

$$\frac{\partial\mathbf{F}_0}{\partial\mathbf{\Lambda}},\quad \frac{\partial\mathbf{F}_k}{\partial\mathbf{\Lambda}}. \tag{325}$$

These conditions, extensions of Maxwell relations of ordinary thermodynamics, provide severe restrictions on the functions $\mathbf{F}_0, \mathbf{F}_k$.

Substitution of (322) in field equations (311) yields

$$-\frac{\partial^2 h'_0}{\partial\mathbf{\Lambda}\partial\mathbf{\Lambda}}\frac{\partial\mathbf{\Lambda}}{\partial t} - \frac{\partial^2 h'_k}{\partial\mathbf{\Lambda}\partial\mathbf{\Lambda}}\frac{\partial\mathbf{\Lambda}}{\partial x_k} = \hat{\mathbf{f}}, \tag{326}$$

which means that the system is *symmetric* as the coefficients are Hessian matrices. This symmetry is visible if we choose Lagrange multipliers $\mathbf{\Lambda}$ as fields. For this reason these fields are called *main fields.* Together with the convexity assumption this yields the conclusion that the system is **symmetric hyperbolic**.

Hyperbolicity of the set of field equations guarantees finite speeds of propagation of disturbances. Moreover, it yields a desirable mathematical property of the well-posedness of Cauchy problems which means local existence, uniqueness, and continuous dependence of the solutions on the data (stability).

In order to see that disturbances propagate with finite speeds we investigate a wave front of an acceleration wave. This is the surface on which fields, say $\mathbf{\Lambda}$, are continuous and which moves with the speed c in the normal direction and carries a discontinuity of the first derivatives of fields. Hadamard compatibility conditions which we have mentioned in Lecture 1 (see: (51)) yield then

$$\left[\left[\frac{\partial\mathbf{\Lambda}}{\partial x_k}\right]\right] = n_k\delta\mathbf{\Lambda},\quad \left[\left[\frac{\partial\mathbf{\Lambda}}{\partial t}\right]\right] = -c\delta\mathbf{\Lambda}, \tag{327}$$

where n_k are components of the unit normal vector to the wave front, $\delta\mathbf{\Lambda}$ is the so-called amplitude of the discontinuity. Calculating the limits of the equation (326) on both sides of the front and subtracting we obtain

$$\left(\frac{\partial^2 h_0'}{\partial\mathbf{\Lambda}\partial\mathbf{\Lambda}}c - \frac{\partial^2 h_k'}{\partial\mathbf{\Lambda}\partial\mathbf{\Lambda}}n_k\right)\delta\mathbf{\Lambda} = 0. \tag{328}$$

Eigenvalues of this eigenvalue problem which follow from the *dispersion relation*

$$\det\left(\frac{\partial^2 h_0'}{\partial\mathbf{\Lambda}\partial\mathbf{\Lambda}}c - \frac{\partial^2 h_k'}{\partial\mathbf{\Lambda}\partial\mathbf{\Lambda}}n_k\right) = 0, \tag{329}$$

are real and finite due to the symmetry of the real Hessian matrices and nonsingularity of the matrix $\frac{\partial^2 h_0'}{\partial\mathbf{\Lambda}\partial\mathbf{\Lambda}}$. They determine speeds of propagation of *weak* disturbances, i.e. discontinuities of field derivatives with a simultaneous continuity of fields. Due to the hyperbolicity the corresponding eigenvectors which specify the amplitudes are linearly independent.

In order to explain the principle of relativity we have to recall some transformations we have discussed in Lecture 1 (compare formulae (24), (25), (26)). The most restrictive transformation is the Euclidean transformation (24) which follows from the isometry of the space of motions of classical Newtonian mechanics. In Table 8 we present three transformations in the representation in Cartesian coordinates which are of interest in this Lecture.

Table 8: *Transformations of Newtonian continuum mechanics*

transformation:	rotation of coordinates	Galilean transformation	Euclidean transformation
	$x_i^* = O_{ij}x_j$ $t^* = t,$ O_{ij} – const	$x_i^* = O_{ij}x_j + d_i t$ $t^* = t$ O_{ij}, d_i – const	$x_i^* = O_{ij}(t)\,x_j + c_i(t)$ $t^* = t$
name of the invariant object	tensor	Galilean tensor	objective tensor
velocity	$v_i^* = O_{ij}v_j$	$v_i^* = O_{ij}v_j + d_j$	$v_i^* = O_{ij}v_j + \dot{O}_{ij}x_j + \dot{c}_j$
acceleration	$a_i^* = O_{ij}a_j$	$a_i^* = O_{ij}a_j$	$a_i^* = O_{ij}a_j +$ $+\dot{O}_{ij}v_j + \ddot{O}_{ij}x_j + \ddot{c}_j$

An invariant object with respect to any of these transformations has the following transformation rule

$$T^*_{i_1\ldots i_A} = O_{i_1 j_1}\ldots O_{i_A j_A}T_{j_1\ldots j_A}. \tag{330}$$

Inspection of the classical momentum balance equation which yields in continuum mechanics the equation of motion shows that this equation is invariant with respect to the Galilean transformation but not with respect to the Euclidean transformation. The invariance follows from the property of acceleration which is the Galilean vector. Euclidean transformation which yields the noninertial frames of reference produces noninertial forces with which we were already dealing a few times in this course.

As extended thermodynamics contains additional balance equations replacing some classical constitutive relations (for instance, for the heat flux) we expect that these equations will be also Galilean invariant. This is the essence of the principle of relativity for such models.

The Eulerian description yields the natural velocity-dependent contribution to balance equations. Namely, the fluxes have the following form

$$\mathbf{F}_k = \mathbf{F}_0 v_k + \mathbf{G}_k, \quad \varphi_k = \rho\eta v_k + h_k, \tag{331}$$

where $\mathbf{G}_k, h_k$ are *nonconvective fluxes.*

However, this does not mean that $\mathbf{F}_0, \mathbf{G}_k, h_k$ are independent of the velocity. Let us write constitutive relations in the form

$$\begin{aligned} \mathbf{F}_0 &= \mathbf{F}_0\left(\mathbf{v},\mathbf{u}\right), \quad \mathbf{G}_k = \mathbf{G}_k\left(\mathbf{v},\mathbf{u}\right), \quad \hat{\mathbf{f}} = \hat{\mathbf{f}}\left(\mathbf{v},\mathbf{u}\right), \\ \rho\eta &= \rho\eta\left(\mathbf{v},\mathbf{u}\right), \quad h_k = h_k\left(\mathbf{v},\mathbf{u}\right), \quad \hat{\eta} = \hat{\eta}\left(\mathbf{v},\mathbf{u}\right), \end{aligned} \tag{332}$$

where the vector of field $\mathbf{w}$ has been split into $(\mathbf{v},\mathbf{u})$. Galilean transformation to $(\mathbf{v}^*,\mathbf{u}^*)$ yields the following form of these constitutive relations

$$\begin{aligned} \mathbf{F}_0^* &= \mathbf{F}_0\left(\mathbf{v}^*,\mathbf{u}^*\right), \quad \mathbf{G}_k^* = \mathbf{G}_k\left(\mathbf{v}^*,\mathbf{u}^*\right), \quad \hat{\mathbf{f}}^* = \hat{\mathbf{f}}\left(\mathbf{v}^*,\mathbf{u}^*\right), \\ \rho\eta^* &= \rho\eta\left(\mathbf{v}^*,\mathbf{u}^*\right), \quad h_k^* = h_k\left(\mathbf{v}^*,\mathbf{u}^*\right), \quad \hat{\eta}^* = \hat{\eta}\left(\mathbf{v}^*,\mathbf{u}^*\right), \end{aligned} \tag{333}$$

which is similar to material objectivity except that Galilean transformation instead of Euclidean transformation is used. The principle of relativity requires in addition that the field equations and the entropy balance equation in the two frames are equivalent, i.e.

$$\begin{aligned} \frac{\partial \mathbf{F}_0\left(\mathbf{v},\mathbf{u}\right)}{\partial t} + \frac{\partial\left[\mathbf{F}_0\left(\mathbf{v},\mathbf{u}\right)v_k + \mathbf{G}_k\left(\mathbf{v},\mathbf{u}\right)\right]}{\partial x_k} &= \hat{\mathbf{f}}\left(\mathbf{v},\mathbf{u}\right), \\ \frac{\partial \rho\eta\left(\mathbf{v},\mathbf{u}\right)}{\partial t} + \frac{\partial\left[\rho\eta\left(\mathbf{v},\mathbf{u}\right)v_k + h_k\left(\mathbf{v},\mathbf{u}\right)\right]}{\partial x_k} &= \hat{\eta}\left(\mathbf{v},\mathbf{u}\right), \end{aligned} \tag{334}$$

and

$$\begin{aligned} \frac{\partial \mathbf{F}_0\left(\mathbf{v}^*,\mathbf{u}^*\right)}{\partial t} + \frac{\partial\left[\mathbf{F}_0\left(\mathbf{v}^*,\mathbf{u}^*\right)v_k^* + \mathbf{G}_k\left(\mathbf{v}^*,\mathbf{u}^*\right)\right]}{\partial x_k} &= \hat{\mathbf{f}}\left(\mathbf{v}^*,\mathbf{u}^*\right), \\ \frac{\partial \rho\eta\left(\mathbf{v}^*,\mathbf{u}^*\right)}{\partial t} + \frac{\partial\left[\rho\eta\left(\mathbf{v}^*,\mathbf{u}^*\right)v_k^* + h_k\left(\mathbf{v}^*,\mathbf{u}^*\right)\right]}{\partial x_k} &= \hat{\eta}\left(\mathbf{v}^*,\mathbf{u}^*\right). \end{aligned} \tag{335}$$

The exploitation of this condition yields the existence of an $n \times n$ nonsingular matrix $\mathcal{X}\left(\mathbf{v}\right)$ such that we have the representations

$$\begin{aligned} \mathbf{F}_0\left(\mathbf{v},\mathbf{u}\right) &= \mathcal{X}\left(\mathbf{v}\right)\boldsymbol{\rho}_0\left(\mathbf{u}\right), \quad \mathbf{G}_k\left(\mathbf{v},\mathbf{u}\right) = \mathcal{X}\left(\mathbf{v}\right)\boldsymbol{\rho}_k\left(\mathbf{u}\right), \\ \hat{\mathbf{f}}\left(\mathbf{v},\mathbf{u}\right) &= \mathcal{X}\left(\mathbf{v}\right)\mathbf{S}\left(\mathbf{u}\right), \end{aligned} \tag{336}$$

where $\boldsymbol{\rho}_0\left(\mathbf{u}\right), \boldsymbol{\rho}_k\left(\mathbf{u}\right), \mathbf{S}\left(\mathbf{u}\right)$ are functions in the rest frame (i.e. for $\mathbf{v} \equiv \mathbf{0}$). These representations as well as the form of the matrix $\mathcal{X}\left(\mathbf{v}\right)$ have been found by T. Ruggeri in 1989[12]. The latter is as follows

$$\mathcal{X}\left(\mathbf{v}\right) = e^{\mathbf{A}^r v_r} = \mathbf{1} + \mathbf{A}^r v_r + \frac{1}{2}\mathbf{A}^r\mathbf{A}^s v_r v_s + ..., \tag{337}$$

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[12] T. Ruggeri; *Galilean invariance and entropy principle for systems of balance laws. The structure of extended thermodynamics, Cont. Mech. Thermodyn.*, **1**, 1989.

where $\mathbf{A}^r$ are constant matrices dependent on the tensorial character of the corresponding quantity and otherwise independent of the system.

The above decomposition for a symmetric tensor density of arbitrary rank A into velocity-dependent and internal parts has the following form in Cartesian coordinates

$$\begin{aligned} F_{i_1 \dots i_A} &= \rho_{i_1 \dots i_A} + \binom{A}{1} \rho_{(i_1 \dots i_{A-1}} v_{i_A)} + \binom{A}{2} \rho_{(i_1 \dots i_{A-2}} v_{i_{A-1}} v_{i_A)} + \dots + \\ &\quad + \binom{A}{A-1} \rho_{(i_1} v_{i_2} \dots v_{i_{A-1}} v_{i_A)} + \rho v_{i_1} v_{i_{A-1}} v_{i_A}, \end{aligned} \tag{338}$$

and similarly for $\boldsymbol{\rho}_k$ and $\mathbf{S}$.

This completes the presentation of general properties of extended thermodynamics which we need in this course.

We proceed to discuss the most important example motivating the strategy of constructing models by extended thermodynamics. We show the model of ideal nonrelativistic gases.

In order to be able to place the model among models of extended thermodynamics, we formulate the fundamental equations for ideal gases in the notation which we presented in the first part of this Lecture. Consequently, we choose the following fields describing the system

F – the mass density,

F_i – the momentum density,

F_{ij} – the momentum flux density, $F_{ij} = F_{ji}$,

$\frac{1}{2} F_{ijj}$ – the energy flux density.

We assume that these fields satisfy in an arbitrary noninertial frame the following balance equations

$$\begin{aligned} \frac{\partial F}{\partial t} + \frac{\partial F_k}{\partial x_k} &= 0, \\ \frac{\partial F_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} &= F \left(b_i + i_i^0 \right) + 2 F_k \Omega_{ik}, \\ \frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} &= \hat{f}_{\langle ij \rangle} + 2 F_{(i} \left(b_{j)} + i_{j)}^0 \right) + 4 F_{k(i} \Omega_{j)k}, \\ \frac{\partial F_{ijj}}{\partial t} + \frac{\partial F_{ijjk}}{\partial x_k} &= \hat{f}_{ijj} + 3 F_{(ij} \left(b_{j)} + i_{j)}^0 \right) + 6 F_{kjj} \Omega_{ik}. \end{aligned} \tag{339}$$

The vector $\mathbf{i}^0$ of the inertial acceleration is given by the relation

$$i_i^0 = \left(\dot{\Omega}_{ik} - \Omega_{ij} \Omega_{jk} \right) \left(x_k - c_k \right) - 2 \Omega_{ik} \dot{c}_k + \ddot{c}_k. \tag{340}$$

The above set of balance equations has very peculiar symmetry properties. Namely, the flux in the nth tensorial equation acts as the density in the (n+1)th tensorial equation. We shall see that this symmetry limits the applicability to monatomic ideal gases.

The mass balance equation $(339)_1$, the momentum balance equation $(339)_2$ and the trace of $(339)_3$ which is the energy balance equation are conservation laws. It means the productions in these equations are zero. Simultaneously, productions $\hat{f}_{\langle ij\rangle}$ and $\hat{f}_{ijj}$ indicate that remaining balance equations describe quantities which are not conserved.

In order to construct field equations we have to solve the closure problem. To this aim we postulate the following constitutive equations

$$\begin{aligned} F_{\langle ij\rangle k} &= F_{\langle ij\rangle k}\left(F, F_i, F_{ij}, F_{ijj}\right), \\ F_{ijjk} &= F_{ijjk}\left(F, F_i, F_{ij}, F_{ijj}\right), \\ \hat{f}_{\langle ij\rangle} &= \hat{f}_{\langle ij\rangle}\left(F, F_i, F_{ij}, F_{ijj}\right), \\ \hat{f}_{ijj} &= \hat{f}_{ijj}\left(F, F_i, F_{ij}, F_{ijj}\right). \end{aligned} \tag{341}$$

The set (339) and (341) forms the full model for the above chosen fields. They must be still restricted by the following principles

- the Galilean invariance of the field equations,
- the Galilean invariance of the constitutive relations for velocity-independent quantities,
- the thermodynamical admissibility.

The first condition is satisfied if the quantities appearing in the above equations have the form presented in the relation (338). Hence, we have (compare the identical relations (272) in the kinetic approach)

$$\begin{aligned} F &= \rho, \\ F_i &= \rho v_i, \\ F_{ij} &= \rho_{ij} + \rho v_i v_j, \\ F_{ijk} &= \rho_{ijk} + 3\rho_{(ij} v_{k)} + \rho v_i v_j v_k, \\ F_{ijkl} &= \rho_{ijkl} + 4\rho_{(ijk} v_{l)} + 6\rho_{(ij} v_k v_{l)} + \rho v_i v_j v_k v_k. \end{aligned} \tag{342}$$

and

$$\hat{f}_{\langle ij\rangle} = S_{\langle ij\rangle}, \quad \hat{f}_{ijj} = S_{ijj} + 2S_{\langle ij\rangle} v_j. \tag{343}$$

The ρ-quantities as well as S-quantities must satisfy constitutive relations following from (341) and satisfying the principle of material frame indifference.

In the Table 9, we present these quantities in juxtaposition with the standard notation.

Table 9: *Juxtaposition of notation: extended thermodynamics vs. classical thermodynamics*

extended thermodynamics	ρ	ρ_{ij}	$\frac{1}{2}\rho_{ii}$	$\frac{1}{2}\rho_{ijj}$
classical thermodynamics	ρ	$-t_{ij}$	$\rho\varepsilon = \frac{3}{2}p$	q_i

The relation between pressure p and specific energy ε is, as we have shown in the previous Lecture, the characteristic feature of the monatomic gases.

Now, we can reformulate constitutive relations and write them in the following equivalent form

$$\begin{aligned}
\rho_{\langle ijk\rangle} &= \rho_{\langle ijk\rangle}\left(\rho, \rho_{ij}, \rho_{ijj}\right), \\
\rho_{ijjk} &= \rho_{ijjk}\left(\rho, \rho_{ij}, \rho_{ijj}\right), \\
S_{\langle ij\rangle} &= S_{\langle ij\rangle}\left(\rho, \rho_{ij}, \rho_{ijj}\right), \\
S_{ijj} &= S_{ijj}\left(\rho, \rho_{ij}, \rho_{ijj}\right), \\
\rho\eta &= \rho\eta\left(\rho, \rho_{ij}, \rho_{ijj}\right), \\
h_i &= h_i\left(\rho, \rho_{ij}, \rho_{ijj}\right),
\end{aligned} \tag{344}$$

where the last two relations for the entropy density $\rho\eta$ and the nonconvective entropy flux h_i belong to the second law of thermodynamics. We have used here the decomposition: $\rho_{\langle ij\rangle k} = \rho_{\langle ijk\rangle} - \frac{2}{15}\rho_{kll}\delta_{ij} + \frac{3}{15}\rho_{jll}\delta_{ik} + \frac{3}{15}\rho_{ill}\delta_{jk}$ which means that we need only the constitutive relation for the fully deviatoric part $\rho_{\langle ijk\rangle}$.

The constitutive dependence on the velocity, or in the above notation on F_i, has been omitted because of the Galilean invariance. There remains a dependence on one scalar variable, one vector variable, and one variable which is the symmetric tensor of the second rank. Simultaneously, the assumption on the material objectivity of these constitutive relations yields in Cartesian coordinates

$$\begin{aligned}
O_{ir}O_{js}O_{kt}\rho_{\langle rst\rangle}\left(\rho, \rho_{ij}, \rho_{ijj}\right) &= \rho_{\langle ijk\rangle}\left(\rho, O_{ir}O_{js}\rho_{rs}, O_{ir}\rho_{rjj}\right), \\
O_{ir}O_{ks}\rho_{rjjs}\left(\rho, \rho_{ij}, \rho_{ijj}\right) &= \rho_{ijjk}\left(\rho, O_{ir}O_{js}\rho_{rs}, O_{ir}\rho_{rjj}\right), \\
O_{ir}O_{js}S_{\langle rs\rangle}\left(\rho, \rho_{ij}, \rho_{ijj}\right) &= S_{\langle ij\rangle}\left(\rho, O_{ir}O_{js}\rho_{rs}, O_{ir}\rho_{rjj}\right), \\
O_{ir}S_{rjj}\left(\rho, \rho_{ij}, \rho_{ijj}\right) &= S_{ijj}\left(\rho, O_{ir}O_{js}\rho_{rs}, O_{ir}\rho_{rjj}\right), \\
\rho\eta\left(\rho, \rho_{ij}, \rho_{ijj}\right) &= \rho\eta\left(\rho, O_{ir}O_{js}\rho_{rs}, O_{ir}\rho_{rjj}\right), \\
O_{ir}h_r\left(\rho, \rho_{ij}, \rho_{ijj}\right) &= h_i\left(\rho, O_{ir}O_{js}\rho_{rs}, O_{ir}\rho_{rjj}\right),
\end{aligned} \tag{345}$$

where O_{ij} are components of an arbitrary constant orthogonal tensor. Hence, the constitutive quantities are isotropic functions of one vector and one tensor variable. For these functions we have representation theorems which were quoted in Lecture 4. However, we shall not use them here and simplify the model by making an additional *assumption* that the dependence on $\rho_{\langle ij\rangle}$ (i.e. the stress deviator $t_{\langle ij\rangle}$) and on $\frac{1}{2}\rho_{ijj}$ (i.e. on the heat flux q_i) is *linear.* Then the isotropy property yields

$$\begin{aligned}
\rho_{\langle ijk\rangle} &= 0, \\
\rho_{ijjk} &= \alpha\delta_{ik} + \beta\rho_{\langle ik\rangle}, \\
S_{\langle ij\rangle} &= -\frac{1}{\tau_t}\rho_{\langle ij\rangle}, \\
S_{ijj} &= -\frac{1}{\tau_q}\rho_{ijj},
\end{aligned} \tag{346}$$

where the coefficients $\alpha, \beta, \tau_t, \tau_q$ may be functions of ρ and ρ_{ll}.

It should be stressed that the isotropy results are the same for the requirement of the Galilean invariance and for the material frame indifference with the matrix $\mathbf{O}$ dependent on time. This is different from the ordinary thermodynamics in which the material frame indifference requiring the invariance with respect to the Euclidean transformation is more restrictive than the Galilean invariance. In this sense, the material frame indifference is not required in the extended thermodynamics and this explains as well the appearance of nonobjetive contributions to constitutive relations of extended thermodynamics.

It remains to exploit the entropy principle. We begin with the direct evaluation of the entropy inequality restricted by the field equations (339), (341). In the inertial frame and without external forces we obtain the following inequality

$$\frac{\partial \rho\eta}{\partial t}+\frac{\partial \varphi_k}{\partial x_k}-\Lambda\left(\frac{\partial F}{\partial t}+\frac{\partial F_k}{\partial x_k}\right)-\Lambda_i\left(\frac{\partial F_i}{\partial t}+\frac{\partial F_{ik}}{\partial x_k}\right)-$$

$$-\Lambda_{ij}\left(\frac{\partial F_{ij}}{\partial t}+\frac{\partial F_{ijk}}{\partial x_k}-\hat{f}_{\langle ij\rangle}\right)-\Lambda_{lli}\left(\frac{\partial F_{ijj}}{\partial t}+\frac{\partial F_{ijjk}}{\partial x_k}-\hat{f}_{ijj}\right)\geq 0, \tag{347}$$

which must hold for all fields $\left\{F, F_i, F_{ij}, \frac{1}{2}F_{ijj}\right\}$. If we insert the constitutive relations this inequality becomes linear with respect to the following derivatives

$$\frac{\partial F}{\partial t},\frac{\partial F_i}{\partial t},\frac{\partial F_{ij}}{\partial t},\frac{\partial F_{ijj}}{\partial t},\frac{\partial F}{\partial x_k},\frac{\partial F_i}{\partial x_k},\frac{\partial F_{ij}}{\partial x_k},\frac{\partial F_{ijj}}{\partial x_k}. \tag{348}$$

This yields the thermodynamical identities which can be written in the following compact form

$$d\left(\rho\eta\right)=\Lambda dF+\Lambda_i dF_i+\Lambda_{ij}dF_{ij}+\Lambda_{lli}dF_{ijj}, \tag{349}$$

$$d\varphi_k=\Lambda dF_k+\Lambda_i dF_{ik}+\Lambda_{ij}dF_{ijk}+\Lambda_{lli}dF_{ijjk}. \tag{350}$$

Roughly speaking, the relation (349) determines the multipliers and the relation (350) gives rise to thermodynamical identities restricting constitutive relations.

There remains the residual inequality

$$\mathcal{D}=\Lambda_{ij}\hat{f}_{\langle ij\rangle}+\Lambda_{lli}\hat{f}_{ijj}\geq 0, \tag{351}$$

which represents the dissipation (nonnegative entropy production).

As we have shown above the Galilean invariance yields an explicit dependence on the velocity field. This concerns also Lagrange multipliers. Bearing this property in mind, after rather tedious calculations we can write the above results of the entropy principle in the following form

$$\begin{aligned} d\left(\rho\eta\right) &= \lambda d\rho+\lambda_{ij}d\rho_{ij}+\lambda_{lli}d\rho_{ijj}, \\ dh_k &= \lambda_i d\rho_{ik}+\lambda_{ij}d\rho_{ijk}+\lambda_{lli}d\rho_{ijjk}, \end{aligned} \tag{352}$$

$$\begin{aligned} \lambda_k\rho+\lambda_{jji}\left(2\rho_{ik}+\rho_{ll}\delta_{ik}\right) &= 0, \\ 2\lambda_{kj}\rho_{ji}+\lambda_{llm}\left(2\rho_{mki}+\rho_{ijj}\delta_{mk}\right) &= \left[\rho\eta-\lambda\rho-\lambda_{jl}\rho_{jl}-\lambda_{llm}\rho_{mjj}\right]\delta_{ki}, \end{aligned} \tag{353}$$

$$\mathcal{D}=\lambda_{ij}S_{\langle ij\rangle}+\lambda_{lli}S_{ijj}\geq 0. \tag{354}$$

In these relations, λ-multipliers are velocity independent *internal* parts of Λ-multipliers and the two are related in the following way

$$\begin{aligned}
\lambda &= \Lambda + \Lambda_{ij} v_i v_j + \Lambda_{lli} v_i v^2, \\
\lambda_i &= \Lambda_i + 2\Lambda_{ij} v_j + \Lambda_{llj} \left(v^2 \delta_{ji} + 2 v_j v_i \right), \\
\lambda_{ij} &= \Lambda_{ij} + \Lambda_{llk} 3 v_{(k} \delta_{ij)}, \qquad (355) \\
\lambda_{lli} &= \Lambda_{lli}.
\end{aligned}$$

Clearly, relations (352) indicate that the internal parts of multipliers are functions of constitutive variables $\{\rho, \rho_{ij}, \rho_{ijj}\}$.

Principally, we are done with the entropy principle. However, there remains a technically difficult part of evaluation of the above results. For details, we have to refer to the literature. We present here only the most important conclusions.

First of all, we investigate properties of the thermodynamical equilibrium, i.e. processes in which the dissipation $\mathcal{D}$ is zero. This corresponds to the vanishing sources $S_{\langle ij \rangle}$ and S_{ijj}. Such an analysis is easier if we transform the fields $\{\rho, \rho_{ij}, \rho_{ijj}\} \rightarrow \{\lambda, \lambda_i, \lambda_{lli}\}$. We have used a similar transformation at the beginning of this Lecture. Then we have to transform the four-potential in the following manner

$$\begin{aligned}
h' &= -\rho\eta + \lambda\rho + \lambda_{ij}\rho_{ij} + \lambda_{jji}\rho_{ill}, \qquad (356) \\
h'_k &= -h_k + \lambda_{ij}\rho_{ijk} + \lambda_{jji}\rho_{illk},
\end{aligned}$$

and rewrite (349), (350) in the alternative form

$$\begin{aligned}
dh' &= \rho d\lambda + \rho_{ij} d\lambda_{ij} + \rho_{lli} d\lambda_{jji}, \\
dh'_k &= \left[\lambda_{jji} a_{im} \frac{\partial \rho_{mk}}{\partial \lambda} \right] d\lambda + \left[\rho_{ijk} + \lambda_{llm} a_{mn} \frac{\partial \rho_{nk}}{\partial \lambda_{ij}} \right] d\lambda_{ij} + \qquad (357) \\
&\quad + \left[\rho_{ijjk} + \lambda_{llm} a_{mn} \frac{\partial \rho_{nk}}{\partial \lambda_{ppi}} \right] d\lambda_{qqi}, \\
-h'\delta_{ik} &= 2\lambda_{ij}\rho_{jk} + \lambda_{jjl} \left(2\rho_{lik} + \rho_{kpp}\delta_{li} \right).
\end{aligned}$$

The multiplier λ_i has been eliminated and has brought the tensor a_{ij} defined by the relation

$$a_{ij} = \frac{1}{\rho} \left(2\rho_{ij} + \rho_{ll}\delta_{ij} \right). \qquad (358)$$

We return now to the definition of equilibrium. In new variables, the condition $\mathcal{D} = \lambda_{\langle ij \rangle}\big|_E S_{\langle ij \rangle}\big|_E + \lambda_{lli}|_E S_{ijj}|_E = 0$ implies that this is a minimum of this function which yields

$$\lambda_{\langle ij \rangle}\big|_E = 0, \quad \lambda_{lli}|_E = 0. \qquad (359)$$

Hence, with $\rho_{ii} = 2\rho\varepsilon$ we conclude (see: (352))

$$d(\rho\eta)|_E = \frac{2}{3} \lambda_{ii}|_E \, d(\rho\varepsilon) + \lambda_E d\rho. \qquad (360)$$

Comparison with the Gibbs equation yields

$$\lambda_{ii}|_E = \frac{2}{3}\frac{1}{T}, \quad \lambda_E = -\frac{g}{T}, \quad g = \varepsilon - T\eta_E + \frac{p_E}{\rho}, \qquad (361)$$

where T is the absolute temperature and g is the Gibbs free energy (specific free enthalpy).

The above results conclude the identification of multipliers in equilibrium.

Before we apply this knowledge, we investigate the Gibbs equation which we can now write in the form

$$d\eta_E = \frac{1}{T}\left(d\varepsilon - \frac{p_E}{\rho^2}d\rho\right). \tag{362}$$

This equation implies the integrability condition

$$\left(\frac{\partial \varepsilon}{\partial \rho}\right)_T = \frac{1}{\rho^2}\left(p_E - T\left(\frac{\partial p_E}{\partial T}\right)_\rho\right). \tag{363}$$

For a monatomic gas we have $p_E = \frac{2}{3}\rho\varepsilon$ and then we can integrate the above equation. The result is

$$p_E = T^{5/2}\Phi\left(z\right), \quad \eta_E = \frac{3}{2}\int\left(\frac{\Phi'\left(z\right)}{z} - \frac{5}{3}\frac{\Phi\left(z\right)}{z^2}\right)dz + C_1, \quad z := \frac{\rho}{T^{3/2}}, \tag{364}$$

where $\Phi\left(z\right)$ is an arbitrary function, $\Phi' = \frac{d\Phi}{dz}$, and C_1 is an arbitrary constant. Consequently, the thermal equation of state is determined by a function of a single variable. It follows as well

$$\frac{g}{T} = \frac{\Phi}{z} + \int\frac{\Phi}{z^2}dz - C_1. \tag{365}$$

We limit our attention to nonequilibrium processes described up to terms of the first order with respect to the deviation from equilibrium. Calculations of this approximation are based on the so-called Maxwell iteration procedure which we do not present here. The final results are

$$\begin{aligned}
\rho_{\langle ijk\rangle} &= O\left(2\right), \\
\rho_{\langle ijjk\rangle} &= \left[5T^{7/2}\left(\int\frac{\Phi\Phi'}{z}dz + C_1\right) + C_2\right]\delta_{ik} + \\
&\quad +7\frac{T}{\Phi}\left[\int\frac{\Phi\Phi'}{z}dz + C_1\right]\rho_{\langle ij\rangle} + O\left(2\right), \\
S_{\langle ij\rangle} &= -\frac{\varsigma_t}{2T^{7/2}\Phi}\rho_{\langle ij\rangle} + O\left(2\right), \\
S_{ijj} &= -\frac{\varsigma_q}{5T^{9/2}\left[7\left(\int\frac{\Phi\Phi'}{z}dz + C_1\right) - 5\frac{\Phi^2}{z}\right]}\rho_{ill} + O\left(2\right),
\end{aligned} \tag{366}$$

where $O\left(2\right)$ denotes contribution of the second and higher orders with respect to variables $\rho_{\langle ij\rangle}$ and ρ_{ill}, and ς_t, ς_q are proportionality coefficients related to characteristic times τ_t, τ_q appearing in the representations (346) of the production terms

$$\tau_t = 2T^{7/2}\Phi\frac{1}{\varsigma_t}, \quad \tau_q = 5T^{9/2}\left[7\left(\int\frac{\Phi\Phi'}{z}dz + C_1\right) - 5\frac{\Phi^2}{z}\right]\frac{1}{\varsigma_q}. \tag{367}$$

The above results yield the following relations for the entropy and the entropy flux

$$\begin{aligned} \rho\eta &= \rho\left[\frac{3}{2}\int\left(\frac{\Phi'}{z}-\frac{5}{3}\frac{\Phi}{z^2}\right)dz+C_3\right]-\frac{\rho_{\langle ij\rangle}\rho_{\langle ij\rangle}}{\underline{4T^{7/2}\Phi}} \\ &\quad -\frac{\rho_{kki}\rho_{lli}}{\underline{10T^{7/2}\Phi\left[7\frac{T}{\Phi}\left(\int\frac{\Phi\Phi'}{z}dz+C_1\right)-5T\frac{\Phi}{z}\right]}}+O\left(3\right), \qquad (368) \\ h_k &= \frac{1}{T}\frac{1}{2}\rho_{llk}-\frac{2}{5}\frac{\rho_{\langle ki\rangle}\frac{1}{2}\rho_{lli}}{\underline{T^{7/2}\Phi}}+O\left(3\right). \end{aligned}$$

There remains the convexity condition with respect to the densities F, F_i, F_{ij}, F_{ill} or $\rho, \rho_{ij}, \rho_{lii}$. In the case of nonequilibrium variables $\rho_{\langle ij\rangle}, \rho_{lli}$, it follows immediately from (368)

$$\Phi\left(z\right)>0, \quad 7\left(\int\frac{\Phi\Phi'}{z}dz+C_1\right)-5\frac{\Phi^2}{z}>0. \qquad (369)$$

In addition, Hessian of $\rho\eta$ with respect to ρ, ρ_{kk} must be negative definite. After some calculations, it follows

$$0<\Phi'<\frac{5}{3}\frac{\Phi}{z}. \qquad (370)$$

In the simplest case of a classical ideal gas the thermal state equation has the form

$$p=\frac{k}{m}\rho T \quad \text{i.e.} \quad \Phi\left(z\right)=\frac{k}{m}z. \qquad (371)$$

Nothing is known about the constant C_1 but in the kinetic theory it is zero. Then the function Φ of the relation (371) identically satisfies conditions (369), (370).

Let us write the field equations which we have obtained in the above analysis in the form customary in the classical thermodynamics. In an arbitrary noninertial frame, they are as follows

$$\dot{\rho}+\rho\frac{\partial v_k}{\partial x_k}=0, \qquad (372)$$

$$\rho\left[\dot{v}_i-\dot{i}_i^0-2\Omega_{ik}v_k\right]-\frac{\partial}{\partial x_k}\left(t_{\langle ik\rangle}-T^{5/2}\Phi\left(z\right)\delta_{ik}\right)=0, \qquad (373)$$

$$\rho\frac{3}{2}\left(T\frac{\Phi\left(z\right)}{z}\right)^{\bullet}+\frac{\partial q_k}{\partial x_k}-\left(t_{\langle ik\rangle}-T^{5/2}\Phi\left(z\right)\delta_{ik}\right)\frac{\partial v_i}{\partial x_k}=0, \qquad (374)$$

$$\rho\left[\left(\frac{t_{\langle ik\rangle}}{\rho}\right)^{\bullet}+2\frac{t_{j\langle i}}{\rho}\frac{\partial v_{k\rangle}}{\partial x_j}-4\frac{t_{j\langle i}}{\rho}\Omega_{k\rangle j}\right]-\frac{4}{5}\frac{\partial q_{\langle i}}{\partial x_{k\rangle}}=-\frac{1}{\tau_t}t_{\langle ik\rangle}, \qquad (375)$$

$$
\begin{aligned}
&\rho\left[\left(\frac{q_i}{\rho}\right)^{\bullet}+\frac{q_k}{\rho}\frac{\partial v_i}{\partial x_k}-2\frac{q_k}{\rho}\Omega_{ik}\right]-\\
&-\frac{\partial}{\partial x_j}\left[\frac{7}{2}\left(\frac{T}{\Phi\left(z\right)}t_{\langle ij\rangle}-\frac{5}{7}T^{7/2}\delta_{ij}\right)\left(\int\frac{\Phi\Phi'}{z}dz+C_1\right)\right]+\\
&+\frac{2}{5}q_i\frac{\partial v_k}{\partial x_k}+\frac{4}{5}q_k\frac{\partial v_{(i}}{\partial x_{k)}}-\frac{1}{\rho}\left(t_{\langle ij\rangle}-T^{5/2}\Phi\left(z\right)\delta_{ij}\right)\frac{\partial}{\partial x_k}\left(t_{\langle jk\rangle}-T^{5/2}\Phi\left(z\right)\delta_{jk}\right)+\\
&+\frac{3}{2}\frac{T^{5/2}\Phi\left(z\right)}{\rho}\frac{\partial}{\partial x_k}\left(t_{\langle ik\rangle}-T^{5/2}\Phi\left(z\right)\delta_{ik}\right)=-\frac{1}{\tau_q}q_i,\qquad z=\frac{\rho}{T^{3/2}}.
\end{aligned}\tag{376}
$$

In order to see clearly the structure of these equations we rewrite the system in the absolute notation and substitute $\Phi=kz/m$, $p=2\rho\varepsilon/3$, $C_1=0$, $\mathbf{T}=\mathbf{T}^D-p\mathbf{1}$. It follows

$$
\begin{aligned}
&\dot{\rho}+\rho\operatorname{div}\mathbf{v}=0,\\
&\rho\left[\dot{\mathbf{v}}-\mathbf{i}^0-2\boldsymbol{\Omega}\mathbf{v}\right]-\operatorname{div}\mathbf{T}=0,\\
&\rho\dot{\varepsilon}+\operatorname{div}\mathbf{q}-\mathbf{T}\cdot\mathbf{L}=0,\\
&\rho\left(\frac{\mathbf{T}^D}{\rho}\right)^{\bullet}+\left[2\left(\mathbf{L}-2\boldsymbol{\Omega}\right)\mathbf{T}\right]^D-\frac{4}{5}\left(\operatorname{grad}\mathbf{q}\right)^D=-\frac{1}{\tau_t}\mathbf{T}^D,\\
&\rho\left(\frac{\mathbf{q}}{\rho}\right)^{\bullet}+\left(\mathbf{L}-2\boldsymbol{\Omega}\right)\mathbf{q}-\operatorname{div}\left[\frac{p}{\rho}\left(\frac{7}{2}\mathbf{T}+p\mathbf{1}\right)\right]+\\
&+\frac{2}{5}\mathbf{q}\operatorname{div}\mathbf{v}-\frac{1}{\rho}\left(\mathbf{T}-\frac{3}{2}p\mathbf{1}\right)\operatorname{div}\mathbf{T}=-\frac{1}{\tau_q}\mathbf{q},
\end{aligned}\tag{377}
$$

where $\left(\operatorname{grad}\mathbf{q}\right)^D=\frac{1}{2}\left(\operatorname{grad}\mathbf{q}+\left(\operatorname{grad}\mathbf{q}\right)^T\right)-\frac{1}{3}\mathbf{1}\operatorname{div}\mathbf{q}$ and similarly for $\left[2\left(\mathbf{L}-2\boldsymbol{\Omega}\right)\mathbf{T}\right]^D$.

This completes the thermodynamical analysis of the model. We have obtained results which are explicit up to three constants C_1, C_2, C_3 and the function $\Phi\left(z\right)$. The latter is fully determined by the equilibrium thermal state equation. It remains to compare these results with the kinetic theory and with the ordinary thermodynamics. We proceed to do so.

Comparison with the results of the kinetic theory discussed in the previous Lecture (viz. relation (296) for the entropy and the entropy flux and (300), (301) for the remaining quantities) reveals an almost perfect agreement. Indeed if we set the constant C_1 equal to zero we obtain both in the kinetic theory and in the extended thermodynamics of ideal gases with $\Phi\left(z\right)=\frac{k}{m}z$ the following relations for the entropy and the entropy flux

$$
\begin{aligned}
\eta&=\left[\frac{k}{m}\ln\frac{T^{3/2}}{\rho}+C_3\right]-\frac{t_{\langle ij\rangle}t_{\langle ij\rangle}}{4p\rho T}-\frac{q_iq_i}{5p^2T},\\
h_i&=\frac{q_i}{T}+\frac{2}{5pT}t_{\langle ij\rangle}q_j.
\end{aligned}\tag{378}
$$

Consequently, it is clear that the continuity of the heat flux q_i and of the entropy flux h_i on the material walls do not yield the continuity of the temperature T as it is the case in the ordinary thermodynamics. Only in the linear approximation we obtain such a result.

There exists a small difference between the two approaches as far as the relaxation times are concerned: in the kinetic theory they are equal to $\tau_t = \tau$ and $\tau_q = \frac{3}{2}\tau$, respectively, while in the extended thermodynamics they are independent. As a matter of fact, they are related to the viscosity and the heat conductivity, respectively. This can be seen if we perform the so-called Maxwell iteration on constitutive relations (375), (376). Namely, if we evaluate these relations in an infinitesimal neighborhood of equilibrium (i.e. at $t_{\langle ij\rangle} = 0, q_i = 0$) we obtain as the first step of iteration

$$\begin{aligned} t_{\langle ij\rangle} &\approx 2\mu\frac{\partial v_{(i}}{\partial x_{j)}}, \quad \mu = T^{5/2}\Phi\tau_t \quad = p\tau_t \quad \text{for} \quad \Phi = \frac{k}{m}z, \\ q_i &\approx -K\frac{\partial T}{\partial x_i}, \quad K = -\frac{5}{4}T^{5/2}\left[5\frac{\Phi^2}{z} - 7\left(\int\frac{\Phi\Phi'}{z}dz + C_1\right)\right]\tau_q = \\ &= \frac{5}{2}\frac{p^2}{\rho T}\tau_q \quad \text{for} \quad \Phi = \frac{k}{m}z. \end{aligned} \tag{379}$$

The second step of the iteration follows when we insert the first step on the right-hand side of relations (375), (376) and calculate the stress deviator and the heat flux again. We shall not do so in this Lecture but we mention a few properties which follow from this procedure. First of all, the second iteration step contains the dependence on at least squares of relaxation times τ_t, τ_q. This continues in further iteration steps. Hence, the Maxwell procedure is a kind of polynomial expansion with respect to these times. Secondly, already in the second iterate there appear nonobjective contributions depending on Ω_{ij}. Let us demonstrate this nonobjectivity on a simple example. We consider a process of the rigid rotation with the constant temperature of the material element of the fluid, i.e.

$$\frac{\partial v_{(i}}{\partial x_{j)}} = 0, \quad \dot{T} = 0. \tag{380}$$

Then the relation for the heat flux (376) reduces to the following form

$$\begin{aligned} q_i &= \pi\tau_q\left[\frac{\partial T}{\partial x_i} + 2\tau_q\left(\Omega_{ik} - \frac{\partial v_{[k}}{\partial x_{i]}}\right)\frac{\partial T}{\partial x_k}\right], \\ \pi &= \frac{5}{4}T^{5/2}\left[5\frac{\Phi^2}{z} - 7\int\frac{\Phi\Phi'}{z}dz + C_1\right]. \end{aligned} \tag{381}$$

The second contribution is the frame-dependent objective vector and it indicates that the heat flux is not parallel to the temperature gradient. Such an effect has been discussed by I. Müller who indicated that the transition from the microscopic description yields these contributions as a consequence of Coriolis forces appearing in microscopic equations of motion.

Finally, the second iterates contain coupling terms between the stress and heat flux relations.

Modeling presented above shows clearly adavantages of the application of extended thermodynamics. However, there are also weak points of this approach which have not been removed as yet. The assumption that field equations follow from balance laws means that for each subsequent level of the hierarchy we need additional boundary conditions. This means that either we have to add some additional control on the boundary (e.g. simultaneously a temperature and a heat flux) or that there exist some microscopical mechanisms which produce constraints on the boundary automatically. These may be, for instance, some conditions imposed on fluctuations as a part of the physical definition of the boundary. As the first possibility seems to be physically meaningless the second one has been tested. Various simple examples have been considered (for instance, the so-called minimax principle of Weiss and Struchchtrup) but none of them seems to be indeed a solution of the problem. We return to the discussion of this issue in relation to boundary conditions for porous materials.

Lecture 8: Thermodynamical model of viscoelastic materials

In the previous two Lectures we have demonstrated the construction of a macroscopic model of heat conducting viscous ideal gases. The kinetic theory has motivated the macroscopic modelling called extended thermodynamics. This strategy of constructing macroscopic models can be extended to materials for which the kinetic motivation is remote or even none at all. Viscoelastic materials belong to this class. In the present Lecture, we discuss the thermodynamical construction of the model whose behavior is solid-like and therefore the Lagrangian description is appropriate. We focus the attention on isotropic materials and investigate their general model following from extended thermodynamics. In particular two special cases will be considered: viscous fluids and linear viscoelastic solids. In viscous heat-conducting fluids the resulting equations have the same structure as these presented in previous Lectures for ideal gases but the theory is less restrictive about some scalar coefficients. As the special case of the model of viscoelastic solids we obtain the standard linear solid of viscoelasticity. This construction of the model has been performed by I-Shih Liu in 1989[13].

We consider the construction of the model for the following 21 fields

- F_{iK} – deformation gradient (9 components),
- v_i – velocity (3 components),
- T – temperature (1 component),
- $t^v_{\langle ij\rangle}$ – viscous (Cauchy) stress deviator (5 components),
- $q_i = J^{-1}Q_K F_{iK}$ – heat flux (3 components).

Both Lagrangian and Eulerian indices are referring to Cartesian coordinates.

Field equations follow from the set of balance equations

$$\frac{\partial F_{iK}}{\partial t} - \frac{\partial v_i}{\partial X_K} = 0, \tag{382}$$

$$\frac{\partial G_i}{\partial t} - \frac{\partial P_{iK}}{\partial X_K} = \rho_0 \left(b_i + i^0_i\right) + 2\Omega_{ij} G_j, \tag{383}$$

$$\frac{\partial G_{ij}}{\partial t} + \frac{\partial \Psi_{ijK}}{\partial X_K} - S_{\langle ij\rangle} = 2G_{(i}\left(b_{j)} + i^0_{j)}\right) - 2\Omega_{k(i}\left(G_{j)}v_k + G_{j)k} - P_{j)K}F_{kK}\right), \tag{384}$$

$$\frac{\partial G_{ijj}}{\partial t} + \frac{\partial \Psi_{ijjK}}{\partial X_K} - S_{ijj} = 3G_{(ij}\left(b_{j)} + i^0_{j)}\right) - 3\Omega_{k(i}\left(G_{jj)}v_k + G_{jj)k} + \Psi_{jj)K}F_{kK}\right). \tag{385}$$

The first relation is, obviously, the integrability condition for the deformation gradient. The second one represents the momentum conservation in a noninertial frame with

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[13] I-Shih Liu; *An Extended Fields Theory of Viscoelastic Materials*, Int. J. Engng. Sci., **26**, 331-342, 1988.
I-Shih Liu; *Extended Thermodynamics of viscoelastic materials*, *Continuum Mech. Thermodyn.*, **1**, 143-164, 1989.

the quantity $G_i = \rho_0 v_i$ representing momentum density. The remaining notation is the same as in the previous Lectures.

The trace of (384) represents the energy conservation law. Therefore we identify $\frac{1}{2}G_{ii} = \rho_0 \left(\varepsilon + \frac{1}{2}v^2\right)$ as the total energy density and $\frac{1}{2}\Psi_{jjK} = Q_K - P_{jK}v_j$ as its flux.

Bearing Galilean invariance of balance laws in mind, we obtain on the basis of the Ruggeri Theorem the following explicit dependence on the velocity

$$\begin{aligned} G_{ij} &= \rho_0 v_i v_j + \rho_{ij}, \quad G_{ijj} = \rho_{ijj} + 3\rho_{(ij}v_{j)} + \rho_0 v_i v^2, \\ \Psi_{ijK} &= R_{ijK} - 2v_i P_{j)K}, \quad \Psi_{ijjK} = R_{ijjK} + 3v_{(i}R_{jj)K} - 3v_{(i}v_j P_{j)K}, \\ S_{\langle ij\rangle} &= s_{\langle ij\rangle}, \quad S_{ijj} = s_{ijj} + 3s_{(ij}v_{j)}, \end{aligned} \tag{386}$$

where $\rho_{ij}, \rho_{ijj}, R_{ijK}, R_{ijjK}, P_{jK}, s_{\langle ij\rangle}, s_{ijj}$ are velocity-independent and Galilean invariant. These relations yield the following identifications

$$\varepsilon = \frac{1}{2\rho_0}\rho_{ii}, \quad Q_K = Jq_i F_{Ki}^{-1} = \frac{1}{2}R_{iiK}, \tag{387}$$

where ε is the *specific internal energy* and Q_K denotes the *material heat flux*, i.e. the heat flux vector in the Lagrangian description. In addition, apart from the Piola-Kirchhoff stress tensor P_{iK} we frequently apply the symmetric Cauchy stress tensor $T_{ij} = J^{-1}P_{iK}F_{jK} = T_{ji}$.

In order to construct field equations we have to close the system of balance laws (382)-(385) by constitutive relations. We select the following set of constitutive variables

$$\mathcal{C}' = \left\{F_{iK}, T, t^v_{\langle ij\rangle}, q_i\right\}, \tag{388}$$

where $t^v_{\langle ij\rangle}$ is supposed to represent the deviatoric viscous stress tensor which we identify later. For technical reasons it is more convenient to choose the variables appearing in (386) instead of the above physical variables. We shall do so and after the evaluation of thermodynamical principles we return to this more suggestive choice. Hence, we choose the following set

$$\mathcal{C} = \left\{F_{iK}, \rho_{ij}, \rho_{ijj}\right\}, \tag{389}$$

and assume that the following constitutive quantities

$$\mathcal{F} = \left\{P_{iK}, R_{ijK}, R_{ijjK}, s_{\langle ij\rangle}, s_{ijj}\right\}, \tag{390}$$

are sufficiently smooth functions of constitutive variables

$$\mathcal{F} = \mathcal{F}(\mathcal{C}). \tag{391}$$

The velocity v_i or, equivalently, the vector G_i does not appear anymore among constitutive variables which is the consequence of the Galilean invariance. Some other restrictions following from this invariance shall be presented later. Simultaneously, the constitutive dependence contains only fields (comp. (388)) or their transformations (389). There is no dependence on gradients or time derivatives of fields. This is the characteristic feature of the extended thermodynamics and, for this reason, we call constitutive relations (391) local.

As usual the constitutive relations must satisfy the condition of thermodynamical admissibility which is formulated by means of the entropy inequality

$$\rho_0 \frac{\partial \eta}{\partial t} + \frac{\partial H_K}{\partial X_K} \geq 0, \tag{392}$$

where

$$\eta = \eta\left(\mathcal{C}\right), \quad H_K = H_K\left(\mathcal{C}\right). \tag{393}$$

It is obvious that the entropy flux in the Lagrangian description is independent of the velocity. It contains only the nonconvective part which depends on constitutive variables $\mathcal{C}$.

Entropy inequality must hold for all thermodynamical processes, i.e. for all solutions of field equations. As before this constraint is eliminated by Lagrange multipliers which are also constitutive functions. Easy calculations yield then

$$\begin{aligned} \rho_0 d\eta &= \lambda_{iK} dF_{iK} + \lambda_{ij} d\rho_{ij} + \lambda_{ikk} d\rho_{ijj}, \\ dH_K &= -\lambda_i dP_{iK} + \lambda_{ij} dR_{ijK} + \lambda_{ikk} dR_{ijjK}, \end{aligned} \tag{394}$$

where the multiplier of the momentum balance equation does not contribute to the above relations and the remaining multipliers $\lambda_{iK}, \lambda_{ij}, \lambda_{ikk}$ are velocity independent parts of multipliers corresponding to constraints imposed by (382), (384) and (385), respectively. It follows as well that the multiplier of the momentum balance equation contains the velocity independent part given by the relation

$$\lambda_i = -\frac{3}{\rho_0} \rho_{(ij} \lambda_{j)kk}, \tag{395}$$

and the multiplier λ_{iK} has the form

$$\lambda_{iK} = -2\lambda_{ij} P_{jK} + 3\lambda_{kk(j} R_{ij)K}. \tag{396}$$

There remains the residual inequality of the following form

$$\begin{aligned} &\lambda_{ij} s_{\langle ij \rangle} + \lambda_{ijj} s_{ijj} + \\ &+ \left[2\lambda_{ij}\left(\rho_{ij} - P_{jK} F_{iK}\right) + \lambda_{ill}\left(\rho_{kjj} + R_{jjK} F_{kK}\right) + 2\lambda_{jll} R_{ijK} F_{kK}\right] \Omega_{ik} \geq 0. \end{aligned} \tag{397}$$

Since the inequality must hold for all frames it must be independent of the matrix of angular velocities Ω_{ik}. Consequently, the following identity must be satisfied

$$\left[2\lambda_{ij}\left(\rho_{ij} - P_{jK} F_{iK}\right) + \lambda_{ill}\left(\rho_{kjj} + R_{jjK} F_{kK}\right) + 2\lambda_{jll} R_{ijK} F_{kK}\right] \varepsilon_{ikl} = 0, \tag{398}$$

where ε_{ikl} is the permutation symbol. Simultaneously, the residual inequality becomes

$$\mathcal{D} = \lambda_{ij} s_{\langle ij \rangle} + \lambda_{ijj} s_{ijj} \geq 0, \tag{399}$$

and this relation defines the dissipation $\mathcal{D}$ in the system.

As we know already it is convenient to change variables $\{F_{iK}, \rho_{ij}, \rho_{ijj}\} \to \{F_{iK}, \lambda_{ij}, \lambda_{ikk}\}$ which is possible due to the convexity assumption. Then we can define the conjugate four-potential

$$\begin{aligned} h' &= \lambda_{ij}\rho_{ij} + \lambda_{ikk}\rho_{ijj} - \rho_0\eta, \\ H'_K &= -\lambda_i P_{iK} + \lambda_{ij} R_{ijK} + \lambda_{ikk} R_{ijjK} - H_K, \end{aligned} \tag{400}$$

It follows

$$\begin{aligned} dh' &= \rho_{ij} d\lambda_{ij} + \rho_{ijj} d\lambda_{ikk} - \lambda_{iK} dF_{ik}, \\ dH'_K &= -P_{iK} d\lambda_i + R_{ijK} d\lambda_{ij} + R_{ijjK} d\lambda_{ikk}. \end{aligned} \tag{401}$$

We proceed to analyze the thermodynamical equilibrium defined by the condition $\mathcal{D} = 0$ which corresponds to the requirement of vanishing productions $s_{\langle ij\rangle}\big|_E = 0$, $s_{ijj}\big|_E = 0$. As the inequality (399) is the condition for the minimum of the dissipation in the equilibrium we conclude that the multipliers $\lambda_{\langle ij\rangle}, \lambda_{ijj}$ also vanish in equilibrium. This makes the new choice of variables so attractive from the technical point of view.

Bearing $(394)_1$ and (396) in mind, we obtain in equilibrium

$$d\eta_E = \frac{2}{3}\lambda_{ii}\left(d\varepsilon_E - \frac{1}{\rho_0}\, P_{iK}\big|_E\, dF_{iK}\right). \tag{402}$$

Therefore we can identify

$$\frac{2}{3}\lambda_{ii} = \frac{1}{T}, \tag{403}$$

where T is the absolute temperature. The relation (402) becomes Gibbs equation. Consequently, we can introduce the equilibrium Helmholtz free energy $\psi_E = \varepsilon_E - T\eta_E$ which yields

$$P_{iK}\big|_E = \rho_0 \frac{\partial \psi_E}{\partial F_{iK}}, \quad \varepsilon_E = \psi_E - T\frac{\partial \psi_E}{\partial T}, \quad h'_E = \rho_0 \frac{\psi_E}{T}, \tag{404}$$

where relations $\frac{1}{2}\rho_{jj} = \rho_0\varepsilon$ and (403) have been used. In addition, the evaluation of the identity (398) in equilibrium leads to the relation

$$\rho_{\langle ij\rangle}\big|_E = \frac{\rho_0}{\rho}\, T_{\langle ij\rangle}\big|_E\,, \quad T_{ij} \equiv J^{-1} P_{iK} F_{jK} \equiv \frac{\rho}{\rho_0} P_{iK} F_{jK}. \tag{405}$$

Further analysis will be limited to a few key results of an approximate theory. We construct constitutive relations in the *second order approximation* with respect to the deviation from equilibrium which is measured by multipliers $\lambda_{\langle ij\rangle}$ and λ_{ijj} vanishing in equilibrium. Detailed structure, in particular symmetry properties of material parameters in the nonlinear theory as well as the derivation of restrictions following from the hyperbolicity condition (convexity assumption) are technically so involved that it would be impossible to present them in the form of the single Lecture. We refer for details to the publications of I-Shih Liu.

In this approximation we have

$$\begin{aligned} h' &= \rho_0\left(\frac{\psi_E}{T} + \frac{1}{\rho}\, T_{\langle ij\rangle}\big|_E\, \lambda_{\langle ij\rangle} + \frac{1}{2} h_{ijkl}\lambda_{\langle ij\rangle}\lambda_{\langle kl\rangle} + \frac{1}{2} k_{ij}\lambda_{ikk}\lambda_{jll}\right) + O(3), \\ H'_i &= J^{-1} H'_K F_{iK} = \left(\chi_{ij} + \chi'_{ijkl}\lambda_{\langle kl\rangle}\right)\lambda_{jmm} + O(3), \end{aligned} \tag{406}$$

where the coefficients $h_{ijkl}, k_{ij}, \chi_{ij}, \chi'_{ijkl}$ as well as ψ_E and $\left.T_{\langle ij\rangle}\right|_E$ are isotropic functions of the Cauchy-Green deformation tensor $B_{ij} = F_{iK}F_{jK}$ and of the temperature T. The first coefficient, h_{ijkl}, is, in addition, traceless symmetric in both pairs of indices and it is symmetric with respect to these pairs. k_{ij} is symmetric.

The above relations for the four-potential yield constitutive relations for all constitutive quantities of the model except of productions. They enable the exploitation of relations (403) which are the generalization of the Gibbs equation to nonequilibrium processes with multipliers as process variables. We proceed to exploit these relations.

In the second order approximation, the first equation (401) yields after easy calculations

$$\varepsilon = \varepsilon_E - \frac{T^2}{\rho}\frac{\partial \left.T_{\langle ij\rangle}\right|_E}{\partial T}\lambda_{\langle ij\rangle} -$$

$$-\frac{T^2}{2}\frac{\partial h_{ijkl}}{\partial T}\lambda_{\langle ij\rangle}\lambda_{\langle kl\rangle} - \frac{T^2}{2}\frac{\partial k_{ij}}{\partial T}\lambda_{ikk}\lambda_{jll} + O(3),$$

$$\begin{aligned}
\rho_{\langle ij\rangle} &= \rho_0\left(\frac{1}{\rho}\left.T_{\langle ij\rangle}\right|_E + h_{ijkl}\lambda_{\langle kl\rangle}\right) + O(2),\\
\rho_{ijj} &= \rho_0 k_{ij}\lambda_{jll} + O(2),
\end{aligned}$$

$$\lambda_{kK} = -\frac{\rho_0}{T}\frac{\partial\psi_E}{\partial F_{kK}} - \frac{\partial\left(\left.T_{iL}\right|_E F_{jL}\right)}{\partial F_{kK}}\lambda_{\langle ij\rangle} -$$

$$-\frac{\rho}{2}\left(\frac{\partial h_{ijlm}}{\partial F_{kK}}\lambda_{\langle ij\rangle}\lambda_{\langle lm\rangle} + \frac{\partial k_{ij}}{\partial F_{kK}}\lambda_{imm}\lambda_{jpp}\right) + O(3). \tag{407}$$

Combination of these results yields the relation for the Helmholtz free energy

$$\psi = \psi_E - \frac{T}{2}h_{ijkl}\lambda_{\langle ij\rangle}\lambda_{\langle kl\rangle} - \frac{T}{2}k_{ij}\lambda_{imm}\lambda_{jpp} + O(3). \tag{408}$$

Inspection of (396) shows that up to second order terms we have

$$t^v_{ij} = T_{ij} - \left.T_{ij}\right|_E = T\left(-\left.T_{ij}\right|_E + \rho\frac{\partial^2\psi_E}{\partial F_{iK}\partial F_{kL}}F_{jK}F_{lL}\right)\lambda_{\langle kl\rangle} + O(2). \tag{409}$$

We have anticipated that R_{ijK} is vanishing in equilibrium. We return later to this point.

Thus the stress is decomposed into an equilibrium part $\left.T_{ij}\right|_E$ and a non-equilibrium part t^v_{ij}. The former is referred to as the *elastic stress* and the latter as the *viscous stress.* One can introduce the following *spatial elasticity tensors (first* and *second)*

$$\begin{aligned}
A_{ijkl} &= \rho\frac{\partial^2\psi_E}{\partial F_{iK}\partial F_{kL}}F_{jK}F_{lL}, \\
C_{ijkl} &= A_{ijkl} - \left.T_{jl}\right|_E\delta_{ik}.
\end{aligned} \tag{410}$$

Then

$$t^v_{ij} = TC_{ijkl}\lambda_{\langle kl\rangle} + O(2). \tag{411}$$

Now we are in the position to specify the second order approximation of the multiplier λ_i given by (395)

$$\lambda_i = \left(r_{ik} + r'_{jlki}\lambda_{\langle jl\rangle}\right)\lambda_{kpp} + O\left(2\right), \tag{412}$$

where

$$r_{ik} = -\frac{10}{3}\varepsilon_E\delta_{ik} - \frac{2}{\rho}\left.T_{\langle ik\rangle}\right|_E, \quad r'_{ijkl} = \frac{10}{3}\frac{T^2}{\rho}\frac{\partial\left.T_{\langle ij\rangle}\right|_E}{\partial T}\delta_{kl} - 2h_{ijkl}. \tag{413}$$

This completes the constitutive consequences of the first equation (401) in terms of multipliers $\lambda_{\langle kl\rangle}, \lambda_{kpp}$ as variables describing the deviation of processes from the equilibrium.

These results make possible the exploitation of the second equation (401).

We easily obtain the following relations for quantities transformed to Eulerian description (e.g. $R_{ijk} = J^{-1}R_{ijK}F_{kK}$, $R_{ijjk} = J^{-1}R_{ijjK}F_{kK}$)

$$q_i = \left(\kappa_{ki} + \kappa'_{jlki}\lambda_{\langle jl\rangle}\right)\lambda_{kpp} + O\left(3\right), \tag{414}$$

$$R_{\langle ijk\rangle} = \alpha_{ijkl}\lambda_{lpp} + O\left(2\right), \tag{415}$$

$$R_{kppl} = \beta_{kl} + \beta'_{ijkl}\lambda_{\langle ij\rangle} + O\left(2\right), \tag{416}$$

where

$$\begin{aligned}
\kappa_{ki} &= -T^2\left(\frac{\partial r_{kj}}{\partial T}\left.T_{ji}\right|_E + \frac{\partial\chi_{ki}}{\partial T}\right), \\
\kappa'_{ijkl} &= -T^2\left(\frac{\partial r'_{ijkp}}{\partial T}\left.T_{pl}\right|_E + \frac{\partial\chi'_{ijkl}}{\partial T} + TC_{pl\langle ij\rangle}\frac{\partial r_{kp}}{\partial T}\right), \\
\alpha_{ijkl} &= r'_{ijkp}\left.T_{pl}\right|_E + \chi'_{ijkl}, \quad \beta_{ij} = r_{ip}\left.T_{pl}\right|_E + \chi_{ij}, \quad \beta'_{ijkl} = \alpha_{ijkl} + Tr_{kp}C_{pl\langle ij\rangle}.
\end{aligned} \tag{417}$$

By means of the above relations we can construct the viscous stress in an explicit form. The result is

$$t^v_{ij} = T\left(C_{ijkl}\lambda_{\langle kl\rangle} + C'_{ijkl}\lambda_{kpp}\lambda_{lmm} + C''_{ijklmn}\lambda_{\langle kl\rangle}\lambda_{\langle mn\rangle}\right) + O\left(3\right), \tag{418}$$

where the following abbreviations for the coefficients of the second order have been introduced

$$\begin{aligned}
C'_{ijkl} &= \frac{\rho}{2}\frac{\partial k_{kl}}{\partial F_{iK}}F_{jK} + 2\alpha_{i\langle kl\rangle j} + \frac{10}{3}\kappa_{i\langle k}\delta_{l\rangle j}, \\
C''_{ijklmn} &= \frac{\rho}{2}\frac{\partial h_{klmn}}{\partial F_{iK}}F_{jK} - 2T\delta_{i\langle k}C_{l\,j\rangle\langle mn\rangle}.
\end{aligned} \tag{419}$$

Finally, the comparison of results (400), (406) and (414) yields

$$H_k = \frac{1}{T}q_k + \lambda_{\langle ij\rangle}R_{\langle ij\rangle k} + O\left(3\right). \tag{420}$$

We conclude that the classical Fourier relation $H_k = q_k/T$ holds only in the first order.

It remains to eliminate the multipliers and return to the physical variables which we have mentioned at the beginning of the Lecture. We obtain from (411) and (414)

$$\lambda_{\langle ij\rangle} = \frac{1}{T} C^{-1}_{\langle ij\rangle\langle kl\rangle} t^{v}_{\langle kl\rangle} + O(2), \quad \lambda_{ijj} = \kappa^{-1}_{ij} q_j + O(2), \tag{421}$$

where

$$C^{-1}_{\langle ij\rangle\langle mn\rangle} C_{\langle mn\rangle\langle kl\rangle} = \frac{1}{2}\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl}\right). \tag{422}$$

The higher order terms can be also obtained by the iteration which we do not present here.

In order to complete field equations of the approximate model we need constitutive relations for productions $s_{\langle ij\rangle}$ and s_{ijj}. We know that they have to satisfy the inequality (399) for the dissipation $\mathcal{D}$. Zero value corresponding to equilibrium is the minimum of this function. Consequently, the matrices

$$\sigma_{ijkl} = \frac{1}{\rho_0} \left.\frac{\partial s_{\langle ij\rangle}}{\partial \lambda_{\langle kl\rangle}}\right|_E, \quad \tau_{ij} = \frac{1}{\rho_0} \left.\frac{\partial s_{ikk}}{\partial \lambda_{jmm}}\right|_E, \tag{423}$$

are positive definite, i.e. for arbitrary matrices $A_{\langle ij\rangle}$ and arbitrary vectors B_i

$$\sigma_{ijkl} A_{\langle ij\rangle} A_{\langle kl\rangle} > 0, \quad \tau_{ij} B_i B_j > 0. \tag{424}$$

Hence, for linear relations we obtain by means of relations (421)

$$\begin{aligned} s_{\langle ij\rangle} &= \frac{\rho_0}{T} \sigma_{ijkl} C^{-1}_{\langle kl\rangle\langle mn\rangle} t^{v}_{\langle mn\rangle} + O(2), \\ s_{ijj} &= \rho_0 \tau_{ij} \kappa^{-1}_{jm} q_m + O(2). \end{aligned} \tag{425}$$

It is helpful to collect in the juxtaposition the material parameters of the second order model for nonequilibrium variables λ_{ijj} and $\lambda_{\langle ij\rangle}$. We do so in the following Table 10.

Table 10: *Nonequilibrium material parameters for constitutive quantities of the second order model in terms of variables* $\lambda_{\langle ij\rangle}$ *and* λ_{ijj}

entropy	h'	$\frac{1}{2}k_{ij}$	$\frac{1}{2}h_{ijkl}$
entropy flux	H'_i	χ_{ij}	χ'_{ijkl}
specific internal energy	ε	$-T^2/2\ \partial k_{ij}/\partial T$	$-T^2/2\ \partial h_{ijkl}/\partial T$
Helmholtz free energy	ψ	$-T/2\ k_{ij}$	$-T/2\ h_{ijkl}$
viscous stress tensor	t^v_{ij}		TC_{ijkl}
heat flux	q_i	κ_{ij}	κ'_{ijkl}
stress source	$s_{\langle ij\rangle}$		$\rho_0\sigma_{ijkl}$
heat flux source	s_{ijj}	$\rho_0\tau_{ij}$	

As shown before, they are not all independent.

The above considerations complete the construction of the model. We do not show here the final form of field equations as further results for this set are nonexistent in the general case. Instead, we present two important particular cases: viscous fluids and linear viscoelastic solids.

Let us begin with the **viscous fluid**. For this material, a constitutive dependence on the deformation tensor B_{ij} reduces to its determinant (volume changes) or, equivalently, to the dependence on the current mass density ρ. Simultaneously, all constitutive tensors of the second order model become isotropic functions for which we know representations. The resulting constitutive relations are as follows

$$\begin{aligned}
T_{ij}|_E &= -p\delta_{ij}, \quad T_{ij} = -p\delta_{ij} + t^v_{\langle ij\rangle}, \quad p = p(\rho, T), \quad \frac{\partial p}{\partial \rho} > 0, \\
\varepsilon &= \varepsilon_E(\rho, T), \quad \frac{\partial \varepsilon_E}{\partial T} > 0, \\
\rho_{\langle ij\rangle} &= \frac{\rho_0}{\rho}\left(1 + \frac{\gamma}{2\rho}\right) t^v_{\langle ij\rangle}, \quad \gamma = \gamma(\rho, T), \quad 2p + \gamma < 0, \\
\rho_{ijj} &= \frac{\rho_0}{\rho}\left(\frac{\alpha_2}{\kappa} - \frac{10}{3}\right) q_i, \quad \alpha_2 = \alpha_2(\rho, T), \quad \alpha_2 - \frac{10}{3}\kappa < 0, \\
R_{\langle ij\rangle k} &= \frac{1}{4}\frac{\alpha_1}{\kappa}\left(q_i\delta_{jk} + q_j\delta_{ik} - \frac{2}{3}q_k\delta_{ij}\right), \quad \alpha_1 = \alpha_1(\rho, T), \\
R_{ikkj} &= \beta\delta_{ij} + \left(\frac{\alpha_1}{4\rho T} - \frac{10}{3}\varepsilon_E + 2\frac{p}{\rho}\right) t^v_{\langle ij\rangle}, \quad \beta = \beta(\rho, T), \\
s_{\langle ij\rangle} &= \frac{\rho_0}{2pT}\sigma t^v_{\langle ij\rangle}, \quad \sigma = \sigma(\rho, T) > 0, \\
s_{ijj} &= \frac{\rho_0}{\kappa}\tau q_i, \quad \tau = \tau(\rho, T) > 0,
\end{aligned} \tag{426}$$

where

$$\kappa = -T^2\left(\frac{\partial \beta}{\partial T} - \frac{10}{3}\varepsilon_E\frac{\partial p}{\partial T}\right). \tag{427}$$

Hence, apart from the thermal equation of state $p(\rho, T)$ and caloric equation of state $\varepsilon_E(\rho, T)$ the model requires the knowledge of 6 equilibrium material parameters: β, γ, α_1, α_2, σ, τ, the latter two related to the relaxation times τ_t, τ_q, discussed in previous Lectures.

Bearing these constitutive relations in mind, we obtain from the balance equations the following equations

$$\begin{aligned}
&\underline{t^v_{\langle ij\rangle} = \frac{4p^2T}{\rho\sigma}\left[\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\right.} + \frac{2p+\gamma}{4p^2}\left(\dot{t}^v_{\langle ij\rangle} - \frac{\partial v_{[i}}{\partial x_{k]}}t^v_{\langle kj\rangle} - \frac{\partial v_{[j}}{\partial x_{k]}}t^v_{\langle ki\rangle}\right) + \\
&\left. + \frac{\alpha_1}{4p\kappa}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}}\right] + \frac{\gamma T}{\rho\sigma}\left[\left(\frac{\partial v_{[i}}{\partial x_{k]}} - \Omega_{ik}\right)t^v_{\langle jk\rangle} + \left(\frac{\partial v_{[j}}{\partial x_{k]}} - \Omega_{jk}\right)t^v_{\langle ik\rangle}\right],
\end{aligned} \tag{428}$$

$$\underline{q_i = -\frac{\kappa^2}{\rho\tau T^2}\left[\frac{\partial T}{\partial x_i}\right.} - \frac{T^2}{\kappa^2}\left(\alpha_2 - \frac{10}{3}\kappa\right)\left(\dot{q}_i - \frac{\partial v_{[i}}{\partial x_{k]}}q_k\right) -$$

$$-\frac{\alpha_1 T}{4p\kappa}\frac{\partial t^v_{\langle ik\rangle}}{\partial x_k}\Bigg] + \frac{1}{\rho\tau}\left(\alpha_2 - \frac{5}{3}\alpha_1\right)\left(\frac{\partial v_{[i}}{\partial x_{\,k]}} - \Omega_{ik}\right) q_k. \tag{429}$$

Obviously, the underlined terms represent the Navier-Stokes relation and the Fourier relation of the classical thermodynamics. The above generalization contains, in addition, rate terms for $t^v_{\langle ij\rangle}$ and q_i, the coupling of both relations and the contribution of noninertial frame which makes the above relations material frame indifferent.

However, the model does not account properly for the so-called *normal stress effects* (Weissenberg effects) which appear in the classical Maxwell model of viscoelastic fluids as well as in the so-called Rivlin-Ericksen fluids. This problem has been discussed separately[14]. Unfortunately, there is no uniform approach to this problem of extended thermodynamics which would account for all properties of both classes of models.

We proceed to present the **linear viscoelastic solid**. We assume the initial configuration to be stress-free and, for small deformations,

$$B_{ij} \approx \delta_{ij} + 2\varepsilon_{ij}. \tag{430}$$

It follows

$$\begin{aligned} T_{ij} &= \lambda\varepsilon_{kk}\delta_{ij} + 2\mu\varepsilon_{ij} + t^v_{\langle ij\rangle}, \quad \text{i.e.} \\ C_{ijkl} &\approx A_{ijkl} = \lambda\delta_{ij}\delta_{kl} + \mu\left(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il}\right), \end{aligned} \tag{431}$$

where λ, μ are Lamé moduli, $\varepsilon_0 = \varepsilon_0\left(T\right)$ and

$$\begin{aligned} \rho_{\langle ij\rangle} &= 2\mu\varepsilon_{\langle ij\rangle} + \left(1 + \frac{\gamma}{2\mu}\right) t^v_{\langle ij\rangle}, \\ \rho_{ijj} &= -\left(\frac{10}{3} + \frac{\alpha_2}{T}\left(\frac{d\beta}{dT}\right)^{-1}\right) q_i, \\ R_{\langle ij\rangle k} &= \frac{\alpha_1}{4T^2}\left(\frac{d\beta}{dT}\right)^{-1}\left(q_i\delta_{jk} + q_j\delta_{ik} - \frac{2}{3}q_k\delta_{ij}\right), \\ R_{ikkj} &= \beta\delta_{ij} - \frac{10}{3}\varepsilon_0\left(\lambda\varepsilon_{kk}\delta_{ij} + 2\mu\varepsilon_{ij}\right) + \left(\frac{\alpha_1}{4\mu T} - \frac{10}{3}\varepsilon_0\right) t^v_{\langle ij\rangle}, \\ s_{\langle ij\rangle} &= \frac{\rho}{2\mu T}\sigma t^v_{\langle ij\rangle}, \\ s_{ikk} &= -\frac{\rho}{T^2}\left(\frac{d\beta}{dT}\right)^{-1}\tau q_i. \end{aligned} \tag{432}$$

All material parameters can be arbitrary functions of temperature and the following restrictions must be satisfied

$$\frac{d\varepsilon_0}{dT} > 0, \quad \lambda + \frac{2}{3}\mu > 0, \quad \mu > 0, \quad 2\mu + \gamma < 0, \tag{433}$$

$$\alpha_2 + \frac{10}{3}T^2\frac{d\beta}{dT} < 0, \quad \sigma > 0, \quad \tau > 0. \tag{434}$$

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[14] I. Müller, K. Wilmanski; *Extended Thermodynamics of a non-Newtonian Fluid,* Rheologica Acta, **25**, 1986.
K. Wilmanski; *Thermodynamics of a Heat Conducting Maxwellian Fluid*, Arch. Mech., **40**, 1988.

Now the balance equations for stresses and the heat flux yield

$$\tau_t \dot{T}_{\langle ij\rangle} + T_{\langle ij\rangle} - 2\mu\varepsilon_{\langle ij\rangle} - 2\left(\tau_t + \nu\right)\dot{\varepsilon}_{\langle ij\rangle} = 2\nu\frac{\alpha_1}{4\mu T^2}\left(\frac{d\beta}{dT}\right)^{-1}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}}, \tag{435}$$

$$\tau_q \dot{q}_i + K\frac{\partial T}{\partial x_i} + q_i = -\frac{\alpha_1 K}{4\mu T}\left(\frac{d\beta}{dT}\right)^{-1}\frac{\partial t^v_{\langle ij\rangle}}{\partial x_j}, \quad t^v_{\langle ij\rangle} = T_{ij} - 2\mu\varepsilon_{\langle ij\rangle}, \tag{436}$$

where

$$\begin{aligned} \nu &= \frac{2\mu^2 T}{\rho\sigma}, \quad K = \frac{T^2}{\rho\tau}\left(\frac{d\beta}{dT}\right)^2 \\ \tau_t &= -\frac{T}{\rho\sigma}\left(2\mu + \gamma\right), \quad \tau_q = -\frac{1}{\rho\tau}\left(\alpha_2 + \frac{10}{3}T^2\frac{d\beta}{dT}\right). \end{aligned} \tag{437}$$

The *viscosity coefficient* ν*, the thermal conductivity* K, *the stress relaxation time* τ_t, and *the thermal relaxation time* τ_q are all non-negative.

The equation (435) describes the so-called *standard linear solid* in viscoelasticity[15]. For isothermal processes, this can be integrated and we obtain the following stress-strain relation of the *hereditary type (a linear material with fading memory)*

$$T_{\langle ij\rangle} = 2\left(\mu + \frac{\nu}{\tau_t}\right)\varepsilon_{\langle ij\rangle} - 2\frac{\nu}{\tau_t^2}\int_0^t \varepsilon_{\langle ij\rangle}\left(s\right)e^{-\frac{t-s}{\tau_s}}ds. \tag{438}$$

Simultaneously, the equation (436) without the right-hand side is the Cattaneo equation.

In any case, the above models are hyperbolic which means that disturbances propagate with finite speeds.

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[15] e.g. see: Christensen, R. M.; *Theory of Viscoelasticity*, Academic Press, New York, 1971.

Lecture 9: Thermodynamics of miscible mixtures

Continuum models of multicomponent systems rely on the assumption that particles of distinguishable species are sufficiently densely distributed to enable the volume averaging. For instance, let us consider a domain $\mathcal{P}(\mathbf{x},t)$ which contains at the instant of time t a chosen point $\mathbf{x}$ of the space. Now let us choose an α-species and denote by $\rho^{\alpha}_{micro}(\mathbf{z},t)$ the real mass density of the α-species at the point $\mathbf{z}$ and the instant of time t. The domain $\mathcal{P}(\mathbf{x},t)$ is assumed to be sufficiently large to contain many subdomains of the substance α. Then the macroscopic average mass density of the α-species over the domain $\mathcal{P}(\mathbf{x},t)$ is defined in the following way

$$\rho^{\alpha}(\mathbf{x},t)=\frac{1}{\operatorname{vol}\mathcal{P}(\mathbf{x},t)}\int_{\mathcal{P}(\mathbf{x},t)}\rho^{\alpha}_{micro}(\mathbf{z},t)\,\chi^{\alpha}(\mathbf{z},t)\,dV_z, \tag{439}$$

where $\chi^{\alpha}(\mathbf{z},t)$ is the characteristic function of the α-species, i.e. it equals 1 at the point in which a particle of the α-species appears and it is 0 otherwise. $\operatorname{vol}\mathcal{P}(\mathbf{x},t)$ is the volume of the domain $\mathcal{P}(\mathbf{x},t)$. Obviously, this definition works also in the discrete case when the microscopic density has the form

$$\rho^{\alpha}_{micro}(\mathbf{z},t)\,\chi^{\alpha}(\mathbf{z},t)=\sum_{\mathbf{z}_n\in\mathcal{P}(\mathbf{x},t)}m^{\alpha}\delta\left(\mathbf{z}-\mathbf{z}^{\alpha}(t)\right), \tag{440}$$

where $\mathbf{z}^{\alpha}(t)$ is the location of an α-molecule at the instant of time t and m^{α} is the corresponding molecular mass. The quantity $\rho^{\alpha}(\mathbf{x},t)$ can be considered to be a smooth field of mass density provided the domain $\mathcal{P}(\mathbf{x},t)$ is sufficiently small from the macroscopic point of view and, simultaneously, sufficiently large from the microscopic point of view to include many subdomains of α-species or many α-molecules. We return further to a more detailed discussion of this averaging procedure for porous materials.

In this Lecture we consider *miscible* mixtures which means that a microstructure described by the characteristic functions $\chi^{\alpha}(\mathbf{z},t)$ does not influence macroscopic properties of the mixture. It is different from *immiscible* mixtures such as porous and granular materials or suspensions where these characteristic functions extend the set of macroscopic fields on, say, porosity, tortuosity, etc. We consider such mixtures later in this course.

It is convenient to describe mixtures of fluids, as we do in the fluid dynamics, in the Eulerian reference. It means that the current configuration is the reference configuration for the motion. All fields of the model are functions of the spacial variable $\mathbf{x}\in\mathcal{B}_t$ and the time variable $t\in\mathcal{T}$. The domain of the mixture $\mathcal{B}_t$ depends on time and in any instant of time each point of this domain is occupied simultaneously by particles of all species of the mixture which means there are no subdomains of $\mathcal{B}_t$ of the nonzero volume measure in which one of the species does not appear. The species of the mixture on the macroscopic level of description will be called *components*. The above assumption means that each component of the mixture is described by a set of *partial fields* with a common domain of the definition $\mathcal{B}_t$ at any instant of time t. We distinguish the components by the index α running from 1 to A, where A is the number of components.

In the case of thermomechanical systems considered in this Lecture the *thermodynamical process* is assumed to be described by the following fields

$$\left\{\rho^{\alpha},\mathbf{v}^{\alpha},T\right\},\quad \alpha=1,...,A, \tag{441}$$

where ρ^α are the current partial mass densities of components referring to the common unit volume in the current configuration $\mathcal{B}_t$, $\mathbf{v}^\alpha$ are the velocity fields of components and T denotes the absolute temperature common for all components. The last quantity requires an assumption that all components possess the same temperature. In many practical applications this assumption is not satisfied. However, the problem of thermodynamical modeling of multicomponent systems with multiple temperatures is still not fully solved.

Field equations for the fields (441) follow from the partial balance equations of mass and momentum and from the energy balance equation for the mixture. The partial balance equations for $\alpha = 1, ..., A$ have the form

$$\frac{d}{dt}\int_{\mathcal{P}_t^\alpha} \rho^\alpha dV = \int_{\mathcal{P}_t^\alpha} \hat{\rho}^\alpha dV, \tag{442}$$

$$\frac{d}{dt}\int_{\mathcal{P}_t^\alpha} \rho^\alpha \mathbf{v}^\alpha dV = \oint_{\partial\mathcal{P}_t^\alpha} \mathbf{T}^\alpha \mathbf{n} dS + \int_{\mathcal{P}_t^\alpha} \left(\rho^\alpha \mathbf{b}^\alpha + \hat{\mathbf{p}}^\alpha\right) dV, \tag{443}$$

$$\frac{d}{dt}\int_{\mathcal{P}_t^\alpha} \rho^\alpha \left(\varepsilon^\alpha + \tfrac{1}{2}\mathbf{v}^\alpha \cdot \mathbf{v}^\alpha\right) dV = \oint_{\partial\mathcal{P}_t^\alpha} \left(\mathbf{T}^\alpha \mathbf{v}^\alpha - \mathbf{q}^\alpha\right) \cdot \mathbf{n} dS +$$

$$+ \int_{\mathcal{P}_t^\alpha} \left(\rho^\alpha \mathbf{b}^\alpha \cdot \mathbf{v}^\alpha + \rho^\alpha r^\alpha + \hat{\varepsilon}^\alpha\right) dV, \tag{444}$$

where $\mathcal{P}_t^\alpha \subset \mathcal{B}_t$ is a measurable subset of the current configuration which moves with the kinematics of the α-component and $\partial\mathcal{P}_t^\alpha$ denotes its surface with the unit outward normal vector $\mathbf{n}$. The quantities with the hat are volume densities of sources (productions) and, according to the fundamental assumption of Truesdell's mixture theory they must satisfy the following conservation laws

$$\sum_{\alpha=1}^{A} \hat{\rho}^\alpha = 0, \quad \sum_{\alpha=1}^{A} \hat{\mathbf{p}}^\alpha = 0, \quad \sum_{\alpha=1}^{A} \hat{\varepsilon}^\alpha = 0. \tag{445}$$

The remaining quantities $\mathbf{T}^\alpha, \mathbf{b}^\alpha, \varepsilon^\alpha, \mathbf{q}^\alpha, r^\alpha$ denote the symmetric partial Cauchy stress tensor in the α-component, the body force per unit mass of the α-component, the partial density of the internal energy of the α-component, the partial heat flux in the α-component, and the density of energy radiation in the α-component, respectively.

The assumption that partial densities satisfy balance laws yields, according to the Cauchy Theorem which we have discussed in Lecture 2, the existence of partial stress tensors $\mathbf{T}^\alpha$ and partial heat flux vectors $\mathbf{q}^\alpha$.

In the case of the single temperature field the partial energy balance equations are not used and we need only the energy conservation of the mixture. This must have, of course, the classical form

$$\frac{d}{dt}\int_{\mathcal{P}_t} \rho \left(\varepsilon + \tfrac{1}{2}\mathbf{v} \cdot \mathbf{v}\right) dV = \oint_{\partial\mathcal{P}_t} \left(\mathbf{T}\mathbf{v} - \mathbf{q}\right) \cdot \mathbf{n} dS + \int_{\mathcal{P}_t} \rho \left(\mathbf{b} \cdot \mathbf{v} + \mathbf{r}\right) dV. \tag{446}$$

We obtain indeed this relation if we add equations (444) and introduce the definitions

$$\rho = \sum_{\alpha=1}^{A} \rho^\alpha, \quad \rho\mathbf{v} = \sum_{\alpha=1}^{A} \rho^\alpha \mathbf{v}^\alpha, \quad \rho\varepsilon = \sum_{\alpha=1}^{A} \rho^\alpha \left(\varepsilon^\alpha + \tfrac{1}{2}\mathbf{u}^\alpha \cdot \mathbf{u}^\alpha\right),$$

$$\mathbf{T} = \sum_{\alpha=1}^{A} \left(\mathbf{T}^\alpha - \rho^\alpha \mathbf{u}^\alpha \otimes \mathbf{u}^\alpha \right), \quad \mathbf{q} = \sum_{\alpha=1}^{A} \left(\mathbf{q}^\alpha + \rho^\alpha \left(\varepsilon^\alpha + \tfrac{1}{2} \mathbf{u}^\alpha \cdot \mathbf{u}^\alpha \right) \mathbf{u}^\alpha - \mathbf{T}^\alpha \mathbf{u}^\alpha \right),$$

$$\rho r = \sum_{\alpha=1}^{A} \rho^\alpha \left(r^\alpha + \mathbf{b}^\alpha \cdot \mathbf{u}^\alpha \right), \quad \mathbf{u}^\alpha = \mathbf{v}^\alpha - \mathbf{v}, \quad \sum_{\alpha=1}^{A} \rho^\alpha \mathbf{u}^\alpha = 0. \tag{447}$$

The presence of convective terms containing the *diffusion velocities* $\mathbf{u}^\alpha$ follows from the fact that subsets $\mathcal{P}_t$ of the current configuration $\mathcal{B}_t$ possess the kinematics of the *barycentric velocity field* $\mathbf{v}$ and it means that fluxes contain additional contributions – none of these subsets is *material* with respect to any of the components.

It can be easily checked that the above definitions yield as well the classical conservation of mass and momentum for the whole mixture

$$\frac{d}{dt} \int_{\mathcal{P}_t} \rho dV = 0, \quad \frac{d}{dt} \int_{\mathcal{P}_t} \rho \mathbf{v} dV = \oint_{\partial \mathcal{P}_t} \mathbf{T} \mathbf{n} dS + \int_{\mathcal{P}_t} \rho \mathbf{b} dV, \quad \rho \mathbf{b} = \sum_{\alpha=1}^{A} \rho^\alpha \mathbf{b}^\alpha. \tag{448}$$

Let us remark that the presence of diffusion yields a macroscopic heat flux $\mathbf{q}$ even in the case when the partial heat conduction contributions $\mathbf{q}^\alpha$ are absent. This property is essential for a peculiar form of the second law of thermodynamics of mixtures which we discuss further.

The above global balance equations yield in a standard way local laws. They have different form in *regular* points in which fields are continuous and in *singular* points on surfaces on which fields may suffer jumps. Namely

$$\begin{aligned}
&\frac{\partial \rho^\alpha}{\partial t} + \operatorname{div} \left(\rho^\alpha \mathbf{v}^\alpha \right) = \hat{\rho}^\alpha, \\
&\frac{\partial \rho^\alpha \mathbf{v}^\alpha}{\partial t} + \operatorname{div} \left(\rho^\alpha \mathbf{v}^\alpha \otimes \mathbf{v}^\alpha - \mathbf{T}^\alpha \right) = \rho^\alpha \mathbf{b}^\alpha + \hat{\mathbf{p}}^\alpha, \\
&\frac{\partial \rho \varepsilon}{\partial t} + \operatorname{div} \left(\rho \varepsilon \mathbf{v} + \mathbf{q} \right) = \mathbf{T} \cdot \operatorname{grad} \mathbf{v} + \rho r,
\end{aligned} \tag{449}$$

in regular points. The last equation, the so called balance of internal energy, follows by elimination of the contribution of kinetic energy by means of mass and momentum conservation laws.

In singular points the balance equations have the form of jump conditions across the surface. We use them here only for the bulk mass and the bulk energy of the mixture but, of course, they may be easily derived for all other equations as well. We have for these two quantities (comp. Table 4, Lecture 2)

$$\begin{aligned}
&[[\rho \left(\mathbf{v} \cdot \mathbf{n} - c \right)]] = 0, \quad [[...]] = (...)^+ - (...)^-, \\
&[[\mathbf{q} \cdot \mathbf{n}]] = [[\mathbf{T} \left(\mathbf{v} - c\mathbf{n} \right)]] \cdot \mathbf{n} - \left[\left[\varepsilon + \tfrac{1}{2} \left(\mathbf{v} - c\mathbf{n} \right) \cdot \left(\mathbf{v} - c\mathbf{n} \right) \right] \right] \rho \left(\mathbf{v} \cdot \mathbf{n} - c \right),
\end{aligned} \tag{450}$$

where c denotes the speed of the surface and $\mathbf{n}$ is the unit normal vector to this surface. As indicated the double parenthesis denotes the difference of limits on both sides of the singular surface.

As we know already from thermodynamical theories of single component systems the system of balance laws may be transformed into field equations by means of the closure. This means that we have to specify constitutive relations for a set of constitutive quantities.

We begin the discussion of this problem with the specification of mass sources for chemical reactions. Components of the mixture are then not the most fundamental ingredients of the macroscopic picture. These are rather molecules (constituents) which satisfy laws of mass conservation. To see this structure let us consider the simplest example of formation of water from hydrogen H and oxygen O. These two are molecules (constituents) while the mixture consists of the following components: H, O, H_2, O_2, OH, H_2O. They are participating in chemical reactions which can be symbolically written in the form

$$\begin{array}{l} H_2 - 2H = 0, \\ O_2 - 2O = 0, \\ H + O - OH = 0, \\ H + OH - H_2O = 0, \\ 2H_2 + O_2 - 2H_2O = 0, \end{array} \qquad (\gamma^r_\alpha) = \begin{pmatrix} -2 & 0 & 1 & 0 & 0 & 0 \\ 0 & -2 & 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 & -1 & 0 \\ 1 & 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 2 & 1 & 0 & -2 \end{pmatrix}, \tag{451}$$

The matrix of coefficients γ^r_α, $\alpha = 1, ..., 6$, $r = 1, ..., 5$ in this set of relations is called the *stoichiometric matrix*. Its rank determines the number of independent reactions. In our example this rank is equal to 4. The conservation of mass for molecules (constituents) in each reaction can be written in the form

$$\sum_{\alpha=1}^{A} \gamma^r_\alpha M_\alpha \mu_H = 0, \quad r = 1, ..., \mathcal{R}, \tag{452}$$

where M_α denotes the molecular weight of the component α, μ_H is the mass of a hydrogen atom and $\mathcal{R}$ is the number of reactions.

Further we consider only the set of independent chemical reactions and we denote their number by ν. The contribution of each reaction to the production of components depends also on the *rate of reaction* which we denote by $\lambda^r, r = 1, ..., \nu$. Then the mass source in partial mass balance equations can be written in the form

$$\hat{\rho}^\alpha = \sum_{r=1}^{\nu} \gamma^r_\alpha M_\alpha \mu_H \lambda^r. \tag{453}$$

It is clear that the conservation relations (452) imply $(445)_1$.

Let us now return to the general closure problem. We transform the balance equations (449) into field equations for the fields (441). We use the strategy of continuum thermodynamics and assume that the *constitutive quantities*

$$\mathcal{F} = \left\{ \lambda^r, \mathbf{T}^\alpha, \hat{\mathbf{p}}^\alpha, \varepsilon, \mathbf{q} \right\}, \tag{454}$$

are sufficiently smooth functions of *constitutive variables*. The choice of the constitutive variables specifies the class of substances admissible in the model under construction. We consider here only an example of inviscid fluids. However, in contrast to the thermodynamical modeling of the single inviscid (ideal) fluid we include among constitutive variables the gradients of partial mass densities. It has been shown by I. Müller that this yields a desirable structure of interactions of components. We return later to this point. The chosen set of constitutive variables is as follows

$$\mathcal{C} = \{\rho^{\alpha}, \operatorname{grad}\rho^{\alpha}, \mathbf{v}^{\alpha}, T, \operatorname{grad}T\}\,. \tag{455}$$

Hence the *closure* of the set of balance equations has the form

$$\mathcal{F} = \mathcal{F}(\mathcal{C})\,. \tag{456}$$

These relations must satisfy the conservation restrictions $(445)_2$.

In order to describe viscous fluids we would have to add a dependence on gradients of velocity to the set of constitutive variables. This can be easily done but the results are not so transparent as in the present case.

The constitutive relations (456) in the thermodynamical modeling procedure must satisfy principles which we were already discussing for single component continua. For fluid mixtures two of them will be presented in details

- material objectivity (material frame indifference),
- thermodynamical admissibility.

As we know already the principle of material objectivity (material frame indifference) concerns the behavior of field equations under the so-called Euclidean transformation, i.e the transformation described by the following relation for an arbitrary point of the configuration space

$$\mathbf{x}^{*} = \mathbf{O}(t)\,\mathbf{x} + \mathbf{c}(t)\,, \quad \mathbf{O}^{T} = \mathbf{O}^{-1}. \tag{457}$$

Let us recall that the scalar, a, the vector, $\mathbf{w}$, and the tensor, $\mathbf{T}$, transform in an objective manner if they satisfy the following transformation rules

$$a^{*} = a, \quad \mathbf{w}^{*} = \mathbf{O}\mathbf{w}, \quad \mathbf{T}^{*} = \mathbf{O}\mathbf{T}\mathbf{O}^{T}. \tag{458}$$

Obviously, neither the velocity nor the acceleration transform in an objective manner. Differentiation of (457) with respect to time yields

$$\begin{aligned} \mathbf{v}^{*} &= \mathbf{O}\mathbf{v} + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}}, \quad \dot{\mathbf{O}} = \frac{d\mathbf{O}}{dt}, \quad \dot{\mathbf{c}} = \frac{d\mathbf{c}}{dt} \\ \mathbf{a}^{*} &= \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}^{*}\cdot \operatorname{grad}\mathbf{v}^{*} = \mathbf{O}\mathbf{a} + 2\dot{\mathbf{O}}\mathbf{v} + \ddot{\mathbf{O}}\mathbf{x} + \ddot{\mathbf{c}}. \end{aligned} \tag{459}$$

Consequently, the momentum balance equations do not transform in an objective manner. The transformation from an inertial to a noninertial frame yields centrifugal, Coriolis, Euler, and translational forces which form together the inertial forces discussed already in previous Lectures. Simultaneously, the mass and energy balance equations transform in an objective manner.

In the case of chemical reactions there appears an additional problem related to the contribution of mass sources to the momentum balance equations. It becomes clear when we use the chain rule of differentiation on the left hand side of $(449)_2$ and substitute mass balance equations $(449)_1$. Then the above described structure remains unchanged under the Euclidean transformation if we assume that the following vector

$$\hat{\mathbf{p}}^\alpha - \hat{\rho}^\alpha \mathbf{v}^\alpha, \tag{460}$$

is objective rather than the momentum source itself. We do so in further considerations.

The principle of material objectivity (material frame indifference) requires that functions

$$\mathcal{F}_o = \left\{\lambda^r, \mathbf{T}^\alpha, \hat{\mathbf{p}}^\alpha - \hat{\rho}^\alpha \mathbf{v}^\alpha, \varepsilon, \mathbf{q}\right\} = \mathcal{F}_o\left(\mathcal{C}\right), \tag{461}$$

remain unchanged under an arbitrary Euclidean transformation, i.e.

$$\mathcal{F}_o^* = \mathcal{F}_o\left(\mathcal{C}^*\right). \tag{462}$$

Note that the constitutive *function* $\mathcal{F}_o(.)$ is the same in (461) and (462).

An immediate consequence of the above principle is the elimination of one of velocities among constitutive variables. Instead of partial velocities this set may contain only relative velocities which are objective. These may be diffusion velocities $\mathbf{u}^\alpha$, or, as they are only $A-1$ independent variables of this art, relative velocities

$$\mathbf{w}^\alpha = \mathbf{v}^\alpha - \mathbf{v}^A, \tag{463}$$

which are more convenient in the calculations.

The full representation of constitutive functions in their objective form is a rather complicated task and we shall not do so in this Lecture. We limit our attention to constitutive functions which are **linear** in $\operatorname{grad}\rho^\alpha, \mathbf{w}^\alpha, \operatorname{grad}T$. In this case the most general form of the constitutive equations compatible with the material objectivity is as follows

$$\begin{aligned}
\lambda^r &= \lambda^r\left(\rho^\beta, T\right), \\
\mathbf{T}^\alpha &= -p^\alpha\left(\rho^\beta, T\right)\mathbf{1}, \\
\hat{\mathbf{p}}^\alpha - \hat{\rho}^\alpha \mathbf{v}^\alpha &= \sum_{\beta=1}^{A} M_\rho^{\alpha\beta} \operatorname{grad}\rho^\beta + \sum_{\beta=1}^{A-1} M_w^{\alpha\beta}\mathbf{w}^\beta + M_T^\alpha \operatorname{grad}T, \\
\mathbf{q}_I &= \sum_{\beta=1}^{A} q_\rho^\beta \operatorname{grad}\rho^\beta + \sum_{\beta=1}^{A-1} q_w^\beta \mathbf{w}^\beta + q_T \operatorname{grad}T, \\
\varepsilon_I &= \varepsilon_I\left(\rho^\beta, T\right),
\end{aligned} \tag{464}$$

where the index I denotes the so-called *intrinsic* part of the quantity

$$\begin{aligned}
\mathbf{q}_I &= \mathbf{q} - \sum_{\alpha=1}^{A} \tfrac{1}{2}\rho^\alpha\left(\mathbf{u}^\alpha \cdot \mathbf{u}^\alpha\right)\mathbf{u}^\alpha = \sum_{\alpha=1}^{A}\mathbf{q}^\alpha + \sum_{\alpha=1}^{A}\left(\rho^\alpha\varepsilon^\alpha\mathbf{1} - \mathbf{T}^\alpha\right)\mathbf{u}^\alpha, \\
\varepsilon_I &= \varepsilon - \sum_{\alpha=1}^{A} \tfrac{1}{2}\frac{\rho^\alpha}{\rho}\mathbf{u}^\alpha \cdot \mathbf{u}^\alpha = \sum_{\alpha=1}^{A}\frac{\rho^\alpha}{\rho}\varepsilon^\alpha.
\end{aligned} \tag{465}$$

The coefficients appearing in relations (464) may be dependent on ρ^β and T. However, they are not independent due to the previously discussed restrictions on sources. Namely we have

$$\begin{aligned} \sum_{\alpha=1}^{A} M_\rho^{\alpha\beta} &= 0, \quad \beta = 1, ..., A, \\ \sum_{\alpha=1}^{A} M_w^{\alpha\beta} + \hat{\rho}^\beta &= 0, \quad \beta = 1, ..., A-1, \\ \sum_{\alpha=1}^{A} M_T^{\alpha} &= 0. \end{aligned} \tag{466}$$

In spite of the above assumed linearity the whole model remains nonlinear due to various nonlinear explicit contributions.

We proceed to impose the condition of thermodynamical admissibility on the above constitutive relations. As in the case of the single component continua we assume that the *second law of thermodynamics* is based upon the entropy inequality. As discussed earlier, the strategy of continuum thermodynamics in construction of macroscopic models relies on the assumption that solutions of the field equations identically satisfy the second law of thermodynamics called also the entropy principle. This law consists of four parts:

i/ There exist a nontrivial entropy density function η and the entropy flux $\mathbf{h}$ which are both constitutive. In the case of miscible mixtures, considered in this Section, they must have the following general form

$$\eta = \eta\left(\rho^\beta, T\right), \quad \mathbf{h} = \sum_{\alpha=1}^{A} h_\rho^\alpha \operatorname{grad} \rho^\alpha + \sum_{\alpha=1}^{A-1} h_w^\alpha \mathbf{w}^\alpha + h_T \operatorname{grad} T, \tag{467}$$

where $h_\rho^\alpha, h_w^\alpha$, and h_T may be functions of ρ^β, T.

ii/ The entropy density satisfies the balance equation whose form in regular points is as follows

$$\frac{\partial \rho\eta}{\partial t} + \operatorname{div}\left(\rho\eta\mathbf{v} + \mathbf{h}\right) = \hat{\eta}, \tag{468}$$

where $\hat{\eta}$ denotes the entropy source.

iii/ The entropy source is nonnegative for all solutions of field equations, i.e. for all thermodynamic processes. Consequently, the following inequality holds

$$\forall_{\text{all thermodynamic processes}} \frac{\partial \rho\eta}{\partial t} + \operatorname{div}\left(\rho\eta\mathbf{v} + \mathbf{h}\right) \geq 0. \tag{469}$$

iv/ There exist *ideal walls* on which there is no entropy production and the temperature is continuous across it, i.e.

$$[[\mathbf{h} \cdot \mathbf{n}]] + [[\eta]]\, \rho\left(\mathbf{v} \cdot \mathbf{n} - c\right) = 0, \quad [[T]] = 0. \tag{470}$$

The method of Lagrange multipliers applied to the inequality (469) yields the following extended form of the inequality

$$\forall_{\text{all fields}} \frac{\partial \rho\eta}{\partial t} + \operatorname{div}\left(\rho\eta\mathbf{v} + \mathbf{h}\right) - \sum_{\alpha=1}^{A} \Lambda^{\rho^\alpha} \left(\frac{\partial \rho^\alpha}{\partial t} + \operatorname{div}\left(\rho^\alpha \mathbf{v}^\alpha\right) - \sum_{r=1}^{\nu} \gamma_\alpha^r M_\alpha \mu_H \lambda^r \right) -$$

$$-\sum_{\alpha=1}^{A} \mathbf{\Lambda}^{v^\alpha} \cdot \left(\frac{\partial \rho^\alpha \mathbf{v}^\alpha}{\partial t} + \operatorname{div}\left(\rho^\alpha \mathbf{v}^\alpha \otimes \mathbf{v}^\alpha - \mathbf{T}^\alpha \right) - \hat{\mathbf{p}}^\alpha \right) - \tag{471}$$

$$-\Lambda^\varepsilon \left(\frac{\partial \rho\varepsilon}{\partial t} + \operatorname{div}\left(\rho\varepsilon \mathbf{v} + \mathbf{q} \right) - \mathbf{T} \cdot \operatorname{grad} \mathbf{v} \right) \geq 0.$$

The Lagrange multipliers $\Lambda^{\rho^\alpha}, \mathbf{\Lambda}^{v^\alpha}, \Lambda^\varepsilon$ are functions of constitutive variables $\rho^\beta, \operatorname{grad} \rho^\beta$, $\mathbf{v}^\beta, T, \operatorname{grad} T$. After the exploitation of the above inequality these multipliers must be eliminated as auxiliary quantities.

Insertion of constitutive relations into the inequality (471) leads to an inequality which is explicitly linear in the derivatives

$$\left\{ \frac{\partial T}{\partial t}, \operatorname{grad} \otimes \operatorname{grad} T, \frac{\partial \rho^\beta}{\partial t}, \operatorname{grad} \otimes \operatorname{grad} \rho^\beta, \frac{\partial \mathbf{v}^\beta}{\partial t}, \operatorname{grad} \mathbf{v}^\beta \right\}. \tag{472}$$

Since the inequality (471) must hold for arbitrary fields these derivatives can be chosen arbitrarily. Consequently, the inequality can be violated if these contributions do not vanish identically. This yields a series of identities which, on the one hand side, determine multipliers and, on the other hand, restrict constitutive relations. In addition, there remains a nonlinear part of the inequality, the so-called *residual* inequality which determines the *dissipation* density of processes.

The identities following from the entropy inequality have the following form

$$\frac{\partial \eta}{\partial T} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial T} = 0, \tag{473}$$

$$\frac{\partial \mathbf{h}}{\partial \mathbf{g}} - \Lambda^\varepsilon \frac{\partial \mathbf{q}}{\partial \mathbf{g}} = 0, \quad \mathbf{g} = \operatorname{grad} T, \tag{474}$$

$$\frac{\partial \eta}{\partial \rho^\alpha} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \rho^\alpha} + \frac{1}{\rho}\left(\eta - \Lambda^\varepsilon \varepsilon \right) - \frac{1}{\rho}\Lambda^{\rho^\alpha} - \frac{1}{\rho}\mathbf{v}^\alpha \cdot \mathbf{\Lambda}^{v^\alpha} = 0, \quad \alpha = 1, ..., A-1 \tag{475}$$

$$\frac{\partial \mathbf{h}}{\partial \operatorname{grad} \rho^\alpha} - \Lambda^\varepsilon \frac{\partial \mathbf{q}}{\partial \operatorname{grad} \rho^\alpha} = 0, \quad \alpha = 1, ..., A \tag{476}$$

$$\frac{\partial \eta}{\partial \mathbf{w}^\alpha} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{w}^\alpha} - \frac{\rho^\alpha}{\rho}\mathbf{\Lambda}^{v^\alpha} = 0, \quad \alpha = 1, ..., A-1, \tag{477}$$

$$-\sum_{\beta=1}^{A} \left(\frac{\partial \eta}{\partial \mathbf{w}^\beta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{w}^\beta} \right) - \frac{\rho^A}{\rho}\mathbf{\Lambda}^{v^A} = 0, \tag{478}$$

$$\left(\frac{\partial \eta}{\partial \rho^\alpha} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \rho^\alpha} \right) \mathbf{1} - \frac{1}{\rho^2}\Lambda^\varepsilon \mathbf{T} - \tag{479}$$

$$-\frac{1}{\rho\rho^\alpha} \left(\frac{\partial \mathbf{h}}{\partial \mathbf{w}^\alpha} - \Lambda^\varepsilon \frac{\partial \mathbf{q}}{\partial \mathbf{w}^\alpha} \right) + \frac{1}{\rho}\mathbf{\Lambda}^{v^\alpha} \otimes \mathbf{u}^\alpha = 0, \quad \alpha = 1, ..., A-1,$$

$$\left(\frac{\partial\eta}{\partial\rho^A}-\Lambda^\varepsilon\frac{\partial\varepsilon}{\partial\rho^A}\right)\mathbf{1}-\sum_{\beta=1}^{A-1}\frac{1}{\rho\rho^A}\left(\frac{\partial\mathbf{h}}{\partial\mathbf{w}^\beta}-\Lambda^\varepsilon\frac{\partial\mathbf{q}}{\partial\mathbf{w}^\beta}\right)-\frac{1}{\rho}\boldsymbol{\Lambda}^{v^A}\otimes\mathbf{u}^A-\frac{1}{\rho^2}\Lambda^\varepsilon\mathbf{T}=0.\tag{480}$$

There remains the residual inequality which has the following form

$$\begin{aligned}&\sum_{\beta=1}^{A}\left[\left(\frac{\partial\mathbf{h}}{\partial\rho^\beta}-\Lambda^\varepsilon\frac{\partial\mathbf{q}}{\partial\rho^\beta}\right)-\rho\left(\frac{\partial\eta}{\partial\rho^\beta}-\Lambda^\varepsilon\frac{\partial\varepsilon}{\partial\rho^\beta}\right)\mathbf{u}^\beta-\right.\\&\left.-\sum_{\alpha=1}^{A}\boldsymbol{\Lambda}^{v^\alpha}\frac{\partial p^\alpha}{\partial\rho^\beta}+\Lambda^\varepsilon\frac{1}{\rho}\mathbf{T}\mathbf{u}^\beta\right]\cdot\operatorname{grad}\rho^\beta+\\&+\left(\frac{\partial\mathbf{h}}{\partial T}-\Lambda^\varepsilon\frac{\partial\mathbf{q}}{\partial T}-\sum_{\alpha=1}^{A}\boldsymbol{\Lambda}^{v^\alpha}\frac{\partial p^\alpha}{\partial T}\right)\cdot\mathbf{g}+\sum_{\alpha=1}^{A}\Lambda^{\rho^\alpha}\hat{\rho}^\alpha+\sum_{\alpha=1}^{A}\boldsymbol{\Lambda}^{v^\alpha}\cdot\hat{\mathbf{p}}^\alpha\geq 0.\end{aligned}\tag{481}$$

We use further the following relation following from the above identities

$$\Lambda^\varepsilon\sum_{\alpha=1}^{A}p^\alpha=-\sum_{\alpha=1}^{A}\rho^\alpha\Lambda_I^{\rho^\alpha}+\rho\left(\eta-\Lambda^\varepsilon\varepsilon_I\right),\tag{482}$$

where

$$\Lambda_I^{\rho^\beta}=\Lambda^{\rho^\beta}-\frac{1}{T}\left(\mathbf{v}^\beta\cdot\mathbf{u}^\beta-\tfrac{1}{2}\mathbf{u}^\beta\cdot\mathbf{u}^\beta\right)=\Lambda_I^{\rho^\beta}\left(\rho^\alpha,T\right).\tag{483}$$

Before the discussion of thermodynamical properties of the mixture let us check the form of the above relations for a single fluid, i.e. we set $A=1$. We obtain

$$\begin{aligned}\boldsymbol{\Lambda}^v&=0,\\d\eta&=\Lambda^\varepsilon\left(d\varepsilon-\frac{p}{\rho^2}d\rho\right),\\\mathbf{h}&=\Lambda^\varepsilon\mathbf{q},\\&\frac{\partial\Lambda^\varepsilon}{\partial\rho}\mathbf{q}\cdot\operatorname{grad}\rho+\frac{\partial\Lambda^\varepsilon}{\partial T}\mathbf{q}\cdot\operatorname{grad}T\geq 0.\end{aligned}\tag{484}$$

We use now the part iv/ of the second law of thermodynamics. Let us consider an impermeable ideal wall which separates two different single fluids I and II. Such a wall moves with the speed $c=\mathbf{v}\cdot\mathbf{n}$ (material surface). The jump condition (470) yields then

$$[[\mathbf{h}]]\cdot\mathbf{n}=0\quad\text{and}\quad[[T]]=0.\tag{485}$$

Bearing (450) and $(484)_3$ in mind, we obtain

$$\Lambda_I^\varepsilon\left(\rho_I,T\right)=\Lambda_{II}^\varepsilon\left(\rho_{II},T\right).\tag{486}$$

This relation must hold for an arbitrary independent choice of ρ_I and ρ_{II}. Hence it can be satisfied only if it is independent of mass densities at all. We conclude

$$\Lambda_I^\varepsilon\left(T\right)=\Lambda_{II}^\varepsilon\left(T\right).\tag{487}$$

Consequently, the function $\Lambda^{\varepsilon}(T)$ is the same for all ideal fluids and, for this reason, we call it *universal.*

In order to determine this function it is sufficient to inspect $(484)_2$ for the case of ideal gases. Then it is identical with $1/T$. Hence it follows in general

$$\Lambda^{\varepsilon} = \frac{1}{T}. \tag{488}$$

Relations (484) become

$$d\eta = \frac{1}{T}\left(d\varepsilon - \frac{p}{\rho^2}d\rho\right), \quad \mathbf{h} = \frac{1}{T}\mathbf{q}, \quad \mathbf{q}\cdot \operatorname{grad} T \leq 0. \tag{489}$$

These are the results identical with those of the classical thermodynamics. The first relation is, of course, the Gibbs equation.

If we consider an impermeable wall separating a mixture I from a single fluid II and account for the jump conditions we obtain immediately

$$\Lambda_I^{\varepsilon}(\rho_I^{\alpha}, T) = \frac{1}{T}. \tag{490}$$

Hence the multiplier Λ^{ε} remains universal also for mixtures.

One cannot argue in the same way in a general model of mixtures in which each component possesses its own temperature. The multipliers of the partial energy balance equations are not in general universal functions of the absolute temperature. This means as well that temperature cannot be measured on the surface of contact between two different systems because such a surface, even if it is an ideal wall, does not yield the continuity of temperatures. Consequently, we cannot construct thermometers.

Let us now consider a semipermeable wall separating two mixtures I and II. The wall is assumed to be permeable for a single chosen component γ. On such a wall

$$\mathbf{v}^{\alpha}\cdot\mathbf{n} = c \quad \text{for} \quad \alpha \neq \gamma, \quad \mathbf{v} = c\mathbf{n} + \frac{\rho^{\gamma}}{\rho}\left(\mathbf{v}^{\gamma} - c\mathbf{n}\right). \tag{491}$$

The jump of internal energy $(450)_2$ reads

$$[[\mathbf{q}]]\cdot\mathbf{n} - \left[\left[\frac{\mathbf{n}\cdot\mathbf{T}\mathbf{n}}{\rho} - \varepsilon - \tfrac{1}{2}(\mathbf{v}-c\mathbf{n})\cdot(\mathbf{v}-c\mathbf{n})\right]\right]\rho(\mathbf{v}\cdot\mathbf{n}-c) = 0,$$

or, bearing the separation (465) and the relation

$$\mathbf{T} = -\sum_{\alpha=1}^{A}\left(p^{\alpha}\mathbf{1} + \rho^{\alpha}\mathbf{u}^{\alpha}\otimes\mathbf{u}^{\alpha}\right),$$

in mind, we obtain

$$[[\mathbf{q}_I]]\cdot\mathbf{n} + \left[\left[\frac{1}{\rho}\sum_{\alpha=1}^{A}p^{\alpha} + \varepsilon_I + \tfrac{1}{2}(\mathbf{v}-c\mathbf{n})\cdot(\mathbf{v}-c\mathbf{n})\right]\right]\rho(\mathbf{v}\cdot\mathbf{n}-c) = 0. \tag{492}$$

Simultaneously, the jump of the entropy is of the following form

$$[[\mathbf{h}]]\cdot\mathbf{n} + [[\eta]]\,\rho(\mathbf{v}\cdot\mathbf{n}-c) = 0. \tag{493}$$

These two relations can be now substituted in one of the identities following from the evaluation of the entropy inequality. The result is

$$\left[\left[\varepsilon_I - T\eta + \tfrac{1}{2}\left(\mathbf{v}-c\mathbf{n}\right)\cdot\left(\mathbf{v}-c\mathbf{n}\right) + \frac{1}{\rho}\sum_{\alpha=1}^{A} p^{\alpha} - T\sum_{\alpha=1}^{A}\left(\delta^{\gamma\beta} - \frac{\rho^{\beta}}{\rho}\right)\Lambda_I^{\rho^{\beta}}\right]\right] = 0. \quad (494)$$

Bearing (482) in mind, this relation can be transformed as follows

$$[[\mu^{\gamma}]] = 0, \quad (495)$$

where

$$\mu^{\gamma} = \mu_I^{\gamma} + \tfrac{1}{2}\left(\mathbf{v}-c\mathbf{n}\right)\cdot\left(\mathbf{v}-c\mathbf{n}\right), \quad \mu_I^{\gamma} = -T\Lambda_I^{\rho^{\gamma}}, \quad (496)$$

This quantity continuous across ideal semipermeable walls is called the *chemical potential of the component* γ. This can be determined experimentally. Namely according to the relation (482) we have

$$\sum_{\alpha=1}^{A} \rho^{\alpha}\mu_I^{\alpha} = \rho\left(\varepsilon_I - T\eta\right) + \sum_{\alpha=1}^{A} p^{\alpha}, \quad (497)$$

and, for the single fluid,

$$\mu_I = \varepsilon - T\eta + \frac{p}{\rho}, \quad (498)$$

which is, of course, the free enthalpy, and, hence, a measurable quantity. We can now argue in the same way as we did for the temperature. The contact between the mixture and the fluid identical with the γ-component of the mixture through the semipermeable wall for this component yields the measurement of the chemical potential of this component.

The remaining results of the exploitation of the second law of thermodynamics can now be written in the following compact form

$$\begin{aligned}
\mathbf{\Lambda}^{v^{\alpha}} &= -\frac{1}{T}\mathbf{u}^{\alpha}, \\
d\left(\rho\eta\right) &= \frac{1}{T}\left(d\left(\rho\varepsilon_I\right) - \sum_{\alpha=1}^{A}\mu_I^{\alpha} d\rho^{\alpha}\right), \\
\rho\left(\varepsilon_I - T\eta\right) &= \sum_{\alpha=1}^{A}\rho^{\alpha}\mu_I^{\alpha} - p, \\
\mathbf{h} &= \frac{1}{T}\left(\mathbf{q} - \sum_{\alpha=1}^{A}\rho^{\alpha}\mu_I^{\alpha}\mathbf{u}^{\alpha}\right).
\end{aligned} \quad (499)$$

Equation $(499)_2$ is the Gibbs equation for the mixtures. We investigate further its consequences. Equation $(499)_3$ is called the Gibbs-Duhem equation. Finally, the relation $(499)_4$ between the entropy flux $\mathbf{h}$ and the heat flux $\mathbf{q}$ demonstrates the fundamental difference between the thermodynamics of single component media for which $\mathbf{h} = \mathbf{q}/T$ and the multicomponent media. The presence of the additional term in the above relation proves that we cannot rely in thermodynamics of mixtures on the classical Clausius-Duhem inequality as the form of the second law of thermodynamics. This is one of the main observations made by Ingo Müller in the construction of thermodynamical mixture theories. There is a simple physical explanation of the difference between these fluxes. They describe the transfer through an interface which moves with a velocity either related to the barycentric motion and then the components move with respect to the interface with the diffusion velocity $\mathbf{u}^\alpha$ or related to the motion of one of the components, say β, and then components move with the relative velocity $\mathbf{v}^\alpha - \mathbf{v}^\beta$. In any case the transfer of energy and the transfer of entropy through the interface will be caused not only by conduction in which case the fluxes $\mathbf{h}$ and $\mathbf{q}$ would be proportional but there is a drag transfer through crossing the interface by particles moving with the velocity different from the velocity of the interface. This is exactly what the additional contribution in relation $(499)_4$ is describing.

The above presented Gibbs equation yields immediately the following relations

$$\mu_I^\alpha = \frac{\partial \rho\left(\varepsilon_I - T\eta\right)}{\partial \rho^\alpha}, \quad \rho\eta = -\frac{\partial \rho\left(\varepsilon_I - T\eta\right)}{\partial T}, \tag{500}$$

as well as the integrability conditions (comp. (256))

$$\frac{\partial \rho\varepsilon_I}{\partial \rho^\alpha} = -T^2 \frac{\partial\left(\mu_I^\alpha / T\right)}{\partial T}, \quad \frac{\partial \mu_I^\alpha}{\partial \rho^\beta} = \frac{\partial \mu_I^\beta}{\partial \rho^\alpha}. \tag{501}$$

Hence the derivatives of the Helmholtz free energy density $\rho\left(\varepsilon_I - T\eta\right)$ specify constitutive relations for chemical potentials and for the entropy. In addition, integrability relations demonstrate couplings between components: the chemical potential of component α depends on all other mass densities.

There are some additional restrictions due to the fact that the multiplier Λ^ε is dependent only on the temperature. For this reason the residual inequality contains a contribution linear in $\operatorname{grad}\rho^\alpha$ which must vanish according to the same argument which we made before. This yields the following identity

$$\sum_{\alpha=1}^{A} \frac{\partial \Lambda_I^{\rho^\alpha}}{\partial \rho^\gamma} \rho^\alpha \mathbf{u}^\alpha + \frac{\partial \Lambda^\varepsilon}{\partial T} q_\rho^\gamma \operatorname{grad} T - \Lambda^\varepsilon \sum_{\alpha=1}^{A} \left(M_\rho^{\alpha\gamma} - \frac{\partial p^\alpha}{\partial \rho^\gamma} \right) \mathbf{u}^\alpha = 0. \tag{502}$$

Consequently, we obtain

$$q_\rho^\gamma = 0, \quad M_\rho^{\alpha\gamma} = \frac{\partial p^\alpha}{\partial \rho^\gamma} - \rho^\alpha \frac{\partial \mu_I^\alpha}{\partial \rho^\gamma}. \tag{503}$$

This yields the following form of the energy flux and the sources in momentum equations

$$\begin{aligned} \mathbf{q}_I &= q_T \operatorname{grad} T + \sum_{\beta=1}^{A-1} q_w^\beta \mathbf{w}^\beta, \\ \hat{\mathbf{p}}^\alpha - \hat{\rho}^\alpha \mathbf{v}^\alpha &= M_T^\alpha \operatorname{grad} T + \sum_{\beta=1}^{A-1} M_w^{\alpha\beta} \mathbf{w}^\beta + \sum_{\beta=1}^{A} \left(\frac{\partial p^\alpha}{\partial \rho^\beta} - \rho^\alpha \frac{\partial \mu_I^\alpha}{\partial \rho^\beta} \right) \operatorname{grad} \rho^\beta. \end{aligned} \tag{504}$$

We see that the only place where the gradient of partial mass densities appears in the model is the source of momentum. However even this weak form of influence has an important bearing on interactions in the mixture. Namely, if we assume that the gradient of mass densities does not appear at all in the model we obtain from (504)

$$\frac{1}{\rho^\alpha}\frac{\partial p^\alpha}{\partial \rho^\beta} = \frac{\partial \mu_I^\alpha}{\partial \rho^\beta}. \tag{505}$$

This relation yields the following integrability condition

$$-\frac{1}{\rho^{\alpha 2}}\delta^{\alpha\gamma}\frac{\partial p^\alpha}{\partial \rho^\beta} = -\frac{1}{\rho^{\alpha 2}}\delta^{\alpha\beta}\frac{\partial p^\alpha}{\partial \rho^\gamma}. \tag{506}$$

Hence it follows

$$\frac{\partial p^\alpha}{\partial \rho^\beta} = 0 \quad \text{when} \quad \alpha \neq \beta. \tag{507}$$

This means that the partial pressure p^α depends in this case on its mass density ρ^α but not on the mass densities of other components. We say then that the mixture is *simple.* Molecules in such mixtures do not feel forces of interactions created in the material due to heterogeneity. This observation made by Ingo Müller in 1968 has solved one of the fundamental problems of the classical theory of mixtures of fluids. We see further that a similar problem arises for immiscible mixtures.

Obviously the relation (505) yields for simple mixtures $\mu_I^\alpha = \mu_I^\alpha\left(\rho^\alpha, T\right)$. Hence

$$\frac{\partial^2 \rho\left(\varepsilon_I - T\eta\right)}{\partial \rho^\alpha \partial \rho^\beta} = 0 \quad \text{for} \quad \alpha \neq \beta. \tag{508}$$

Consequently the free energy is the sum of functions which depend on only one mass density and temperature. The entropy density possesses the same property and so does the internal energy. Therefore we can write

$$\rho\varepsilon_I = \sum_{\alpha=1}^{A} \rho^\alpha \varepsilon^\alpha\left(\rho^\alpha, T\right), \quad \rho\eta = \sum_{\alpha=1}^{A} \rho^\alpha \eta^\alpha\left(\rho^\alpha, T\right). \tag{509}$$

This decomposition shows that there is no energy of interaction between components in simple mixtures. It yields as well the following relation for chemical potentials

$$\mu_I^\alpha = \varepsilon^\alpha - T\eta^\alpha + \frac{p^\alpha}{\rho^\alpha}, \tag{510}$$

which means that in simple mixtures the chemical potential and the partial free enthalpy are identical.

We proceed to investigate the residual inequality which remains after the analysis presented above. It has the form

$$\mathcal{D} := \begin{pmatrix} \operatorname{grad} T \\ \mathbf{w}^\alpha \end{pmatrix} \cdot \begin{pmatrix} -\frac{q_T}{T} & A^\beta \\ A^\alpha & -\frac{1}{T}M_w^{\alpha\beta} \end{pmatrix} \begin{pmatrix} \operatorname{grad} T \\ \mathbf{w}^\beta \end{pmatrix} -$$

$$-\frac{1}{T}\sum_{r=1}^{\nu}\left(\sum_{\alpha=1}^{A-1}\left(\mu_I^\alpha - \mu_I^A + \tfrac{1}{2}\mathbf{w}^\alpha \cdot \mathbf{w}^\alpha\right)\gamma_\alpha^r M_\alpha \mu_H \lambda^r\right) \geq 0, \tag{511}$$

where

$$A^\alpha = -\frac{1}{2T}\left\{\frac{q_w^\alpha}{T} + \left[\left(\frac{M_T^\alpha}{\rho^\alpha} - \frac{M_T^\gamma}{\rho^\gamma}\right) - \left(\frac{1}{\rho^\alpha}\frac{\partial p^\alpha}{\partial T} - \frac{1}{\rho^\gamma}\frac{\partial p^\gamma}{\partial T}\right) + \right.\right.$$

$$\left.\left. + T\frac{\partial \frac{\mu_I^\alpha - \mu_I^\gamma}{T}}{\partial T}\right] \sum_{\gamma=1}^{A-1}\left(\rho^\alpha \delta^{\alpha\gamma} - \frac{\rho^\alpha \rho^\gamma}{\rho}\right)\right\}. \tag{512}$$

The function $\mathcal{D}$ is called the *dissipation density* and it consists of four contributions:

- chemical reactions which are primarily characterized by the difference of chemical potentials $\mu_I^\alpha - \mu_I^A$,

- heat conduction which contributes with the square of the temperature gradient $\operatorname{grad} T$,

- diffusion which contributes with the square of the relative velocity $\mathbf{w}^\alpha$,

- thermal diffusion which contributes with the product of the temperature gradient and relative velocity.

The vanishing dissipation defines the *thermodynamical equilibrium*

$$\operatorname{grad} T|_E = 0, \quad \left(\mu_I^\alpha - \mu_I^A\right)\big|_E = 0, \quad \mathbf{w}^\alpha|_E = 0, \quad \alpha = 1, ..., A-1. \tag{513}$$

Such processes correspond to the minimum of dissipation and this yields additional conditions – thermodynamic stability conditions of equilibrium.

Let us add that, in addition to this classical approach to thermodynamics of mixtures there exists also a relativistic extended thermodynamics of mixtures of ideal fluids and this theory gives an important physical insight to the description of chemical reactions. Details can be found in the book of I. Müller and T. Ruggeri.

Lecture 10: Thermodynamics of immiscible mixtures: introduction and models without the field of porosity

The main topic of the following Lectures is the construction of continuous models of multicomponent systems in which one of the components is a solid creating skeleton (a solid confinement) for the motion of fluid components. As we allow for large deformations of the solid phase we shall mostly use the Lagrangian description of motion. Such models are called *porous material models*.

Theories of porous and granular materials can be constructed on different levels of observation. *Microscopic* models rely on Newton's equations of motion of material points or molecules and use methods of molecular dynamics. Such models can be transferred on a *semimacroscopic* level by multiscaling and averaging procedures. Some numerical methods such as Monte Carlo are also used in practical applications. On a *macroscopic* level continuum field models are constructed. These may either follow from semimacroscopic models by homogenizing, averaging over Representative Elementary Volumes (REV), construction of moments of kinetic distribution functions or they may be constructed by means of a phenomenological macroscopic approach. In these Lectures we present solely the latter type of models with a marginal reference to averaging procedures.

The construction of macroscopic continuous models of systems with a solid component in its most sophisticated form stems from models of multicomponent systems. Differences are primarily connected with an art of interactions within the solid component. Models must be clearly different in the cases of suspensions, of granular materials or of porous materials. In the first case solid particles interact with each other either through the fluid or through collisions and there is no permanent contact between them. In the second case a granular solid component may behave as a solid which cannot carry a tensile loading (unilateral constraint on constitutive relations) or it may fluidize and then behave as a suspension. Finally, a porous material behaves in average as a usual solid and it forms a deformable carrier for fluid components. We limit our attention to the last case.

The most important feature of *porous materials* is the appearance of different kinematics for the solid component - the *skeleton*, and fluid components in channels of the skeleton. This yields *diffusion processes* characterized by relative velocities of components. In most cases of a practical bearing the dependence on the relative velocity is reduced to a linear contribution to momentum balance equations (momentum sources) or even to a simpler form called the *Darcy law*.

The problem of *thermodiffusion* within such models is still very much open. This is related to difficulties with an appropriate definition of the temperature on the macroscopic level of description. The most important property of the classical *thermodynamical temperature*, its continuity on ideal thermal walls and, consequently, its experimental measurability, is not fulfilled in porous materials. Simultaneously, such processes as phase transitions or chemical reactions in porous materials are characterized by real thermodynamical temperatures (e.g. melting and freezing points, evaporation, etc.) of components on a semimacroscopic level of description. It means that even if we have introduced a macroscopic notion of temperature we would have to know a rule of transformation of this quantity to the semimacroscopic level. This is mathematically an ill-posed problem. Even though one can formally work with notions such as partial heat fluxes, specific heats etc. their operational meaning is not clarified yet. This seems to be the most important challenge of modelling porous and granular materials.

In addition, we have to deal frequently with the problem of different temperatures for different components. In contrast to gases a local thermodynamical equilibrium is reached in porous and granular materials after macroscopically long relaxation times. For instance, a hot water flowing through a cold porous material does not reach locally a common temperature with the skeleton within seconds or minutes. Consequently, we should construct thermodynamical models with different temperatures of components. Such a construction, as we have indicated in the previous Lecture, is missing even in the case of fluid mixtures. One of the reasons is again the problem of measurability.

Let us mention in passing that in theories of granular materials stemming from a kinetic equation it is common to work with a *kinetic temperature* rather than a thermodynamical temperature. It is defined in a way similar to this of the kinetic theory of gases (275) as a mean kinetic energy of granulae. There are numerous difficulties connected with such a notion. For example a natural equilibrium state of a granular material in which particles do not move would have a temperature equal to zero. Consequently, deviations from the equilibrium state which are used in the construction of macroscopic moment equations of the kinetic theory (comp. (293)) would have to be constructed by means of a trivial distribution function. Certainly, this cannot give any reasonable physical results. For this reason moment equations are constructed by a reference to a Maxwell-like distribution describing processes of simple shearing flows rather than real equilibrium states. In contrast to, say, Grad's 13 moment method of rarified gases such procedures are not justified in any way. Moreover the questions of measurability of kinetic temperature, a relation to the thermodynamical temperature etc. are not even asked as yet[16].

Within multicomponent continuous models an exchange of mass is described by mass sources in partial mass balance equations. These contributions, as demonstrated for fluid mixtures, must contain additional *microstructural* variables. This requires an extension of the set of field equations. In many cases additional equations for microstructural variables have the form of evolution equations. Then there is no need to introduce additional boundary conditions. Such microstructural variables cannot be controlled, they develop spontaneously from initial data. On the other hand, the latter can be usually easily formulated because many microstructural variables are defined in such a way that they vanish in thermodynamical equilibria.

Further in these Lectures, we present in some details a model of processes of exchange of mass called *adsorption*. These processes appear in cases of components which, in contrast to chemical bindings, form weak van der Waals bindings solely with the skeleton. Such are, for example, processes of transport of many pollutants in soils. According to the simplest model of these processes, developed by Langmuir, they are described by an additional field of the so-called *number of bare sites*. In the case of materials with very small diameters of channels adsorption processes possess a hysteresis loop in the relation between the partial pressure of adsorbate in the fluid phase and an amount of mass adsorbed by the skeleton and this plays a very important role in controlling technological processes in such materials. Such loops are caused by *capillary effects*. For this reason,

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[16] e.g. see: N. Bellomo, M. Pulvirenti; *Generalized Boltzmann Models in Applied Sciences: A Kinetic Theory Approach (Modeling and Simulation in Science, Engineering and Technology)*, Birkhäuser, Boston, 2000.

they do not appear in materials with moderate and large channels which is characteristic for usual soils but they do appear, for instance, in concrete.

As already mentioned above multicomponent models of porous materials contain more than one velocity field. This yields field equations following from partial momentum balance equations with a corresponding number of partial accelerations. Consequently, one expects that in such models additional modes of weak discontinuity waves (*acoustic waves*) have to appear. This is indeed the case. One of these modes was predicted by M. A. Biot in 1941. Due to the tradition stemming from geophysics this mode is called P2 compressional (Biot's) wave as the usual longitudinal wave registered in seismograms was called P1. Existence of this mode was confirmed in numerous experiments. It has been found out that it is the slowest of three modes P1, S (transversal wave) and P2. It is also very strongly attenuated.

As consequence of existence of additional bulk modes there exist as well additional modes of *surface waves*. Apart from the classical Rayleigh wave there exist the so-called Stoneley waves, various leaky waves and, in general, a number of possible modes of surface waves depends on properties of neighboring systems, i.e. on the structure of *boundary conditions*. We discuss this problem further in these Lectures. Let us mention that surface waves are much weaker attenuated than bulk waves and for this reason they are easier attainable in measurements. In recent years one can observe a vehement progress in these measuring techniques.

Couplings of dynamical properties of porous and granular materials with mass exchange between components play an important role in various combustion and explosion problems. These are connected with the propagation of strong discontinuities such as *shock waves* and *combustion fronts* in combustion of solid fuels or deformations of soils due to impacts of meteorites. Models for such processes are still rather weakly developed. Most important contributions are based on the model proposed by M. A. Goodman and C. Cowin which refers to some additional microstructural properties called the *principle of equilibrated pressures*. The model leads to a quasilinear hyperbolic set of equations which admits the existence of shock waves. Incidentally, a similar model is used in the description of avalanches, landslides and mud flows. However, apart from some simple properties of propagation conditions, usually one-dimensional, results are rather scarce.

Some elementary properties of one-dimensional Rankine-Hugoniot conditions have been also investigated within the frame of the model with the porosity balance equation. However a comprehensive theory of shock waves is still missing and one of the reasons is lack of a selection (entropy) criterion.

Many processes in porous and granular materials are connected with the development of instabilities. They lead to fluidization of saturated sands, to the creation of patterns in porous materials and to some instabilities, such as Saffmann-Taylor, in flows of fluid components. As usual they are connected with nonlinearities appearing in the model.

One of the most spectacular phenomena accompanying earthquakes is the fountain-like explosion of water and mud from the sand. It has been found that prior to this phenomenon the character of permeability of the soil changes in an unstable manner. In the first stage the homogeneity of the system breaks down and a pattern of chimney-like channels with a very high permeability is formed. In the second stage one of these channels becomes dominant and this leads to an explosion-like eruption of water from the ground. This behavior seems to be connected with a nonlinear coupling of the diffusion velocity with the gradient of porosity.

Another class of instabilities appears in the model with the balance equation of porosity. These are connected with the coupling between dynamical changes of porosity and partial stresses in components. Let us mention one of those instabilities. In a case of a Riemann problem the system develops soliton-like waves of porosity. These are connected with the loss of symmetry of the front of propagation if the two-dimensional front is concave. Most likely in the vicinity of the symmetry axis the system develops a mushy region. Multicomponent modeling of porous materials is based on the assumption that additionally to usual fields of theories of fluid mixtures there exists a microstructure which is reflected in the simplest case by a single additional field of porosity and by solid-like properties of one of the components. In some models this microstructural extension is even broader and corresponding models contain, for instance, the so-called volume fractions of all components, double porosity, tortuosity as a simplest measure of complexity of geometrical structure of channels, couple stresses etc.

We begin the presentation of models of porous materials with an example of a two-component system whose theory is based on the assumption of incompressibility of components. Models of this art appear quite frequently in applications to soil mechanics or glaciology.

First of all, let us make a comment on the calculation of averages in modeling porous materials. The microstructure of these materials has usually characteristic dimensions of an almost macroscopic nature. Typical dimensions of granulae or radii of channels are in the order of micrometers and sometimes even millimeters. This means that we can, in principle, apply a continuum model on this semimacroscopic level and consider either a single component continuum (skeleton) or a mixture of fluids (fluid components in channels of the skeleton). This is not being done because extremely complicated shapes of channels practically rule out the possibility of formulation of boundary value problems for semimacroscopic field equations. Instead we construct volume averages over the so-called Representative Elementary Volumes. These are three-dimensional sets whose dimensions are sufficiently large to be able to assume the randomness of the microstructural geometry and, simultaneously, sufficiently small when compared with macroscopic dimensions in order to be able to prescribe average properties to values of corresponding macroscopic fields. In Figure 10, we show schematically such a REV-domain and the distributions of the skeleton and channels on the semimacroscopic level. These distributions are described by characteristic functions $\chi^{\alpha}(\mathbf{Z},t)$ which, for the α-component, has the value 1 if the point $\mathbf{Z}$ is in the instant of time t occupied by the α-component and 0 otherwise. The notation $\mathbf{Z}$ as well as $\mathbf{X}$ appearing further is characteristic for the Lagrangian description of the multicomponent system which we present later in details. In the following derivation, it is immaterial as we consider the time t only as a parameter and the whole considerations concern spatial properties of the system which may be represented in Lagrangian as well as in Eulerian description. This issue will be made precise further in this Lecture.

Let us denote by $\mathcal{M}(\mathbf{X},t)$ the REV-domain which at the instant of time t is located at the point $\mathbf{Z}=\mathbf{X}$. The point $\mathbf{X}$ selecting $\mathcal{M}$ can be chosen arbitrarily but it is usually convenient to make a special choice related to the geometry of REV. Namely, the shape of REV-domains should be chosen in such a way that it does not deviate from natural symmetries of the microstructure. For instance, in the most common case of isotropic microstructure the shape should be spherical. Then $\mathcal{M}(\mathbf{X},t)$ is the ball of the constant radius R whose center lies at $\mathbf{X}$ at the instant of time t

$$\mathcal{M}\left(\mathbf{X},t\right)=\left\{\mathbf{Z}\right|\mathbf{X}\in\!\mathcal{B}_0\ \&\ \left.\left|\mathbf{Z}-\mathbf{X}\right|<R\right\}. \tag{514}$$

By this choice, R must be much larger than, say, typical diameters of channels and much smaller that the macroscopic dimensions of the body.

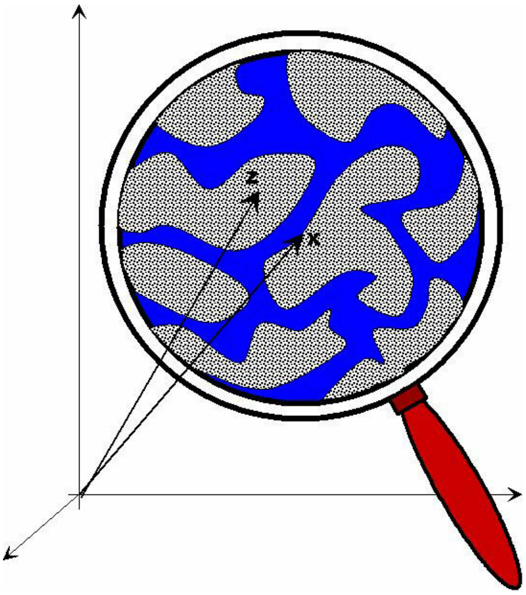

Fig. 10: *Schematic Representative Elementary Volume (REV).*

Obviously, there is a problem of defining REV in the vicinity of the boundary as well as the problem of the definition of the boundary $\partial\mathcal{B}_0$ itself. We return to this question in the discussion of boundary conditions. However, it should be mentioned that these problems yield the existence of *boundary layers* which are replaced by additional surface quantities.

Now let us consider the construction of volume averages. For an arbitrary quantity $\varphi^\alpha\left(\mathbf{Z},t\right)$ characteristic for the α-component we construct the average

$$\left\langle\varphi^\alpha\right\rangle\left(\mathbf{X},t\right)=\frac{1}{V}\int_{\mathcal{M}(\mathbf{X},t)}\varphi^\alpha\left(\mathbf{Z},t\right)\chi^\alpha\left(\mathbf{Z},t\right)dV_Z, \tag{515}$$

where $V=\operatorname{vol}\mathcal{M}\left(\mathbf{X},t\right)$ and, for simplicity it is assumed to be a constant. By means of this definition of the volume average we have to define macroscopic gradients of quantities $\left\langle\varphi^\alpha\right\rangle\left(\mathbf{X},t\right)$ and their time derivatives. The latter is straightforward because we construct instantaneous averages over the spatial domain. However the construction of the gradients is more complicated. Let us choose an infinitesimal vector $\delta\mathbf{X}$ which is constant over $\mathcal{M}\left(\mathbf{X},t\right)$. This vector defines the shift of the REV-domain $\mathcal{M}\left(\mathbf{X},t\right)$. We have

$$\left\langle\varphi^\alpha\right\rangle\left(\mathbf{X}+\delta\mathbf{X},t\right)=\frac{1}{V}\int_{\mathcal{M}(\mathbf{X}+\delta\mathbf{X},t)}\varphi^\alpha\left(\mathbf{Z},t\right)\chi^\alpha\left(\mathbf{Z},t\right)dV_Z=$$

$$=\frac{1}{V}\left\{\int_{\mathcal{M}(\mathbf{X},t)}\varphi^\alpha\left(\mathbf{Z},t\right)\chi^\alpha\left(\mathbf{Z},t\right)dV_Z+\right.$$

$$
+\oint_{\partial\mathcal{M}(\mathbf{X},t)} \varphi^{\alpha}(\mathbf{Z},t)\,\chi^{\alpha}(\mathbf{Z},t)\,\mathbf{N}_Z(\mathbf{Z},t)\cdot\delta\mathbf{X}dS_Z\Big\} + O\left(|\delta\mathbf{X}|^2\right) =
$$

$$
= \langle\varphi^{\alpha}\rangle(\mathbf{X},t) + \frac{1}{V}\left\{\int_{\mathcal{M}(\mathbf{X},t)} \mathrm{Div}\left[\varphi^{\alpha}(\mathbf{Z},t)\,\chi^{\alpha}(\mathbf{Z},t)\,\delta\mathbf{X}\right]dV_Z\right\} + O\left(|\delta\mathbf{X}|^2\right) =
$$

$$
= \langle\varphi^{\alpha}\rangle(\mathbf{X},t) + \frac{1}{V}\delta\mathbf{X}\cdot\int_{\mathcal{M}(\mathbf{X},t)} \mathrm{Grad}\left[\varphi^{\alpha}(\mathbf{Z},t)\,\chi^{\alpha}(\mathbf{Z},t)\right]dV_Z + O\left(|\delta\mathbf{X}|^2\right) =
$$

$$
\begin{aligned}
= {} & \langle\varphi^{\alpha}\rangle(\mathbf{X},t) + \delta\mathbf{X}\cdot\langle\mathrm{Grad}\,\varphi^{\alpha}\rangle(\mathbf{X},t) + \\
& + \frac{1}{V}\delta\mathbf{X}\cdot\int_{\mathcal{M}(\mathbf{X},t)} \varphi^{\alpha}(\mathbf{Z},t)\,\mathrm{Grad}\left[\chi^{\alpha}(\mathbf{Z},t)\right]dV_Z + O\left(|\delta\mathbf{X}|^2\right),
\end{aligned} \tag{516}
$$

where $\mathbf{N}_Z$ is the unit outward normal vector to the surface $\partial\mathcal{M}(\mathbf{X},t)$. In order to evaluate the last integral let us introduce the set

$$
\mathcal{M}^{\alpha}(\mathbf{X},t) = \left\{\mathbf{Z}\in\mathcal{M}(\mathbf{X},t)\,|\,\chi^{\alpha}(\mathbf{Z},t)=1\right\}. \tag{517}
$$

Then the above relation yields

$$
\begin{aligned}
& \langle\varphi^{\alpha}\rangle(\mathbf{X}+\delta\mathbf{X},t) - \langle\varphi^{\alpha}\rangle(\mathbf{X},t) = \delta\mathbf{X}\cdot\langle\mathrm{Grad}\,\varphi^{\alpha}\rangle(\mathbf{X},t) + \\
& + \frac{1}{V}\delta\mathbf{X}\cdot\int_{\partial\mathcal{M}^{\alpha}(\mathbf{X},t)\cap\mathcal{M}(\mathbf{X},t)} \varphi^{\alpha}(\mathbf{Z},t)\,\mathbf{N}_Z(\mathbf{Z},t)\,dS_Z + O\left(|\delta\mathbf{X}|^2\right).
\end{aligned} \tag{518}
$$

We have used here the formula for the differentiation of the characteristic function $\chi^{\alpha}(\mathbf{Z},t)$. Obviously, the gradient of this function is zero in the interior of $\mathcal{M}^{\alpha}(\mathbf{X},t)$ and $\mathcal{M}(\mathbf{X},t)\setminus\mathcal{M}^{\alpha}(\mathbf{X},t)$, where this function is constant. One has to evaluate only the derivative in the direction orthogonal to the boundary $\partial\mathcal{M}^{\alpha}(\mathbf{X},t)$. We can do this using local coordinates such that at every point of the boundary we choose the origin of the orthogonal frame with the coordinate ξ, whose unit base vector is $\mathbf{N}_Z$. We demonstrate the calculations using the following definition of the characteristic function in the vicinity of the point $\xi=0$

$$
\chi^{\alpha}(\xi,t) = \frac{1}{2}\lim_{\alpha\to\infty}\left[1-\tanh(\alpha\xi)\right], \tag{519}
$$

where the dependence on the other two local coordinates is immaterial. Then

$$
\begin{aligned}
\mathrm{Grad}\left[\chi^{\alpha}(\mathbf{Z},t)\right] &= \left(\mathbf{N}_Z\cdot\mathrm{Grad}\left[\chi^{\alpha}(\mathbf{Z},t)\right]\right)\mathbf{N}_Z = \\
&= \left.\frac{d\chi^{\alpha}(\xi,t)}{d\xi}\right|_{\xi=0}\mathbf{N}_Z = -\frac{1}{2}\lim_{\alpha\to\infty}\left.\frac{\alpha}{\cosh^2(\alpha\xi)}\right|_{\xi=0}\mathbf{N}_Z = \\
&= -\delta_{\partial\mathcal{M}^{\alpha}(\mathbf{X},t)}(\xi)\,\mathbf{N}_Z,
\end{aligned} \tag{520}
$$

where $\delta_{\partial\mathcal{M}^{\alpha}(\mathbf{X},t)}(\xi)$ is the Dirac-delta function for the surface $\partial\mathcal{M}^{\alpha}(\mathbf{X},t)$. This yields the transition from the volume integral in (516) to the surface integral in (518).

The relation (518) for the *directional derivative* of the average $\langle\varphi^{\alpha}\rangle$ gives rise to the following formula

$$
\forall_{\delta\mathbf{X}\text{ - infinitesimal}}\delta\mathbf{X}\cdot\,\mathrm{Grad}\,\langle\varphi^{\alpha}\rangle(\mathbf{X},t) =
$$

$$= \delta\mathbf{X}\cdot \langle \mathrm{Grad}\,\varphi^{\alpha}\rangle (\mathbf{X},t) - \frac{1}{V}\delta\mathbf{X}\cdot \int_{\partial\mathcal{M}^{\alpha}(\mathbf{X},t)\cap\mathcal{M}(\mathbf{X},t)} \varphi^{\alpha}(\mathbf{Z},t)\,\mathbf{N}_{Z}(\mathbf{Z},t)\,dS_{Z} \qquad (521)$$

To demonstrate the meaning of this relation let us consider a special case in which $\varphi^{\alpha}(\mathbf{Z},t)$ is piecewise constant. Then the first contribution vanishes identically and in the second one most contributions vanish due to the outward orientation of the vector $\mathbf{N}_{Z}(\mathbf{Z},t)$. There remain only those whose counterpart lies outside the domain $\mathcal{M}(\mathbf{X},t)$. We explain this argument in the one-dimensional diagram of Fig. 11. Contributions of $\mathcal{M}^{\alpha}(\mathbf{X},t)$-sets: (2),...,(6) vanish due to the opposite orientation of the normal vector on their ends. There remain the contributions of the set (1) and of the set (7) because their ends lie beyond the set $\mathcal{M}(\mathbf{X},t)$ and this gives the contribution $\varphi_{1}^{\alpha}-\varphi_{7}^{\alpha}$ of the integral in (521), where $\varphi_{1}^{\alpha},\varphi_{7}^{\alpha}$ are values of φ^{α} on the subsets (1) and (7), respectively. As V is in this example identical with the length L of the interval in Fig. 11, we obtain the average value of the gradient identical with $\left(\varphi_{7}^{\alpha}-\varphi_{1}^{\alpha}\right)/L$.

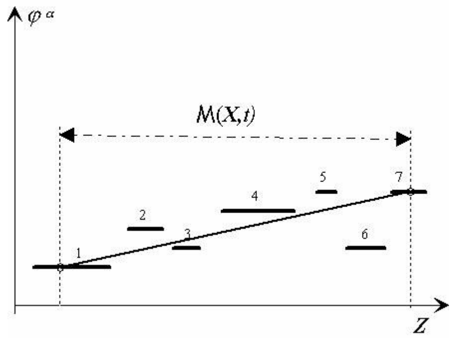

Fig. 11: *Construction of macroscopic gradients in 1D-case*

It is obvious that this construction is extremely singular. One cannot expect ever any differentiable macroscopic functions to follow from such a construction. Consequently, it is essential that characteristic dimensions of the microstructure are much smaller than macroscopic increments $|\delta\mathbf{X}|$. In addition, the heterogeneity of the function $\varphi^{\alpha}(\mathbf{Z},t)$ should be sufficiently small for the contribution $\langle \mathrm{Grad}\,\varphi^{\alpha}\rangle(\mathbf{X},t)$ to be negligible in (521). Such a contribution is characterized by the parameter of heterogeneity of the microstructure $\varepsilon_{\text{heter}} = \left|\langle \mathrm{Grad}\,\varphi^{\alpha}\rangle(\mathbf{X},t)\,/\,\mathrm{Grad}\,\langle\varphi^{\alpha}\rangle(\mathbf{X},t)\right|$ which must be much smaller than the parameter $\varepsilon_{\text{micro}} = R/l \ll 1$, where l is the macroscopic characteristic length. If these conditions are satisfied we can speak about macroscopic fields as volume approximations of real semimacroscopic quantities. We shall not discuss any further the mathematical structure of such constructions and assume sufficient smoothness for all operations which we perform on the fields.

We illustrate the above considerations on some simple models of poroelastic materials with an incompressibility assumption. As in all continuum models we define in *Eulerian description* fields on a common domain $\mathcal{B}_{t}$ which is time dependent and corresponds to a part of the three-dimensional space of motion occupied in a current instant of time by all components. In the case of semipermeable boundary $\partial\mathcal{B}_{t}$ parts of components which flow out of this domain are considered separately and one has to solve contact problems.

In a purely mechanical model which we want to consider in this Lecture processes are described by two current partial mass densities $\rho_{t}^{S}(\mathbf{x},t), \rho_{t}^{F}(\mathbf{x},t), \mathbf{x}\in\mathcal{B}_{t}\subset\Re^{3}, t\in\mathcal{T}\subset\Re$, for the skeleton and the fluid component, respectively, and by two velocity fields

$\mathbf{v}^S(\mathbf{x},t), \mathbf{v}^F(\mathbf{x},t)$ for these two components. All these fields are *macroscopic* which means that they are defined on the common domain $\mathcal{B}_t$ and, for instance the fluid mass and the skeleton mass contained in a subdomain $\mathcal{P}_t \subset \mathcal{B}_t$ are given by the Lebesgue integrals

$$M^F(\mathcal{P}_t) = \int_{\mathcal{P}_t} \rho_t^F dV, \quad M^S(\mathcal{P}_t) = \int_{\mathcal{P}_t} \rho_t^S dV. \tag{522}$$

In the definition of incompressible components one uses a "pseudomesoscopic" quantities which are called *realistic mass densities.* We denote them by ρ_t^{SR} and ρ_t^{FR}. They are also defined in each point of the domain $\mathcal{B}_t$ and not in points of the skeleton or of the fluid, respectively. They may be related to mesoscopic (or semimacroscopic) quantities ρ_m^{SR}, ρ_m^{FR} by the following formulae

$$\begin{aligned} \rho_t^{SR}(\mathbf{x},t) &= \frac{1}{V(\mathcal{M}_t^S)} \int_{\mathcal{M}_t} \rho_m^{SR}(\mathbf{z},t)\left(1-\chi^F\right) dV_{\mathbf{z}}, \\ \rho_t^{FR}(\mathbf{x},t) &= \frac{1}{V(\mathcal{M}_t^F)} \int_{\mathcal{M}_t} \rho_m^{FR}(\mathbf{z},t)\,\chi^F dV_{\mathbf{z}}, \end{aligned} \tag{523}$$

where

$$\begin{aligned} \mathcal{M}_t &= \mathcal{M}_t^S \cup \mathcal{M}_t^F, \quad \mathcal{M}_t^S \cap \mathcal{M}_t^F = \emptyset, \\ V\left(\mathcal{M}_t^F\right) &:= \int_{\mathcal{M}_t}^F \chi^F dV_{\mathbf{z}}, \quad V\left(\mathcal{M}_t^S\right) := \int_{\mathcal{M}_t} \left(1-\chi^F\right) dV_{\mathbf{z}}, \end{aligned} \tag{524}$$

and $\chi^F(\mathbf{z},t)$ is the characteristic function for $\mathcal{M}_t^F$. $\mathcal{M}_t$ is the image of $\mathcal{M}(\mathbf{X},t)$ if we choose to describe the motion of the skeleton, as we customarily do in the Lagrangian description, by the function of motion $\mathbf{f}^S(.,t) : \mathcal{B}_0 \to \mathcal{B}_t$. Then $\mathcal{M}_t = \mathcal{M}\left(\mathbf{f}^{S-1}(\mathbf{x},t), t\right)$. In contrast to ρ_t^{SR}, ρ_t^{FR} which do not possess any physical interpretation in points of the real fluid for the first quantity and in points of the skeleton for the second one, the mass densities ρ_m^{SR}, ρ_m^{FR} are defined solely in points of the real skeleton, and of the real fluid, respectively. Consequently, they possess a usual physical interpretation. For instance, ρ_m^{FR} is equal to $1000\frac{kg}{m^3}$ for water in normal conditions.

It is easy to check the following relations

$$\begin{aligned} &V\left(\mathcal{M}_t^S\right) = (1-n)\,V(\mathcal{M}_t), \quad V\left(\mathcal{M}_t^F\right) = nV(\mathcal{M}_t), \\ &n := \frac{1}{V(\mathcal{M}_t)} \int_{\mathcal{M}_t} \chi^F dV, \quad V(\mathcal{M}_t) := \int_{\mathcal{M}_t} dV. \end{aligned} \tag{525}$$

The quantity n defined in $(525)_3$ is called the *porosity.*

Consequently

$$\begin{aligned} \rho_t^S &:= \frac{1}{V(\mathcal{M}_t)} \int_{\mathcal{M}_t} \rho_m^{SR}\left(1-\chi^F\right) dV = (1-n)\,\rho_t^{SR}, \\ \rho_t^F &:= \frac{1}{V(\mathcal{M}_t)} \int_{\mathcal{M}_t} \rho_m^{FR}\chi^F dV = n\rho_t^{FR}. \end{aligned} \tag{526}$$

Clearly, the smeared-out, partial mass densities ρ_t^S, ρ_t^F are related to the common macroscopic volume in the current configuration. Their definitions contain the full volume of REV.

By means of the above relations we are now in the position to introduce the notion of incompressibility appearing in some theories of porous and granular materials. Namely it is assumed for such models that

$$\rho_t^{SR} = const., \qquad \rho_t^{FR} = const. \tag{527}$$

Consequently the current mass densities ρ_t^F, ρ_t^S are not independent fields. They can be reduced to the single field of porosity n. In such a case partial mass balance equations (without mass exchange!) reduce to the following form

$$\begin{aligned} \frac{1}{\rho_t^{SR}} \left\{ \frac{\partial \rho_t^S}{\partial t} + \operatorname{div}\left(\rho_t^S \mathbf{v}^S\right) \right\} &\equiv \quad -\frac{\partial n}{\partial t} + \operatorname{div}\left(\left(1-n\right)\mathbf{v}^S\right) = 0, \\ \frac{1}{\rho_t^{FR}} \left\{ \frac{\partial \rho_t^F}{\partial t} + \operatorname{div}\left(\rho_t^F \mathbf{v}^F\right) \right\} &\equiv \quad \frac{\partial n}{\partial t} + \operatorname{div}\left(n\mathbf{v}^F\right) = 0. \end{aligned} \tag{528}$$

We can also combine these two equations to the following one

$$\operatorname{div}\left(n\mathbf{v}^F + \left(1-n\right)\mathbf{v}^S\right) = 0. \tag{529}$$

If we consider equation $(528)_1$ as a candidate for the field equation for the porosity n then equation (529) is a *constraint condition* of the model. This condition yields certain limitations on constitutive relations appearing in the phenomenological model which are not always physically and mathematically acceptable. We show here two examples of models which are thermodynamically admissible. The first one is used frequently in soil mechanics and in the description of suspensions. In order to obtain field equations we need momentum balance equations which have the following form in the Eulerian description

$$\begin{aligned} &\frac{\partial\left(\rho_t^S \mathbf{v}^S\right)}{\partial t} + \operatorname{div}\left(\rho_t^S \mathbf{v}^S \otimes \mathbf{v}^S - \mathbf{T}^S\right) = \hat{\mathbf{p}}^S, \\ &\frac{\partial\left(\rho_t^F \mathbf{v}^F\right)}{\partial t} + \operatorname{div}\left(\rho_t^F \mathbf{v}^F \otimes \mathbf{v}^F - \mathbf{T}^F\right) = \hat{\mathbf{p}}^F, \quad \hat{\mathbf{p}}^S + \hat{\mathbf{p}}^F = 0, \end{aligned} \tag{530}$$

where $\mathbf{T}^S, \mathbf{T}^F$ denote symmetric partial Cauchy stress tensors, $\hat{\mathbf{p}}^S, \hat{\mathbf{p}}^F$ are momentum sources. We make the assumption that these quantities satisfy the following constitutive relations

$$\begin{aligned} \mathbf{T}^S &= \mathbf{T}^S\left(n, \operatorname{grad} n, \mathbf{e}^S, \mathbf{w}\right), \quad \mathbf{T}^F = \mathbf{T}^F\left(n, \operatorname{grad} n, \mathbf{e}^S, \mathbf{w}\right), \\ \hat{\mathbf{p}}^S &= \hat{\mathbf{p}}^S\left(n, \operatorname{grad} n, \mathbf{e}^S, \mathbf{w}\right), \end{aligned} \tag{531}$$

where the symmetric deformation tensor of the skeleton $\mathbf{e}^S$ satisfies for small deformations[17] the equation

$$\frac{\partial \mathbf{e}^S}{\partial t} = \operatorname{sym}\operatorname{grad}\mathbf{v}^S, \tag{532}$$

---

[17] i.e. $\left\|\mathbf{e}^S\right\| \ll 1$, where $\left\|\mathbf{e}^S\right\| = \max\left\{\lambda^{(1)}, \lambda^{(2)}, \lambda^{(3)}\right\}$ and $\lambda^{(1)}, \lambda^{(2)}, \lambda^{(3)}$ are eigenvalues of $\mathbf{e}^S$.

and $\mathbf{w} := \mathbf{v}^F - \mathbf{v}^S$ is the relative velocity of components.

By means of the second law of thermodynamics one can show that the constraint (529) is thermodynamically admissible. This would not be the case were constitutive relations (531) independent of $\operatorname{grad} n$. In this sense we deal with a *higher gradient model.* If we assume in addition the isotropy and linearity with respect to both vector variables $\operatorname{grad} n$ and $\mathbf{w}$ then we obtain a relatively explicit form of constitutive relations

$$\begin{aligned} \mathbf{T}^S &= -(1-n)p\mathbf{1} + \mathbf{T}^S_{eff}\left(n, \mathbf{e}^S\right), \quad \mathbf{T}^F = -np\mathbf{1} + \mathbf{T}^F_{eff}\left(n, \mathbf{e}^S\right), \\ \hat{\mathbf{p}}^S &= -\hat{\mathbf{p}}^F = \pi\left(n, \mathbf{e}^S\right)\mathbf{w} - p \operatorname{grad} n, \end{aligned} \tag{533}$$

where $\mathbf{T}^S_{eff}, \mathbf{T}^F_{eff}$ are the so-called *effective partial stress tensors.* The second one is frequently assumed to be zero and the first one, if it is linear (small deformation of the skeleton $\left\|\mathbf{e}^S\right\| \ll 1$), is given by a Hooke's law with material coefficients depending on the porosity n. The *permeability coefficient* π is also usually assumed to be constant. The *pore pressure* p is the reaction force on the constraint.

In order to account for instabilities of the microstructure one can try to extend the above model by accounting for nonlinear dependence on the relative velocity $\mathbf{w}$. This is justified because such instabilities appear by flows of a high intensity of the fluid component. In a continuum model the latter corresponds to contributions $\rho^F_t \mathbf{w}$. Such an extension yields in the lowest approximation the following constitutive relations

$$\begin{aligned} \mathbf{T}^S &= -(1-n)p\mathbf{1} + \mathbf{T}^S_{eff}\left(n, \mathbf{e}^S\right) + \delta \mathbf{w} \otimes \mathbf{w}, \\ \mathbf{T}^F &= -np\mathbf{1} + \mathbf{T}^F_{eff}\left(n, \mathbf{e}^S\right) - \delta \mathbf{w} \otimes \mathbf{w}, \\ & \\ \hat{\mathbf{p}}^S &= -\hat{\mathbf{p}}^F = \pi\left(n, \mathbf{e}^S\right)\mathbf{w} - \left(p + \Gamma \mathbf{w} \cdot \mathbf{w}\right) \operatorname{grad} n, \end{aligned} \tag{534}$$

where δ and Γ are additional material parameters.

Such a model seems to be appropriate to describe, for instance, instabilities leading to fluidization and eruption in water saturated sands by earthquakes.

The above described class of models shall not be discussed any further. In spite of their important role in some problems of soil mechanics these models have some faults which do not seem to be acceptable in cases of wave processes. Most important of them is the lack of hyperbolicity (the part of the operator connected with the constraint is elliptic). This leads to a reduced number of real eigenvalues corresponding to speeds of propagation and, consequently, to the lack of certain modes of propagation of weak discontinuity waves. In particular the P2-wave and some important surface waves cannot be described by such models

Lecture 11: Thermodynamics of poroelastic materials with the balance equation of porosity

In this Lecture we present the model of porous materials developed in the recent years for an elastic skeleton and ideal fluid components. We present its nonlinear foundations for a system with A fluid components. Only a few basic thermodynamical features will be discussed in order to place the model within the rational extended thermodynamics. Thermodynamical details will be discussed in further Lectures for two-component models.

Geometric nonlinearities connected with possibly large deformations of the skeleton indicate that the convenient way to describe processes is to define fields on a *reference configuration* $\mathcal{B}_0$ of the skeleton. For such a configuration the deformation gradient of the skeleton is defined as the unit matrix: $\mathbf{F}^S = \mathbf{1}$. Hence we formulate the *Lagrangian description* of motion of the porous material. Let us mention in passing that there are papers on this subject in which the Lagrangian description is introduced separately for each component. It is not only an unnecessary formal complication but sometimes it yields erroneous results. We do not present this approach in these Lectures.

The aim of the model is to find the following fields defined in points $\mathbf{X}$ of the reference domain $\mathcal{B}_0 \subset \Re^3$ and in instances t of the time interval $\mathcal{T} \subset [0, \infty)$:

1. mass density of the skeleton referred to a unit reference volume: $\rho^S(\mathbf{X}, t)$,
2. mass densities of the fluid components referred to a unit reference volume: $\rho^\alpha(\mathbf{X}, t)$, $\alpha = 1, \dots, A$,
3. velocity of the skeleton: $\acute{\mathbf{x}}^S(\mathbf{X}, t)$,
4. deformation gradient of the skeleton: $\mathbf{F}^S(\mathbf{X}, t)$, $\quad J^S := \det \mathbf{F}^S > 0$,
5. velocities of fluid components $\acute{\mathbf{x}}^\alpha(\mathbf{X}, t)$, $\quad \alpha = 1, \dots, A$,
6. porosity: $n(\mathbf{X}, t)$,
7. temperature common for all components $T(\mathbf{X}, t)$.

Consequently a *thermomechanical process* is described by the mapping

$$\mathbf{w} : (\mathbf{X}, t) \mapsto \Re^{4A+15}, \quad \mathbf{w} := \left\{ \rho^S, \rho^\alpha, \acute{\mathbf{x}}^S, \mathbf{F}^S, \acute{\mathbf{x}}^\alpha, n, T \right\}, \quad \alpha = 1, \dots, A. \tag{535}$$

Field equations for these fields follow from balance equations which we proceed to formulate.

Balance equations are formulated in their global form on material domains of components. For porous materials in the Lagrangian description the family of material domains for the skeleton is defined as a class of subsets of $\mathcal{B}_0$ which is time independent and satisfies conditions identical with those of the classical continuum mechanics. Material domains of the skeleton are time independent because the reference configuration $\mathcal{B}_0$ is defined with respect to the deformation gradient of skeleton $\mathbf{F}^S$. For this configuration $\mathbf{F}^S = \mathbf{1}$.

It is not the case any more for fluid components. They have different kinematics than the skeleton which means that domains in the space of motion containing during the motion the same particles of a particular fluid component move with respect to material domains of the skeleton. In the Eulerian description the velocity field for this motion is given by the difference $\mathbf{v}^{\alpha}(\mathbf{x},t)-\mathbf{v}^{S}(\mathbf{x},t)$ for the fluid component α, where $\mathbf{v}^{\alpha}(\mathbf{x},t)$ is the velocity of the fluid and $\mathbf{v}^{S}(\mathbf{x},t)$ is the velocity of the skeleton at the same spatial position $\mathbf{x}$ and at the same instant of time t. This relative motion yields the time dependence of material domains of fluid components projected on the reference configuration $\mathcal{B}_0$. The projection is carried by the function of motion of the skeleton

$$\begin{aligned} &\forall \mathbf{X}\in\mathcal{B}_0, t\in\mathcal{T}: \quad \mathbf{x}=\mathbf{f}^{S}(\mathbf{X},t)\Longrightarrow \\ &\Longrightarrow \mathbf{F}^{S}=\operatorname{Grad}\mathbf{f}^{S}(\mathbf{X},t), \quad \acute{\mathbf{x}}^{S}=\frac{\partial \mathbf{f}^{S}(\mathbf{X},t)}{\partial t}, \end{aligned} \tag{536}$$

whose existence is assumed in the model. The condition for the existence of the function of motion $\mathbf{f}^{S}$ shall be formulated later.

In order to describe the kinematics of material fluid domains projected on the reference configuration we consider the mappings shown in Fig. 12. In the current configuration $\mathcal{B}_t=\mathbf{f}^{S}(\mathcal{B}_0,t)$ we consider an arbitrary subset $\mathcal{P}_t^{\alpha}\subset\mathcal{B}_t$ which is material with respect to the component α, i.e. by an infinitesimal increment of time Δt it becomes $\mathcal{P}_{t+\Delta t}^{\alpha}:=\{\mathbf{x}\in\mathcal{B}_{t+\Delta t}|\,\mathbf{x}-\mathbf{v}^{\alpha}(\mathbf{x},t+\Delta t)\,\Delta t\in\mathcal{P}_t^{\alpha}\}$. These two subsets of the space of current configurations are maps of the subsets $\mathcal{P}^{\alpha}(t),\mathcal{P}^{\alpha}(t+\Delta t)$ of the reference configuration $\mathcal{B}_0$, one at the instant of time t and the other at the instant of time $t+\Delta t$. Obviously, they contain the same particles of the component α. This construction is shown in Fig. 12. Now, we choose an arbitrary particle of the component α which occupies the position $\mathbf{x}\in\mathcal{P}_t^{\alpha}$ at the instant of time t, i.e. its position in the reference configuration is $\mathbf{X}=\mathbf{f}^{S-1}(\mathbf{x},t)$. Its position $\mathbf{x}+\mathbf{\Delta x}$ at the instant $t+\Delta t$ can be written in the form

$$\begin{aligned} \mathbf{x}+\mathbf{\Delta x} &= \mathbf{x}+\acute{\mathbf{x}}^{\alpha}(\mathbf{X},t)\,\Delta t=\mathbf{f}^{S}(\mathbf{X}+\Delta\mathbf{X},t+\Delta t)= \\ &= \mathbf{x}+\operatorname{Grad}\mathbf{f}^{S}(\mathbf{X},t)\,\Delta\mathbf{X}+\frac{\partial\mathbf{f}^{S}}{\partial t}\Delta t= \\ &= \mathbf{x}+\mathbf{F}^{S}\Delta\mathbf{X}+\acute{\mathbf{x}}^{S}\Delta t. \end{aligned} \tag{537}$$

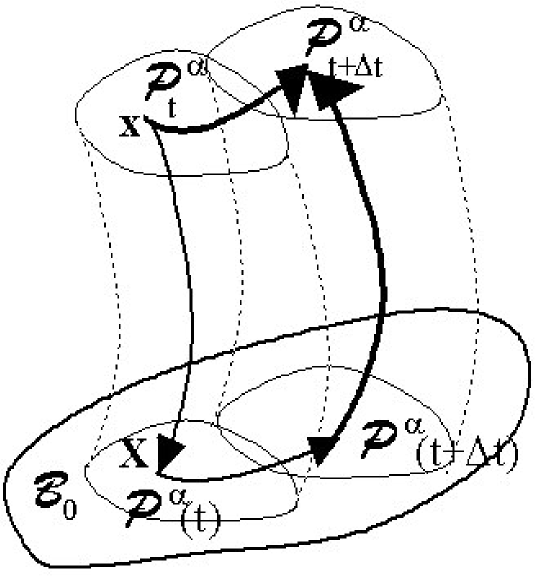

Fig. 12: *Projections of material domains of the α-component (pull-back)*

Consequently, the set $\mathcal{P}^{\alpha}(t) \subset \mathcal{B}_0$ is endowed with the kinematics defined by the following velocity field

$$\forall \mathbf{X} \in \mathcal{B}_0 : \quad \lim_{\Delta t \to 0} \frac{\Delta \mathbf{X}}{\Delta t} =: \acute{\mathbf{X}}^{\alpha}(\mathbf{X}, t) = \mathbf{F}^{S-1}\left(\acute{\mathbf{x}}^{\alpha} - \acute{\mathbf{x}}^{S}\right). \tag{538}$$

Obviously, in the above relations we were using the following transformations

$$\acute{\mathbf{x}}^{S}(\mathbf{X}, t) = \mathbf{v}^{S}\left(\mathbf{f}^{S}(\mathbf{X}, t), t\right), \quad \acute{\mathbf{x}}^{\alpha}(\mathbf{X}, t) = \mathbf{v}^{\alpha}\left(\mathbf{f}^{S}(\mathbf{X}, t), t\right). \tag{539}$$

In order to appreciate the operational meaning of this transformation we formulate balance equations of mass for all components. They have the following form

$$\frac{d}{dt}\int_{\mathcal{P}^S} \rho^S dV = \int_{\mathcal{P}^S} \hat{\rho}^S dV, \tag{540}$$

for every material domain of the skeleton $\mathcal{P}^S \subset \mathcal{B}_0$, and

$$\frac{d}{dt}\int_{\mathcal{P}^{\alpha}(t)} \rho^{\alpha} dV = \int_{\mathcal{P}^{\alpha}(t)} \hat{\rho}^{\alpha} dV, \tag{541}$$

for every material domain of the α fluid component $\mathcal{P}^{\alpha}(t) \subset \mathcal{B}_0, \quad \alpha = 1, \dots A$. In the above relations $\hat{\rho}^S, \hat{\rho}^{\alpha}$ are the mass sources which satisfy the following bulk conservation law

$$\forall \mathbf{X} \in \mathcal{B}_0, t \in \mathcal{T} : \quad \hat{\rho}^S + \sum_{\alpha=1}^{A} \hat{\rho}^{\alpha} = 0. \tag{542}$$

Time dependence of material domains for fluid components yields the following rules of time differentiation

$$\begin{aligned} \frac{d}{dt}\int_{\mathcal{P}^S} \rho^S dV &= \int_{\mathcal{P}^S} \frac{\partial}{\partial t}\rho^S dV, \\ \frac{d}{dt}\int_{\mathcal{P}^{\alpha}(t)} \rho^{\alpha} dV &= \int_{\mathcal{P}^{\alpha}(t)} \frac{\partial}{\partial t}\rho^{\alpha} dV + \oint_{\partial \mathcal{P}^{\alpha}(t)} \rho^{\alpha} \mathbf{N} \cdot \acute{\mathbf{X}}^{\alpha} dS, \end{aligned} \tag{543}$$

where $\mathbf{N}$ denotes the unit normal vector field of the boundary $\partial \mathcal{P}^{\alpha}(t)$.

These relations yield the following local form of mass balance equations for $\alpha = 1, \dots, A$,

$$\frac{\partial \rho^S}{\partial t} = \hat{\rho}^S, \quad \frac{\partial \rho^{\alpha}}{\partial t} + \operatorname{Div}\left(\rho^{\alpha} \acute{\mathbf{X}}^{\alpha}\right) = \hat{\rho}^{\alpha}, \tag{544}$$

in regular points (almost everywhere) of $\mathcal{B}_0$, and

$$U\left[\left[\rho^S\right]\right] = 0, \quad \left[\left[\rho^{\alpha}\left(\acute{\mathbf{X}}^{\alpha} \cdot \mathbf{N} - U\right)\right]\right]) = 0, \tag{545}$$

in points of singular surfaces moving through the reference configuration $\mathcal{B}_0$ with the local speed U. The brackets $[[\cdots]]$ denote the difference of finite limits of quantities in these brackets on the positive and negative side of the surface (comp. (48)).

In a similar manner we obtain the following partial momentum balance equations in their local form. For the regular points of the reference configuration $\mathcal{B}_0$

$$\begin{aligned}
&\frac{\partial\left(\rho^S\acute{\mathbf{x}}^S\right)}{\partial t}-\operatorname{Div}\mathbf{P}^S=\hat{\mathbf{p}}^S+\rho^S\mathbf{b}^S,\\
&\frac{\partial\left(\rho^\alpha\acute{\mathbf{x}}^\alpha\right)}{\partial t}+\operatorname{Div}\left(\rho^\alpha\acute{\mathbf{x}}^\alpha\otimes\acute{\mathbf{X}}^\alpha-\mathbf{P}^\alpha\right)=\hat{\mathbf{p}}^\alpha+\rho^\alpha\mathbf{b}^\alpha,\quad\hat{\mathbf{p}}^S+\sum_{\alpha=1}^{A}\hat{\mathbf{p}}^\alpha=0,
\end{aligned}\tag{546}$$

and for points on singular surfaces

$$\begin{aligned}
&\rho^S U\left[\left[\acute{\mathbf{x}}^S\right]\right]+\left[\left[\mathbf{P}^S\right]\right]\mathbf{N}=0,\\
&\rho^\alpha\left(\acute{\mathbf{X}}^\alpha\cdot\mathbf{N}-U\right)\left[\left[\acute{\mathbf{x}}^\alpha\right]\right]-\left[\left[\mathbf{P}^\alpha\right]\right]\mathbf{N}=0.
\end{aligned}\tag{547}$$

In these relations $\mathbf{P}^S,\mathbf{P}^\alpha$ denote partial Piola-Kirchhoff stress tensors, $\mathbf{b}^S,\mathbf{b}^\alpha$ are partial mass forces, and $\hat{\mathbf{p}}^S,\hat{\mathbf{p}}^\alpha$ denote the momentum sources. Relation $(546)_3$ expresses the bulk conservation of momentum.

We do not need to present details of partial energy balance equations. Under the assumption of a single field of temperature we need solely the bulk energy conservation law. The derivation is based on a principle of the theory of mixtures that bulk quantities must be defined in such a way that balance equations for these quantities have the form of classical conservation laws of the single component continuum thermodynamics.

Bearing this principle in mind we define the following bulk quantities

$$\rho:=\rho^S+\sum_{\alpha=1}^{A}\rho^\alpha,\quad\rho\dot{\mathbf{x}}:=\rho^S\acute{\mathbf{x}}^S+\sum_{\alpha=1}^{A}\rho^\alpha\acute{\mathbf{x}}^\alpha,\quad\rho\dot{\mathbf{X}}:=\sum_{\alpha=1}^{A}\rho^\alpha\acute{\mathbf{X}}^\alpha,\tag{548}$$

which are the bulk mass density, the bulk momentum, and an objective relative momentum connected with the reference of the motion to the skeleton rather than to local centers of gravity;

$$\begin{aligned}
\mathbf{P}&:=\mathbf{P}_I-\mathbf{F}^S\left\{\rho^S\dot{\mathbf{X}}\otimes\dot{\mathbf{X}}+\sum_{\alpha=1}^{A}\rho^\alpha\left(\acute{\mathbf{X}}^\alpha-\dot{\mathbf{X}}\right)\otimes\left(\acute{\mathbf{X}}^\alpha-\dot{\mathbf{X}}\right)\right\},\\
\mathbf{P}_I&:=\mathbf{P}^S+\sum_{\alpha=1}^{A}\mathbf{P}^\alpha;
\end{aligned}\tag{549}$$

this is the bulk Piola-Kirchhoff stress tensor with the so-called intrinsic part $\mathbf{P}_I$;

$$\begin{aligned}
\rho\varepsilon&:=\rho\varepsilon_I+\frac{1}{2}\left\{\rho^S\mathbf{C}^S\cdot\left(\dot{\mathbf{X}}\otimes\dot{\mathbf{X}}\right)+\sum_{\alpha=1}^{A}\rho^\alpha\mathbf{C}^S\cdot\left(\acute{\mathbf{X}}^\alpha-\dot{\mathbf{X}}\right)\otimes\left(\acute{\mathbf{X}}^\alpha-\dot{\mathbf{X}}\right)\right\},\\
\rho\varepsilon_I&:=\rho^S\varepsilon^S+\sum_{\alpha=1}^{A}\rho^\alpha\varepsilon^\alpha,\qquad\mathbf{C}^S:=\mathbf{F}^{ST}\mathbf{F}^S,
\end{aligned}\tag{550}$$

this is the bulk specific internal energy with the intrinsic part $\rho\varepsilon_I$. The symmetric tensor $\mathbf{C}^S$ is the *right Cauchy-Green deformation tensor* of the skeleton;

$$\mathbf{Q} := \mathbf{Q}_I + +\frac{1}{2}\left\{ -\rho^S \dot{\mathbf{X}} \otimes \dot{\mathbf{X}} \otimes \dot{\mathbf{X}} + \sum_{\alpha=1}^{A} \rho^\alpha \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right) \otimes \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right) \otimes \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right) \right\} \mathbf{C}^S,$$

$$\begin{aligned} \mathbf{Q}_I \quad : \quad &= \mathbf{Q}^S + \sum_{\alpha=1}^{A} \mathbf{Q}^\alpha - \rho^S \varepsilon^S \dot{\mathbf{X}} + \sum_{\alpha=1}^{A} \rho^\alpha \varepsilon^\alpha \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right) + \\ &+ \mathbf{P}^{ST} \mathbf{F}^S \dot{\mathbf{X}} - \sum_{\alpha=1}^{A} \mathbf{P}^{\alpha T} \mathbf{F}^S \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right), \end{aligned} \tag{551}$$

and this vector describes the bulk heat flux in the Lagrangian description. Again the intrinsic part $\mathbf{Q}_I$ was separated.

The bulk balance equation of energy can be now written in the following form

$$\frac{\partial}{\partial t} \rho \left(\varepsilon + \frac{1}{2} \dot{x}^2 \right) + Div \left\{ \rho \left(\varepsilon + \frac{1}{2} \dot{x}^2 \right) \dot{\mathbf{X}} + \mathbf{Q} - \mathbf{P}^T \dot{\mathbf{x}} \right\} = \rho \mathbf{b} \cdot \dot{\mathbf{x}} + \rho r, \tag{552}$$

where

$$\begin{aligned} \rho \mathbf{b} &:= \boldsymbol{\rho}^S \mathbf{b}^S + \sum_{\alpha=1}^{A} \rho^\alpha \mathbf{b}^\alpha, \\ \rho r &:= \rho^S r^S + \sum_{\alpha=1}^{A} \rho^\alpha r^\alpha - \rho^S \mathbf{b}^S \cdot \mathbf{F}^S \dot{\mathbf{X}} + \sum_{\alpha=1}^{A} \rho^\alpha \mathbf{b}^\alpha \cdot \mathbf{F}^S \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right), \end{aligned} \tag{553}$$

and r^S, r^α denote the partial radiations.

We skip the presentation of the energy condition on a singular surface because it shall not be used in these notes.

In the Lagrangian description and with the choice of fields (535) we have at disposal the following integrability condition

$$\frac{\partial \mathbf{F}^S}{\partial t} = \operatorname{Grad} \acute{\mathbf{x}}^S. \tag{554}$$

This condition yields the existence of the function of motion (536). By the choice (535) of unknown fields this relation plays the role of the field equation for the deformation gradient $\mathbf{F}^S$.

It is useful to write equation (554) in the following weaker form

$$\frac{d}{dt} \int_{\mathcal{P}^S} \mathbf{F}^S dV = \oint_{\partial \mathcal{P}^S} \acute{\mathbf{x}}^S \otimes \mathbf{N} dV, \tag{555}$$

for every material domain of the skeleton $\mathcal{P}^S \subset \mathcal{B}_0$. This balance equation yields the following condition in points of singular surfaces

$$U \left[\left[\mathbf{F}^S \right] \right] = - \left[\left[\acute{\mathbf{x}}^S \right] \right] \otimes \mathbf{N}. \tag{556}$$

This relation is usually derived by means of the Hadamard Theorem for singular surfaces.

Before we present remaining equations of the model let us discuss some properties of the objects which we have introduce above. It is easy to notice a striking similarity of the structure of bulk quantities to that appearing in the classical theory of mixtures. This concerns terms with explicit contributions of velocities. However in contrast to the mixture theory all velocities of the present model are objective because $\acute{\mathbf{X}}^{\alpha}$ and $\dot{\mathbf{X}}$ are *relative velocities.* Due to constitutive relations these velocities may be also present in the implicit form in intrinsic parts of stress tensors, internal energy and heat flux vector. It is also important to notice that the explicit dependence is at least quadratic. If we consider processes with small deviations from the thermodynamical equilibrium these contributions can be neglected.

In order to turn over mass balance equations (544), momentum balance equations (546), energy balance equation (552) and compatibility condition (554) into field equations for fields (535) we need constitutive relations for partial stress tensors, momentum sources, the bulk internal energy and the bulk heat flux. If we had these relations we would have $14\,(A+1)$ equations. Consequently we would be missing one equation. This is connected with the fact that the porosity n is the additional microstructural variable and this requires an additional equation. We proceed to formulate this equation.

We have seen in the previous Lecture that changes of porosity may be described by a balance equation (528). This was the consequence of incompressibility of components. If the components are compressible we are missing this equation. Compressibility of components is an important feature in the wave analysis and many other problems of practical bearing and linear models (e.g. Biot's model which we present further in these notes) yield in such cases a relation for porosity which does not coincide with this derived for incompressible materials. In addition the porosity equation following from the mass conservation law does not contain a source. Such a source would describe a spontaneous relaxation of porosity. We know from experience with other microstructural variables that this is an important property yielding evolution equations for such variables

All these arguments can be made more precise if we motivate an equation for porosity by a transition from a semimacroscopic model. We do so by means of averaging over the Representative Elementary Volume.

The porosity is the fraction of void spaces in the skeleton. Consequently, if $\chi^{S}\left(\mathbf{Z},t\right)$ denotes the characteristic function of the solid component on the semimacroscopic level (see: Lecture 10) then we have

$$n\left(\mathbf{X},t\right)=\frac{1}{V}\int_{\mathcal{M}(\mathbf{X})}\left(1-\chi^{S}\left(\mathbf{Z},t\right)\right)dV_{Z}, \tag{557}$$

where the averaging is performed over the reference configuration of the skeleton, i.e. $\mathbf{X}\in\mathcal{B}_0$ and it means that the points $\mathbf{Z}$ of the real solid move within $\mathcal{M}\left(\mathbf{X}\right)$ according to semimicroscopic equations of motion. For the purpose of motivation of macroscopic equations it is not necessary to formulate them.

We proceed to investigate time changes of porosity. We have

$$\frac{\partial n}{\partial t}=\frac{1}{V}\int_{\mathcal{M}(\mathbf{X})}\left(-\frac{\partial\chi^{S}}{\partial t}-\operatorname{Grad}_{Z}\chi^{S}\cdot\dot{\mathbf{Z}}\right)dV_{Z}, \tag{558}$$

where Grad_Z denotes the gradient with respect to the variable $\mathbf{Z}$ and $\dot{\mathbf{Z}}$ is the velocity of the real point of the solid. According to (520) we can transform this relation in the following way

$$\begin{aligned}
\frac{\partial n}{\partial t} &= \frac{1}{V}\int_{\mathcal{M}}\left(-\frac{\partial \chi^S}{\partial t} + \delta_{\partial\mathcal{M}^{\alpha}(\mathbf{X},t)}\left(\xi\right)\mathbf{N}_Z\cdot\dot{\mathbf{Z}}\right)dV_Z = \\
&= -\frac{1}{V}\int_{\mathcal{M}}\frac{\partial \chi^S}{\partial t}dV_Z - \frac{1}{V}\int_{\partial\mathcal{M}^S\cap\mathcal{M}}\mathbf{N}_Z\cdot\dot{\mathbf{Z}}dS_Z = \\
&= -\frac{1}{V}\int_{\mathcal{M}(\mathbf{X})}\frac{\partial \chi^S}{\partial t}dV_Z - \frac{1}{V}\oint_{\partial\mathcal{M}^S\cap\mathcal{M}\cup\left(\partial\mathcal{M}\cap\mathcal{M}^S\right)}\mathbf{N}_Z\cdot\dot{\mathbf{Z}}dS_Z +
\end{aligned}$$

$$+\frac{1}{V}\int_{\partial\mathcal{M}\cap\mathcal{M}^S}\mathbf{N}_Z\cdot\dot{\mathbf{Z}}dS_Z =$$

$$= -\frac{1}{V}\int_{\mathcal{M}(\mathbf{X})}\frac{\partial \chi^S}{\partial t}dV_Z - \frac{1}{V}\int_{\mathcal{M}^S}\operatorname{Div}_Z\dot{\mathbf{Z}}dV_Z + \frac{1}{V}\int_{\partial\mathcal{M}\cap\mathcal{M}^S}\mathbf{N}_Z\cdot\dot{\mathbf{Z}}dS_Z. \tag{559}$$

These three contributions have the following macroscopic interpretation. The first one describes the *source* of porosity caused, for instance, by microstructural relaxation processes. We denote this contribution by $\hat{n}$. The second contribution is related to the relative motion of real components on the semimacroscopic level. Bearing the relation (521) in mind, we can identify this term with the contribution of the macroscopic *flux of porosity* $\mathbf{J}$, i.e. we can write approximately

$$\frac{1}{V}\int_{\mathcal{M}^S}\operatorname{Div}_Z\dot{\mathbf{Z}}dV_Z = \operatorname{Div}\mathbf{J}. \tag{560}$$

On the macroscopic level this contribution results from the relative motion of components. Finally, the last contribution is related to internal deformations of the skeleton. As we consider porous materials whose skeleton is elastic this contribution, in contrast to the other two contributions, must appear in equilibrium as well as nonequilibrium processes. We call it *equilibrium changes of the porosity* and denote by $\partial n_E/\partial t$, i.e.

$$\frac{1}{V}\int_{\partial\mathcal{M}\cap\mathcal{M}^S}\mathbf{N}_Z\cdot\dot{\mathbf{Z}}dS_Z = \frac{\partial n_E}{\partial t}. \tag{561}$$

Bearing the above remarks in mind we introduce in regular points the *balance equation of porosity* in the following general form

$$\frac{\partial \Delta_n}{\partial t} + \operatorname{Div}\mathbf{J} = \hat{n}, \quad \Delta_n = n - n_E, \tag{562}$$

where Δ_n is the deviation of porosity from the equilibrium value, the latter together with the flux of porosity $\mathbf{J}$ and the source of porosity $\hat{n}$ must be given by constitutive relations. We expect that n tends to an equilibrium under constant external conditions. The equilibrium value of porosity n_E satisfies the equation (562) with the flux and source equal to zero. The latter as we show later follow indeed from the second law of thermodynamics.

Making an assumption that sources of porosity do not carry surface singularities we can write the following compatibility condition for porosity on such surfaces

$$U\left[\left[\Delta_n\right]\right] - \left[\left[\mathbf{J}\right]\right]\cdot\mathbf{N} = 0, \tag{563}$$

which may suggest the form of natural boundary conditions for porosity.

It is clear that the averaging procedure does not specify the balance equation of porosity but it motivates its structure. This is the typical situation for models which are not based on kinetic microscopical models.

Let us collect balance equations which we have discussed in this Lecture. They are shown in the Tables 11 and 12.

Table 11: *Balance equations for the* $A+1$-component *porous material in regular points of the reference configuration* $\mathbf{X} \in \mathcal{B}_0$

mass of S	$\frac{\partial \rho^S}{\partial t} = \hat{\rho}^S$
mass of α	$\frac{\partial \rho^\alpha}{\partial t} + \operatorname{Div} \rho^\alpha \acute{\mathbf{X}}^\alpha = \hat{\rho}^\alpha$
momentum of S	$\frac{\partial\left(\rho^S \acute{\mathbf{x}}^S\right)}{\partial t} - \operatorname{Div} \mathbf{P}^S = \hat{\mathbf{p}}^S + \rho^S \mathbf{b}^S$
momentum of α	$\frac{\partial(\rho^\alpha \acute{\mathbf{x}}^\alpha)}{\partial t} + \operatorname{Div}\left(\rho^\alpha \acute{\mathbf{x}}^\alpha \otimes \acute{\mathbf{X}}^\alpha - \mathbf{P}^\alpha\right) = \hat{\mathbf{p}}^\alpha + \rho^\alpha \mathbf{b}^\alpha$
bulk energy	$\frac{\partial}{\partial t}\rho\left(\varepsilon + \frac{1}{2}\dot{x}^2\right) + Div\left\{\rho\left(\varepsilon + \frac{1}{2}\dot{x}^2\right)\dot{\mathbf{X}} + \mathbf{Q} - \mathbf{P}^T\dot{\mathbf{x}}\right\} = \rho\mathbf{b}\cdot\dot{\mathbf{x}} + \rho r$
integrability of $\mathbf{F}^S$	$\frac{\partial \mathbf{F}^S}{\partial t} = \operatorname{Grad} \acute{\mathbf{x}}^S$
porosity	$\frac{\partial \Delta_n}{\partial t} + \operatorname{Div} \mathbf{J} = \hat{n}$

Table 12: *Balance equations (dynamic compatibility conditions) in points of the singular surface*

mass of S	$U\left[\left[\rho^S\right]\right] = 0$
mass of α	$\left[\left[\rho^\alpha\left(\acute{\mathbf{X}}^\alpha \cdot \mathbf{N} - U\right)\right]\right] = 0$
momentum of S	$\rho^S U\left[\left[\acute{\mathbf{x}}^S\right]\right] + \left[\left[\mathbf{P}^S\right]\right]\mathbf{N} = 0,$
momentum of α	$\rho^\alpha\left(\acute{\mathbf{X}}^\alpha \cdot \mathbf{N} - U\right)[[\acute{\mathbf{x}}^\alpha]] - [[\mathbf{P}^\alpha]]\,\mathbf{N} = 0$
integrability	$U\left[\left[\mathbf{F}^S\right]\right] = -\left[\left[\acute{\mathbf{x}}^S\right]\right] \otimes \mathbf{N}$
porosity	$U\,[[\Delta_n]] - [[\mathbf{J}]] \cdot \mathbf{N} = 0$

As already indicated we do not quote here the dynamic compatibility relation for the bulk energy.

In order to construct field equations for the fields $\mathbf{w}$ listed in relation (535) we have to solve the *closure problem*, i.e. we have to add to balance equations of the Table 11 constitutive relations. We shall do so for some important particular cases. As the first closure we select the simplest possible one which yields a possibility of exploiting the second law of thermodynamics in a way typical for the rational extended thermodynamics. The other cases shall be investigated by means of the classical approach to the exploitation of the second law of thermodynamics.

In the case of the extended thermodynamics method we proceed as follows.

Let us define the following vectors

$$\begin{aligned}
&\mathsf{F}_0 := \left\{\rho^S, \rho^\alpha, \rho^S \acute{\dot{\mathbf{x}}}^S, \rho^\alpha \acute{\dot{\mathbf{x}}}^\alpha, \rho\left(\varepsilon + \frac{1}{2}\dot{x}^2\right), \mathbf{F}^S, \Delta_n\right\} \in \Re^{4A+15}, \\
&\mathsf{F}_K := \left\{0, \rho^\alpha \acute{\dot{\mathbf{X}}}^\alpha \cdot \mathbf{G}_K, -\mathbf{P}^S \mathbf{G}_K, \left(\rho^\alpha \acute{\dot{\mathbf{x}}}^\alpha \otimes \acute{\dot{\mathbf{X}}}^\alpha - \mathbf{P}^\alpha\right) \mathbf{G}_K,\right. \\
&\left.\left(\rho\left(\varepsilon + \frac{1}{2}\dot{x}^2\right)\dot{\mathbf{X}} + \mathbf{Q} - \mathbf{P}^T \dot{\mathbf{x}}\right) \cdot \mathbf{G}_K, -\acute{\dot{\mathbf{x}}}^S \otimes \mathbf{G}_K, \mathbf{J} \cdot \mathbf{G}_K\right\} \quad \in \quad \Re^{4A+15}, \\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad K \quad = \quad 1,2,3, \\
&\mathsf{f} := \left\{\hat{\rho}^S, \hat{\rho}^\alpha, \hat{\mathbf{p}}^S, \hat{\mathbf{p}}^\alpha, 0, \mathbf{0}, \hat{n}\right\} \in \Re^{4A+15}, \qquad (564) \\
&\mathsf{f}_{ext} := \left\{0, 0, \rho^S \mathbf{b}^S, \rho^\alpha \mathbf{b}^\alpha, \rho \mathbf{b} \cdot \dot{\mathbf{x}} + \rho r, \mathbf{0}, 0\right\} \in \Re^{4A+15},
\end{aligned}$$

where $\mathbf{G}_K$ denote *unit basis vectors* of Lagrangian coordinates. Then the balance equations can be written in the following compact form

$$\frac{\partial \mathsf{F}_0}{\partial t} + \frac{\partial \mathsf{F}_K}{\partial X^K} = \mathsf{f} + \mathsf{f}_{ext}, \tag{565}$$

where $\left\{X^K\right\}_{K=1,2,3}$ denote Lagrangian coordinates. For convenience we have chosen again a Cartesian coordinate system.

In procedures of *extended thermodynamics,* as we presented in Lecture 7, it is assumed that the vectors defined by (564) are sufficiently smooth functions of the vector $\mathbf{w}$ of unknown fields. Then the closure assumption has the form

$$\mathsf{F}_0 = \mathsf{F}_0(\mathbf{w}), \quad \mathsf{F}_K = \mathsf{F}_K(\mathbf{w}), \quad \mathsf{f} = \mathsf{f}(\mathbf{w}). \tag{566}$$

In the case under considerations we obtain the model of *poroelastic materials* without heat conduction. In order to incorporate the heat conduction we would have to introduce either an equation for the heat flux or a dependence on Grad T as a constitutive variable. Similarly we would have to extend the model if we wanted to describe viscous or plastic effects - we would have to add equations for partial stresses or a dependence on gradients of partial velocities. Further we present models in which some aspects of such extensions are indeed discussed within a classical approach to the problem of thermodynamical admissibility.

Let us stress that the structure of constitutive relations (566) is one of the most characteristic features of extended thermodynamics. Namely the constitutive variables are fields themselves but not their derivatives as it is always the case in ordinary nonequilibrium thermodynamics.

In order to expose the structure characteristic for extended thermodynamics we consider a simpler case of the closure in the form (566) under the assumption that processes are *isothermal.* This means that we leave out the temperature in the definition (535) of $\mathbf{w}$ and denote it then $\mathbf{w}_{is}$ as well as we ignore the energy balance equation.

The set of equations (566) for $\mathbf{w}_{is}$ without energy balance has thermodynamically the same structure as the corresponding set of extended thermodynamics. For this reason we can apply the same principles connected with the **thermodynamical admissibility**. They can be formulated as follows:

- *entropy inequality*: there exist a nontrivial entropy function h_0 and a flux $\mathbf{H} = H_K \mathbf{G}_K$ such that for each thermodynamical process (i.e. for each solution of field equations) the following inequality is satisfied

$$\frac{\partial h_0}{\partial t} + \operatorname{Div} \mathbf{H} \geq 0, \quad h_0 = h_0 \left(\mathbf{w}_{is} \right) \in \Re, \quad \mathbf{H} = \mathbf{H} \left(\mathbf{w}_{is} \right) \in \Re^3, \qquad (567)$$

- *convexity and causality*: the entropy function $h_0 = h_0 \left(\mathbf{u}_{is} \right)$ is concave, i.e.

$$\forall \mathbf{v} \in \Re^{14(A+1)}, \mathbf{v} \neq \mathbf{0} : \quad \frac{\partial^2 h_0}{\partial \mathbf{w}_{is} \partial \mathbf{w}_{is}} \cdot (\mathbf{v} \otimes \mathbf{v}) < 0, \qquad (568)$$

- *principle of relativity (Galilean invariance of field equations).*

The last principle yields a decomposition of all quantities of the model into two parts: a convective part which depends explicitly on the absolute velocity fields and a nonconvective part which does not depend on absolute velocities at all. This principle is satisfied identically in the case of Lagrangian description because we deal solely with relative velocities.

Entropy inequality (567) is exploited by means of Lagrange multipliers which eliminate the limitation of this inequality to thermodynamical processes. According to this procedure requirement (567) is equivalent to the following inequality for *all fields*, and not only for solutions of field equations

$$\begin{aligned} \forall \mathbf{w}_{is} &\in \Re^{14(A+1)} : \quad \frac{\partial h_0}{\partial t} + \frac{\partial H_K}{\partial X^K} - \mathbf{\Lambda} \cdot \left(\frac{\partial \tilde{\mathsf{F}}_0}{\partial t} + \frac{\partial \tilde{\mathsf{F}}_K}{\partial X^K} - \tilde{\mathsf{f}} \right) \geq 0, \quad \mathbf{\Lambda} \in \Re^{14(A+1)}, \\ \mathbf{H} &= H_K \mathbf{G}_K, \qquad (569) \end{aligned}$$

where $\mathbf{\Lambda}$ are the Lagrange multipliers, and functions of $\mathbf{w}_{is}$. As mentioned above $\tilde{\mathsf{F}}_0, \tilde{\mathsf{F}}_K, \tilde{\mathsf{f}}$ are truncations of functions (564) to the subspace $\Re^{14(A+1)}$ without the energy balance equation.

The solution of the above problem has the following form

$$dh_0 = \mathbf{\Lambda} \cdot d\tilde{\mathsf{F}}_0, \quad dH_K = d\tilde{\mathsf{F}}_K \cdot \mathbf{\Lambda} \quad \Longrightarrow \quad \frac{\partial \mathbf{\Lambda}}{\partial \mathbf{w}_{is}} = \frac{\partial^2 h_0}{\partial \mathbf{w}_{is} \partial \mathbf{w}_{is}}, \qquad (570)$$

i.e. according to (568), the map $\mathbf{w}_{is} \to \mathbf{\Lambda}$ is globally invertible. Hence after Legendre transformation

$$\begin{aligned} & h_0' \left(\mathbf{\Lambda} \right) = \mathbf{\Lambda} \cdot \tilde{\mathsf{F}}_0 - h_0, \quad H_K' \left(\mathbf{\Lambda} \right) = \mathbf{\Lambda} \cdot \tilde{\mathsf{F}}_K - H_K \quad \Longrightarrow \\ & \Longrightarrow \quad \tilde{\mathsf{F}}_0 = \frac{\partial h_0'}{\partial \mathbf{\Lambda}}, \quad \tilde{\mathsf{F}}_K = \frac{\partial H_K}{\partial \mathbf{\Lambda}}, \quad \mathbf{\Lambda} \cdot \tilde{\mathsf{f}} \left(\mathbf{\Lambda} \right) \geq 0. \qquad (571) \end{aligned}$$

Consequently, the functions $\tilde{\mathsf{F}}_0$, and $\tilde{\mathsf{F}}_K$ which determine the left-hand side of the field equations are given if the *four-potential* $\left(h_0' \left(\mathbf{\Lambda} \right), H_K' \left(\mathbf{\Lambda} \right) \right)$ is known. It leaves unspecified but restricted by the *dissipation inequality* $(571)_5$ only the sources $\tilde{\mathsf{f}} \left(\mathbf{\Lambda} \right)$ of the field equations. This is one of the most important consequences of the second law within the rational extended thermodynamics. Moreover relations (571) yield the symmetry of field equations for the unknown vector $\mathbf{\Lambda}$:

$$\frac{\partial^2 h_0}{\partial \mathbf{\Lambda} \partial \mathbf{\Lambda}} \frac{\partial \mathbf{\Lambda}}{\partial t} + \frac{\partial^2 H'_K}{\partial \mathbf{\Lambda} \partial \mathbf{\Lambda}} \frac{\partial \mathbf{\Lambda}}{\partial X^K} = \tilde{\mathsf{f}}. \tag{572}$$

Consequently under the second part of the condition of thermodynamical admissibility (i.e. nonsingularity of matrix $\frac{\partial^2 h_0}{\partial \mathbf{\Lambda} \partial \mathbf{\Lambda}}$) the system is *symmetric hyperbolic.*

It remains to invert the variables, i.e. to find the map $\mathbf{\Lambda} \to \mathbf{w}_{is}$. This is usually a very difficult technical problem. For this reason we use further a classical approach which does not require the execution of the last step.

Let us mention that the residual inequality $(571)_5$ defines the *dissipation.* This function vanishes in states called *the thermodynamical equilibrium states.* Consequently the necessary and sufficient conditions for the thermodynamical equilibrium within the model discussed in this Section have the form

$$\begin{aligned} \hat{\rho}^\alpha\big|_E &= 0 \quad \text{for } \alpha = 1, \ldots, A, \\ \hat{\mathbf{p}}^\alpha\big|_E &= 0 \quad \text{for } \alpha = 1, \ldots, A, \\ \hat{n}\big|_E &= 0. \end{aligned} \tag{573}$$

They follow directly from definition $(564)_3$ of the vector f truncated to $\tilde{\mathsf{f}}$.

In the following Lectures we discuss some particular models following from the above thermodynamical scheme.

Lecture 12: Two-component poroelastic materials: dependence on objective accelerations and porosity gradient

In order to see the structure of field equations for nonlinear nonisothermal processes in porous materials we consider a particular case of the two-component system which describes thermomechanical processes in *saturated poroelastic materials*. This thermodynamical construction is connected with the classical Biot model of poroelastic materials. Biot's model and some of its linear modifications shall be presented in the next Lecture. However, we have to mention two characteristic features of Biot's model motivating the construction which we present further. Within a purely isothermal framework Biot proposed a two-component linear model in which partial momentum balance equations are coupled by three terms. The first one, diffusive forces, following from the relative motion of components, is classical. The second one follows from the assumption that the momentum source contains a contribution of the relative acceleration of components. This yields the consequence that the matrix of partial mass densities is not diagonal. The off-diagonal part is assumed to be symmetric. The third one appears in partial stresses and describes the reaction of one component on volume changes of the other. This coupling is also assumed to be symmetric.

It is rather straightforward to show that the second contribution violates the principle of material objectivity and the third contribution contradicts the second law of thermodynamics. However, one can construct a nonlinear model whose linear limit is identical with the Biot model. We present this construction in this Lecture. In order to simplify technicalities, we present this construction in two separate steps. First, we construct the model with a contribution of relative accelerations and then a model with couplings of partial stresses.

A nonlinear objective model with a contribution of relative accelerations is thermodynamically admissible if we add some nonlinear contributions to partial stresses and to the free energy. They reflect in the simplest manner the existence of fluctuations of the microstructural kinetic energy caused by the heterogeneity of momentum in the representative elementary volume. The existence of such fluctuations as a result of tortuosity of porous materials has been indicated by O. Coussy in 1989[18]. However, the constitutive part of a model based on such considerations has not been presented. There exist some attempts to derive Biot's model with the contribution of relative acceleration by means of Hamilton's principle based on the fluctuation kinetic energy. As the true variational principle does not hold for dissipative systems the dissipation through fluctuation and diffusion is accounted for by a pseudo-potential and a pseudo-variational principle. This does not seem to be the right way of handling irreversible processes. For this reason we rely rather on the nonequilibrium thermodynamics in our considerations.

We consider a two-component continuum consisting of a solid skeleton and of a fluid. As in the previous Lecture, the motion of the skeleton is assumed to be described by the following twice continuously differentiable function

$$\mathbf{x} = \mathbf{f}^S(\mathbf{X}, t), \quad \mathbf{X} \in \mathcal{B}_0, \quad t \in \mathcal{T}, \tag{574}$$

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[18] O. Coussy; *Poromechanics*, Wiley&Sons, 2003.

where $\mathcal{B}_0$ denotes the reference configuration of the skeleton and $\mathcal{T}$ is the time interval. The velocity, the acceleration and the deformation gradient of the skeleton are defined by the relations

$$\acute{\mathbf{x}}^S := \frac{\partial \mathbf{f}^S}{\partial t}, \quad \acute{\acute{\mathbf{x}}}^S := \frac{\partial \acute{\mathbf{x}}^S}{\partial t}, \quad \mathbf{F}^S := \operatorname{Grad} \mathbf{f}^S. \tag{575}$$

Certainly, the value $\mathbf{F}^S = \mathbf{1}$ corresponds to the reference configuration for, say, $t = t_0$ in which $\mathbf{f}^S(\mathbf{X}, t_0) = \mathbf{X}$.

Motion of the fluid is described by the transformation of the Eulerian velocity field $\mathbf{v}^F = \mathbf{v}^F(\mathbf{x}, t)$ defined on the space of current configurations $\mathbf{f}^S(\mathcal{B}_0, t)$ of the skeleton. We have

$$\mathbf{v}^F = \mathbf{v}^F \left(\mathbf{f}^S(\mathbf{X}, t), t \right) =: \acute{\mathbf{x}}^F(\mathbf{X}, t). \tag{576}$$

The acceleration of the fluid is then given by

$$\acute{\acute{\mathbf{x}}}^F = \frac{\partial \acute{\mathbf{x}}^F}{\partial t} + \acute{\mathbf{X}}^F \cdot \operatorname{Grad} \acute{\mathbf{x}}^F, \quad \acute{\mathbf{X}}^F := \mathbf{F}^{S-1} \left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S \right), \tag{577}$$

where $\acute{\mathbf{X}}^F$ is the Lagrangian velocity of the fluid with respect to the skeleton.

We proceed to determine the transformation rules for the above quantities specified by the Euclidean transformation rule

$$\mathbf{x}^* = \mathbf{O}(t)\, \mathbf{x} + \mathbf{c}(t). \tag{578}$$

The relations (575) and the time differentiation of the relation (578) yield the following quantities in the new reference system

$$\mathbf{F}^{S*} = \mathbf{O}\mathbf{F}^S, \quad \acute{\mathbf{x}}^{S*} = \mathbf{O}\acute{\mathbf{x}}^S + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}}, \quad \acute{\acute{\mathbf{x}}}^{S*} = \mathbf{O}\acute{\acute{\mathbf{x}}}^S + 2\dot{\mathbf{O}}\acute{\mathbf{x}}^S + \ddot{\mathbf{O}}\mathbf{x} + \ddot{\mathbf{c}}, \tag{579}$$

where the dot denotes the time derivative.

We assume that the transformation rule for the velocity field of the fluid component has the same form as it does for the skeleton

$$\acute{\mathbf{x}}^{F*} = \mathbf{O}\acute{\mathbf{x}}^F + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}}. \tag{580}$$

Consequently

$$\acute{\mathbf{x}}^{F*} - \acute{\mathbf{x}}^{S*} = \mathbf{O}\left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S \right) \quad \Rightarrow \quad \acute{\mathbf{X}}^{F*} = \acute{\mathbf{X}}^F. \tag{581}$$

Bearing these relations in mind we can now easily derive the transformation of the acceleration of the fluid. We obtain immediately

$$\begin{aligned} \acute{\acute{\mathbf{x}}}^{F*} &= \frac{\partial}{\partial t}\left(\mathbf{O}\acute{\mathbf{x}}^F + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}} \right) + \acute{\mathbf{X}}^F \cdot \operatorname{Grad}\left(\mathbf{O}\acute{\mathbf{x}}^F + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}} \right) = \\ &= \mathbf{O}\acute{\acute{\mathbf{x}}}^F + 2\dot{\mathbf{O}}\acute{\mathbf{x}}^F + \ddot{\mathbf{O}}\mathbf{x} + \ddot{\mathbf{c}}, \end{aligned} \tag{582}$$

where the definition of the Lagrangian velocity has been used.

Due to the presence of contributions dependent solely on the choice of the frame we say that velocities $\acute{\mathbf{x}}^S, \acute{\mathbf{x}}^F$ and accelerations $\acute{\acute{\mathbf{x}}}^S, \acute{\acute{\mathbf{x}}}^F$ are nonobjective. Consequently, their difference is also nonobjective. We have

$$\acute{\acute{\mathbf{x}}}^{F*} - \acute{\acute{\mathbf{x}}}^{S*} = \mathbf{O}\left(\acute{\acute{\mathbf{x}}}^F - \acute{\acute{\mathbf{x}}}^S \right) + 2\dot{\mathbf{O}}\left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S \right). \tag{583}$$

For this reason the difference of accelerations cannot be used as a constitutive variable in a construction of the macroscopic model of a two-component system.

If we take the gradient of the transformation relations for velocities we obtain

$$\begin{aligned}
&\operatorname{Grad}\acute{\mathbf{x}}^{S*} = \mathbf{O}\operatorname{Grad}\acute{\mathbf{x}}^{S} + \dot{\mathbf{O}}\mathbf{F}^{S} \quad \Rightarrow \quad \dot{\mathbf{O}} = \operatorname{Grad}\left(\acute{\mathbf{x}}^{S*} - \mathbf{O}\acute{\mathbf{x}}^{S}\right)\mathbf{F}^{S-1}, \\
&\operatorname{Grad}\acute{\mathbf{x}}^{F*} = \mathbf{O}\operatorname{Grad}\acute{\mathbf{x}}^{F} + \dot{\mathbf{O}}\mathbf{F}^{S} \quad \Rightarrow \quad \dot{\mathbf{O}} = \operatorname{Grad}\left(\acute{\mathbf{x}}^{F*} - \mathbf{O}\acute{\mathbf{x}}^{F}\right)\mathbf{F}^{S-1}.
\end{aligned} \tag{584}$$

Consequently, we can write

$$\begin{aligned}
&2\dot{\mathbf{O}}\left(\acute{\mathbf{x}}^{F} - \acute{\mathbf{x}}^{S}\right) = (2-\mathfrak{z})\,\dot{\mathbf{O}}\left(\acute{\mathbf{x}}^{F} - \acute{\mathbf{x}}^{S}\right) + \mathfrak{z}\dot{\mathbf{O}}\left(\acute{\mathbf{x}}^{F} - \acute{\mathbf{x}}^{S}\right) = \\
&= (2-\mathfrak{z})\operatorname{Grad}\left(\acute{\mathbf{x}}^{F*} - \mathbf{O}\acute{\mathbf{x}}^{F}\right)\acute{\mathbf{X}}^{F} + \mathfrak{z}\operatorname{Grad}\left(\acute{\mathbf{x}}^{S*} - \mathbf{O}\acute{\mathbf{x}}^{S}\right)\acute{\mathbf{X}}^{F},
\end{aligned} \tag{585}$$

where $\mathfrak{z}$ is arbitrary.

Substitution of this relation in (583) yields

$$\begin{aligned}
&\acute{\acute{\mathbf{x}}}^{F*} - \acute{\acute{\mathbf{x}}}^{S*} - (2-\mathfrak{z})\,\acute{\mathbf{X}}^{F}\cdot\operatorname{Grad}\acute{\mathbf{x}}^{F*} - \mathfrak{z}\acute{\mathbf{X}}^{F}\cdot\operatorname{Grad}\acute{\mathbf{x}}^{S*} = \\
&= \mathbf{O}\left(\acute{\acute{\mathbf{x}}}^{F} - \acute{\acute{\mathbf{x}}}^{S} - (2-\mathfrak{z})\,\acute{\mathbf{X}}^{F}\cdot\operatorname{Grad}\acute{\mathbf{x}}^{F} - \mathfrak{z}\acute{\mathbf{X}}^{F}\cdot\operatorname{Grad}\acute{\mathbf{x}}^{S}\right).
\end{aligned} \tag{586}$$

It means that the quantity

$$\begin{aligned}
&\mathbf{a}_r := \frac{\partial}{\partial t}\left(\acute{\mathbf{x}}^{F} - \acute{\mathbf{x}}^{S}\right) + \acute{\mathbf{X}}^{F}\cdot\operatorname{Grad}\acute{\mathbf{x}}^{F} - (2-\mathfrak{z})\,\acute{\mathbf{X}}^{F}\cdot\operatorname{Grad}\acute{\mathbf{x}}^{F} - \mathfrak{z}\acute{\mathbf{X}}^{F}\cdot\operatorname{Grad}\acute{\mathbf{x}}^{S} \equiv \\
&\equiv \frac{\partial}{\partial t}\left(\acute{\mathbf{x}}^{F} - \acute{\mathbf{x}}^{S}\right) - (1-\mathfrak{z})\,\acute{\mathbf{X}}^{F}\cdot\operatorname{Grad}\acute{\mathbf{x}}^{F} - \mathfrak{z}\acute{\mathbf{X}}^{F}\cdot\operatorname{Grad}\acute{\mathbf{x}}^{S},
\end{aligned} \tag{587}$$

is objective, i.e.

$$\mathbf{a}_r^{*} = \mathbf{O}\mathbf{a}_r. \tag{588}$$

We call this quantity an *objective relative acceleration.* As an objective variable it can be incorporated into the set of constitutive variables. Obviously, there exists a class of such accelerations specified by the constitutive coefficient $\mathfrak{z}$.

It is easy to see that a linear momentum source $\hat{\mathbf{p}}$ in an isotropic material may contain a term $\rho_{12}^{0}\mathbf{a}_r \approx \rho_{12}^{0}\frac{\partial}{\partial t}\left(\acute{\mathbf{x}}^{F} - \acute{\mathbf{x}}^{S}\right)$ as required by relations of Biot's model. The open question is if the second law of thermodynamics admits this type of contribution in a fully nonlinear model.

As we have already mentioned the nonlinear poroelastic two-component model requires the formulation of field equations for the following fields

$$\mathcal{V} := \left\{\rho^{F}, \acute{\mathbf{x}}^{S}, \acute{\mathbf{x}}^{F}, \mathbf{F}^{S}, T, n\right\} \quad \text{for} \quad (\mathbf{X}, t) \in \mathcal{B}_0 \times \mathcal{T}, \tag{589}$$

where ρ^{F} is the partial mass density of the fluid per unit volume in the reference configuration of the skeleton, i.e. in the current configuration it is given by the relation $\rho_t^{F} = \rho^{F} J^{S-1}, J^{S} := \det \mathbf{F}^{S}$. T is the absolute temperature of the medium common for both components, and n is the current porosity. Other symbols have the same meaning as before.

The partial mass density of the skeleton in the reference configuration, ρ^S, does not appear among the fields because it is constant in a homogeneous material without mass exchange between components.

These fields are assumed to fulfil the following set of balance equations

$$R^F := \frac{\partial \rho^F}{\partial t} + \operatorname{Div}\left(\rho^F \acute{\mathbf{X}}^F\right) = 0, \tag{590}$$

$$\mathbf{M}^S := \rho^S \frac{\partial \acute{\mathbf{x}}^S}{\partial t} - \operatorname{Div} \mathbf{P}^S - \hat{\mathbf{p}} = \mathbf{0}, \tag{591}$$

$$\mathbf{M}^F := \rho^F \left(\frac{\partial \acute{\mathbf{x}}^F}{\partial t} + \acute{\mathbf{X}}^F \cdot \operatorname{Grad} \acute{\mathbf{x}}^F\right) - \operatorname{Div} \mathbf{P}^F + \hat{\mathbf{p}} = \mathbf{0}, \tag{592}$$

$$\begin{aligned} E \ &: = \frac{\partial \rho\varepsilon}{\partial t} + \operatorname{Div} \mathbf{Q} - \mathbf{P}^S \cdot \operatorname{Grad} \acute{\mathbf{x}}^S - \mathbf{P}^F \cdot \operatorname{Grad} \acute{\mathbf{x}}^F - \left(\mathbf{F}^{ST} \hat{\mathbf{p}}\right) \cdot \acute{\mathbf{X}}^F = 0, \\ \rho \ &: = \rho^S + \rho^F, \end{aligned} \tag{593}$$

$$\mathbf{F} := \frac{\partial \mathbf{F}^S}{\partial t} - \operatorname{Grad} \acute{\mathbf{x}}^S = \mathbf{0}, \tag{594}$$

$$N := \frac{\partial \Delta_n}{\partial t} + \operatorname{Div} \mathbf{J} - \hat{n} = 0, \quad \Delta_n := n - n_E, \tag{595}$$

where $\mathbf{P}^S, \mathbf{P}^F$ denote the first Piola-Kirchhoff partial stress tensors, $\hat{\mathbf{p}}$ is the momentum source, ε is the specific internal energy per unit mass of the mixture, $\mathbf{Q}$ is the heat flux vector, n_E describes the equilibrium porosity, $\mathbf{J}$ is the porosity flux, and $\hat{n}$ is the porosity source. The porosity balance equation (595) yields the model essentially beyond the frame of Biot's model due to the contribution of relaxation source $\hat{n}$.

As we show in the next Lecture, changes of porosity predicted by the linearized porosity balance equation are identical with those following from Biot's model and Gassmann relations provided the relaxation time of porosity goes to infinity (i.e. $\hat{n} \equiv 0$). However, it should be mentioned that many other approaches to the problem of evolution of volume fractions, porosity, etc. appear in the literature. One of the most popular forms of such an evolution equation follows from the so-called principle of equilibrated pressures introduced by Goodman, Cowin, Nunziato, Passman and others. Even though in some applications such an approach may by advantageous to the porosity balance, we do not discuss it any further in these Lecture notes.

In order to obtain field equations from the above balance equations we have to specify constitutive relations for these quantities, i.e

$$\mathcal{F} := \left\{\mathbf{P}^S, \mathbf{P}^F, \hat{\mathbf{p}}, \varepsilon, \mathbf{Q}, n_E, \mathbf{J}, \hat{n}\right\}, \tag{596}$$

must be functions of constitutive variables. In the model, we are presently discussing, the set of constitutive variables is chosen as follows

$$\mathcal{C} := \left\{\rho^F, \mathbf{F}^S, \acute{\mathbf{X}}^F, \Delta_n, T, \mathbf{G}, \mathbf{a}_r\right\}, \quad \mathbf{G} := \operatorname{Grad} T. \tag{597}$$

Hence the gradient of porosity does not appear among the variables. As we see further it means that we can expect only the so-called simple mixture model to follow from thermodynamical considerations in which some couplings of components are absent. We do so on purpose to avoid technical difficulties of accounting simultaneously for two new contributions: due to $\mathbf{a}_r$ and due to $\mathbf{N} := \operatorname{Grad} n$. Later we consider the model with the dependence on $\mathbf{N}$ but on $\mathbf{a}_r$. One can show that the combined model satisfies the second law of thermodynamics.

Once the function

$$\mathcal{F} = \mathcal{F}\left(\mathcal{C}\right), \tag{598}$$

is given, we obtain a closed system of differential equations for fields $\mathcal{V}$.

Constitutive relations (598) satisfy the second law of thermodynamics in the form of the following entropy inequality

$$\frac{\partial \rho\eta}{\partial t} + \operatorname{Div}\mathbf{H} \geq 0, \quad \eta = \eta\left(\mathcal{C}\right), \quad \mathbf{H} = \mathbf{H}\left(\mathcal{C}\right), \tag{599}$$

which must hold for all solutions of field equations. In this inequality η is the specific entropy and $\mathbf{H}$ its flux.

This requirement is equivalent to the following inequality which must hold for all fields

$$\frac{\partial \rho\eta}{\partial t} + \operatorname{Div}\mathbf{H} - \Lambda^{\rho^F} R^F - \mathbf{\Lambda}^{v^S} \cdot \mathbf{M}^S - \mathbf{\Lambda}^{v^F} \cdot \mathbf{M}^F - \Lambda^{\varepsilon} E - \mathbf{\Lambda}^F \cdot \mathbf{F} - \Lambda^n N \geq 0, \tag{600}$$

where

$$\Lambda^{\rho^F}, \mathbf{\Lambda}^{v^S}, \mathbf{\Lambda}^{v^F}, \Lambda^{\varepsilon}, \mathbf{\Lambda}^F, \Lambda^n \tag{601}$$

are Lagrange multipliers dependent on constitutive variables $\mathcal{C}$.

The exploitation of the second law of thermodynamics in the general case is technically impossible. Therefore we make simplifying assumptions sufficient for the second law to be satisfied and yielding explicit limitations on constitutive relations. They are as follows[19]:

1° The material is isotropic. Consequently, scalar constitutive functions, for instance, depend on vector and tensor variables solely through invariants. This assumption will be applied in some steps of our proofs. Some relations are simpler in a general form and then we do not introduce this limitation.

2° The dependence on the relative velocity $\acute{\mathbf{X}}^F$ is at most quadratic. This assumption is related to the structure of the nonlinear contribution to the objective relative acceleration. We motivate its form further.

3° The dependence on the temperature gradient $\mathbf{G}$ is linear. We could skip this assumption on the cost of some technicalities but the experience with the thermodynamical construction of poroelastic models shows that this simplifying assumption does not yield any undesired results.

4° The dependence on the deviation of porosity n from its equilibrium value n_E, $\Delta_n \equiv n - n_E$, is quadratic.

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[19] K. Wilmanski; *Tortuosity and Objective Relative Accelerations in the Theory of Porous Materials,* Proc. Roy. Soc. **A**, **461**, 1533-1561, 2005.

5° The dependence on the relative acceleration $\mathbf{a}_r$ is linear.

6° Higher order combinations of variables $\mathbf{G}, \acute{\mathbf{X}}^F, \Delta_n, \mathbf{a}_r$ can be neglected.

As we see further these assumptions limit thermodynamical considerations to a vicinity of the thermodynamical equilibrium similar to this appearing in the classical Onsager thermodynamics.

Bearing these assumptions in mind we can write the following representations of constitutive functions

– partial stresses

$$\mathbf{P}^S = \mathbf{P}_0^S\left(\mathcal{C}_E, \Delta_n\right) + \frac{1}{2}\sigma^S\left(\mathcal{C}_E\right)\mathbf{F}^S\acute{\mathbf{X}}^F \otimes \acute{\mathbf{X}}^F, \quad \mathcal{C}_E := \left\{\rho^F, \mathbf{F}^S, T\right\},$$

$$\mathbf{P}^F = \mathbf{P}_0^F\left(\mathcal{C}_E, \Delta_n\right) + \frac{1}{2}\sigma^F\left(\mathcal{C}_E\right)\mathbf{F}^S\acute{\mathbf{X}}^F \otimes \acute{\mathbf{X}}^F, \quad n_E = n_E\left(\mathcal{C}_E\right), \tag{602}$$

– internal energy and entropy

$$\rho\varepsilon = \rho\varepsilon_0\left(\mathcal{C}_E, \Delta_n\right) + \frac{1}{2}\varepsilon_d\left(\mathcal{C}_E\right)\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right)\cdot\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right),$$

$$\rho\eta = \rho\eta_0\left(\mathcal{C}_E, \Delta_n\right) + \frac{1}{2}\eta_d\left(\mathcal{C}_E\right)\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right)\cdot\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right), \tag{603}$$

– fluxes of energy, entropy, porosity

$$\begin{array}{rcl}\mathbf{Q} & = & Q_V\acute{\mathbf{X}}^F - K\mathbf{G} + Q_a\mathbf{F}^{ST}\mathbf{a}_r, \\ \mathbf{H} & = & H_V\acute{\mathbf{X}}^F + H_T\mathbf{G} + H_a\mathbf{F}^{ST}\mathbf{a}_r, \\ \mathbf{J} & = & \Phi\acute{\mathbf{X}}^F + J_T\mathbf{G} + J_a\mathbf{F}^{ST}\mathbf{a}_r,\end{array} \tag{604}$$

where all coefficients are functions of variables $\mathcal{C}_E$,

– momentum source

$$\mathbf{F}^{ST}\hat{\mathbf{p}} = \Pi_V\acute{\mathbf{X}}^F + \Pi_T\mathbf{G} - \rho_{12}^0\mathbf{F}^{ST}\mathbf{a}_r, \tag{605}$$

with coefficients dependent again on variables $\mathcal{C}_E$.

The contributions with the coefficients ε_d, η_d to the energy and entropy are motivated by fluctuations of the microstructural kinetic energy caused by the tortuosity[20]. We do not introduce any additional microstructural variable describing changes of tortuosity. For this reason a macroscopic influence of tortuosity can be solely reflected by the *seepage velocity* which in our model corresponds to the Lagrangian velocity $\acute{\mathbf{X}}^F$. The classical kinetic energy in this model is given by $\frac{1}{2}\left(\rho^S\acute{\mathbf{x}}^S\cdot\acute{\mathbf{x}}^S + \rho^F\acute{\mathbf{x}}^F\cdot\acute{\mathbf{x}}^F\right)$. Consequently, the correction $\frac{1}{2}\varepsilon_d\left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S\right)\cdot\left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S\right)$ may be considered as an *added mass effect* resulting from tortuosity.

As we see further, the dependence of partial stresses on this velocity, introduced in the simplest form by (602), is then required by the consistency of the model with the second law of thermodynamics. In other words, we show further that coefficients σ^S, σ^F in the

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[20] Tortuosity is the geometrical property of flows in channels of porous materials and it may be defined as the ratio of the average length of the streamline within REV to the typical linear dimension of REV. Hence, its minimum value is equal to one. It corresponds to the straight streamline.

stress relations (602) and the coefficient ε_d in the energy relation (603) are connected (see: formula (645)).

The exploitation of the second law of thermodynamics (600) is standard. We apply the chain rule of differentiation to constitutive laws. We skip here rather cumbersome technical details.

Linearity of the second law of thermodynamics with respect to time derivatives

$$\left\{\frac{\partial\rho^F}{\partial t},\frac{\partial\mathbf{F}^S}{\partial t},\frac{\partial\Delta_n}{\partial t},\frac{\partial\acute{\mathbf{x}}^S}{\partial t},\frac{\partial\acute{\mathbf{x}}^F}{\partial t},\frac{\partial T}{\partial t},\frac{\partial\mathbf{G}}{\partial t}\right\}$$

yields

$$\Lambda^{\rho^F}=\Lambda_0^{\rho^F}+\frac{1}{2}\left(\frac{\partial\eta_d}{\partial\rho^F}-\Lambda^\varepsilon\frac{\partial\varepsilon_d}{\partial\rho^F}\right)\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right)\cdot\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right), \tag{606}$$

$$\Lambda_0^{\rho^F}:=\frac{\partial\rho\eta_0}{\partial\rho^F}-\Lambda^\varepsilon\frac{\partial\rho\varepsilon_0}{\partial\rho^F}$$

$$\boldsymbol{\Lambda}^F=\frac{\partial\rho\eta_0}{\partial\mathbf{F}^F}-\Lambda^\varepsilon\frac{\partial\rho\varepsilon_0}{\partial\mathbf{F}^F}+\frac{1}{2}\left(\frac{\partial\eta_d}{\partial\mathbf{F}^F}-\Lambda^\varepsilon\frac{\partial\varepsilon_d}{\partial\mathbf{F}^F}\right)\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right)\cdot\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right), \tag{607}$$

$$\Lambda^n=\frac{\partial\rho\eta_0}{\partial\Delta_n}-\Lambda^\varepsilon\frac{\partial\rho\varepsilon_0}{\partial\Delta_n}, \tag{608}$$

$$\begin{aligned}\left(\rho^S-\rho_{12}^0\right)\boldsymbol{\Lambda}^{v^S}+\rho_{12}^0\boldsymbol{\Lambda}^{v^F}&=-\left(\eta_d-\Lambda^\varepsilon\varepsilon_d\right)\mathbf{F}^S\acute{\mathbf{X}}^F+\rho_{12}^0\Lambda^\varepsilon\mathbf{F}^S\acute{\mathbf{X}}^F-\\&-\operatorname{Div}\left(H_a\mathbf{F}^S\right)+\Lambda^\varepsilon\operatorname{Div}\left(Q_a\mathbf{F}^S\right)+\Lambda^n\operatorname{Div}\left(J_a\mathbf{F}^S\right)=0,\end{aligned} \tag{609}$$

$$\begin{aligned}\left(\rho^F-\rho_{12}^0\right)\boldsymbol{\Lambda}^{v^F}+\rho_{12}^0\boldsymbol{\Lambda}^{v^S}&=\left(\eta_d-\Lambda^\varepsilon\varepsilon_d\right)\mathbf{F}^S\acute{\mathbf{X}}^F-\rho_{12}^0\Lambda^\varepsilon\mathbf{F}^S\acute{\mathbf{X}}^F+\\&+\operatorname{Div}\left(H_a\mathbf{F}^S\right)-\Lambda^\varepsilon\operatorname{Div}\left(Q_a\mathbf{F}^S\right)-\Lambda^n\operatorname{Div}\left(J_a\mathbf{F}^S\right)=0,\end{aligned} \tag{610}$$

$$\frac{\partial\rho\eta_0}{\partial T}-\Lambda^\varepsilon\frac{\partial\rho\varepsilon_0}{\partial T}+\frac{1}{2}\left(\frac{\partial\eta_d}{\partial T}-\Lambda^\varepsilon\frac{\partial\varepsilon_d}{\partial T}\right)\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right)\cdot\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right)=0. \tag{611}$$

These identities still contain linear contributions of $\operatorname{Grad}\mathbf{F}^S$, Δ_n, quadratic contributions of the latter as well as quadratic contributions of Lagrangian velocity. As they should hold for arbitrary fields coefficients of these contributions must vanish separately. After easy analysis we obtain

$$H_a=0,\quad Q_a=0,\quad J_a=0, \tag{612}$$

$$\rho^S\boldsymbol{\Lambda}^{v^S}=-\rho^F\boldsymbol{\Lambda}^{v^F}=\mathfrak{y}\mathbf{F}^S\acute{\mathbf{X}}^F,\quad \mathfrak{y}:=-\frac{\eta_d-\Lambda^\varepsilon\varepsilon_d-\Lambda^\varepsilon\rho_{12}^0}{\rho^S-\rho_{12}^0\left(1+\frac{\rho^S}{\rho^F}\right)}. \tag{613}$$

The second law of thermodynamics is also linear with respect to the following spatial derivatives

$$\operatorname{Grad}\acute{\mathbf{x}}^S,\operatorname{Grad}\acute{\mathbf{x}}^F,\operatorname{Grad}\rho^F,\operatorname{Grad}\mathbf{F}^S,\operatorname{Grad}\mathbf{G},\operatorname{Grad}\Delta_n. \tag{614}$$

We have listed them in the order of the further analysis and, simultaneously, skipped the derivative Grad $\mathbf{a}_r$ because it does not contribute to the second law due to the relations (612). The linearity with respect to (614) yields a set of identities and leaves a residual inequality which is essentially nonlinear. It defines the **dissipation** in the system and has the following form

$$\begin{aligned} \mathcal{D} := & \left(\frac{\partial H_V}{\partial T} - \Lambda^\varepsilon \frac{\partial Q_V}{\partial T} - \Lambda^n \frac{\partial \Phi}{\partial T} + \Pi_T\right) \acute{\mathbf{X}}^F \cdot \mathbf{G} + \\ & + \left(\frac{\partial H_T}{\partial T} + \Lambda^\varepsilon \frac{\partial K}{\partial T} - \Lambda^n \frac{\partial J_T}{\partial T}\right) \mathbf{G} \cdot \mathbf{G} + \\ & + \Lambda^\varepsilon \Pi_V \acute{\mathbf{X}}^F \cdot \acute{\mathbf{X}}^F + \Lambda^n \hat{n} \geq 0. \end{aligned} \tag{615}$$

Hence the state of thermodynamical equilibrium defined by $\mathcal{D} = 0$ appears if

$$\mathbf{G} = 0, \quad \acute{\mathbf{X}}^F = 0, \quad \hat{n} = 0, \tag{616}$$

i.e. the temperature gradient, relative motion (diffusion), and the relaxation of porosity cause the deviation from the equilibrium.

Clearly the assumption 4° yields the linearity of $\hat{n}$ and Λ^n with respect to Δ_n. In addition, the above inequality yields homogeneity of these functions, i.e. we can write

$$\hat{n} = -\frac{\Delta_n}{\tau}, \quad \Lambda^n = \lambda^n \Delta_n, \tag{617}$$

where τ, λ^n can be solely functions of variables $\mathcal{C}_E$. Consequently, we obtain as well

$$\frac{\partial \Phi}{\partial T} = 0, \quad \frac{\partial J_T}{\partial T} = 0. \tag{618}$$

It is worth mentioning that due to (612) the relative acceleration does not contribute to the dissipation. This property of the model follows from the fact that the model does not possess any independent field of tortuosity which could relax to the thermodynamical equilibrium.

Now we return to the coefficients of spatial derivatives of fields. The vanishing coefficient of Grad $\acute{\mathbf{x}}^S$ yields the following results

$$\Lambda^\varepsilon \mathbf{P}_0^S \mathbf{F}^{ST} + \left(\frac{\partial \rho\eta_0}{\partial \mathbf{F}^S} - \Lambda^\varepsilon \frac{\partial \rho\varepsilon_0}{\partial \mathbf{F}^S}\right) \mathbf{F}^{ST} + \left(-H_V + \Lambda^\varepsilon Q_V + \Lambda^n \Phi + \rho^F \Lambda_0^{\rho^F}\right) \mathbf{1} = 0, \tag{619}$$

$$\frac{\partial \eta_d}{\partial I} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial I} = 0, \quad \frac{\partial \eta_d}{\partial II} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial II} = 0, \tag{620}$$

$$2\left(\frac{\partial \eta_d}{\partial III} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial III}\right) III + \rho^F \left(\frac{\partial \eta_d}{\partial \rho^F} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial \rho^F}\right) = \mathfrak{y}\left(\sigma^S + \frac{\rho^S}{\rho^F}\sigma^F\right), \tag{621}$$

$$\mathfrak{z} = -\frac{1}{2\rho_{12}^0} \frac{\sigma^S \Lambda^\varepsilon - \mathfrak{y}\left(\sigma^S + \frac{\rho^S}{\rho^F}\sigma^F\right)}{\mathfrak{y}\left(1 + \frac{\rho^S}{\rho^F}\right) + \Lambda^\varepsilon}, \tag{622}$$

where

$$I := \operatorname{tr} \mathbf{C}^S, \quad II := \frac{1}{2}\left(I^2 - \operatorname{tr} \mathbf{C}^S\right), \quad III := \det \mathbf{C}^S, \quad \mathbf{C}^S := \mathbf{F}^{ST}\mathbf{F}^S, \tag{623}$$

are main invariants of the Cauchy-Green deformation tensor $\mathbf{C}^S$.

The coefficient of $\operatorname{Grad} \acute{\mathbf{x}}^F$ yields

$$\Lambda^\varepsilon \left(\mathbf{P}_0^S + \mathbf{P}_0^F\right) = -\left(\frac{\partial \rho\eta_0}{\partial \mathbf{F}^S} - \Lambda^\varepsilon \frac{\partial \rho\varepsilon_0}{\partial \mathbf{F}^S}\right), \tag{624}$$

$$\frac{\partial \eta_d}{\partial III} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial III} = 0, \tag{625}$$

$$\frac{1}{2}\Lambda^\varepsilon \left(\sigma^S + \sigma^F\right) = -\rho_{12}^0 \left(1 + \frac{\rho^S}{\rho^F}\right)\mathfrak{y} - \rho^S \mathfrak{y} - \rho_{12}^0 \Lambda^\varepsilon. \tag{626}$$

Consequently, bearing (620) and (625) in mind,

$$\frac{\partial \eta_d}{\partial \mathbf{F}^S} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial \mathbf{F}^S} = 0. \tag{627}$$

Next we consider the coefficient of $\operatorname{Grad} \rho^F$. We have

$$\left(\frac{\partial H_V}{\partial \rho^F} - \Lambda^\varepsilon \frac{\partial Q_V}{\partial \rho^F} - \Lambda^n \frac{\partial \Phi}{\partial \rho^F} - \Lambda^{\rho^F}\right)\acute{\mathbf{X}}^F + \mathfrak{y}\frac{\partial \mathbf{P}^{ST}}{\partial \rho^F}\mathbf{F}^S\acute{\mathbf{X}}^F - \mathfrak{y}\frac{\rho^F}{\rho^S}\frac{\partial \mathbf{P}^{FT}}{\partial \rho^F}\mathbf{F}^S\acute{\mathbf{X}}^F = 0, \tag{628}$$

$$\frac{\partial H_T}{\partial \rho^F} + \Lambda^\varepsilon \frac{\partial K}{\partial \rho^F} = 0, \quad \frac{\partial J_T}{\partial \rho^F} = 0. \tag{629}$$

Similarly, the coefficient of $\operatorname{Grad} \mathbf{F}^S$ yields

$$\operatorname{sym}\left\{\left(\frac{\partial H_V}{\partial \mathbf{F}^S} - \Lambda^\varepsilon \frac{\partial Q_V}{\partial \mathbf{F}^S} - \Lambda^n \frac{\partial \Phi}{\partial \mathbf{F}^S}\right)\otimes \acute{\mathbf{X}}^F + \rho^F \Lambda^{\rho^F}\mathbf{F}^{S-T}\otimes \acute{\mathbf{X}}^F + \mathfrak{y}\boldsymbol{\Xi}^S + \mathfrak{y}\boldsymbol{\Xi}^F\right\} -$$

$$- \operatorname{sym}\left\{\left(H_V - \Lambda^\varepsilon - \Lambda^n \Phi\right)\mathbf{F}^{S-T}\otimes \acute{\mathbf{X}}^F\right\} = 0, \tag{630}$$

$$\frac{\partial H_T}{\partial \mathbf{F}^S} + \Lambda^\varepsilon \frac{\partial K}{\partial \mathbf{F}^S} = 0, \quad \frac{\partial J_T}{\partial \mathbf{F}^S} = 0, \tag{631}$$

where the components of tensors $\boldsymbol{\Xi}^S, \boldsymbol{\Xi}^F$ in Cartesian coordinates are given by the relations

$$\Xi_{kKL}^S = \frac{\partial P_{0lL}^S}{\partial F_{kK}^S}F_{lM}^S \acute{X}_M^F, \quad \Xi_{kKL}^F = -\frac{\rho^S}{\rho^F}\frac{\partial P_{0lL}^F}{\partial F_{kK}^S}F_{lM}^S \acute{X}_M^F. \tag{632}$$

Under our assumptions the contribution of $\operatorname{Grad} \Delta_n$ does not yield any restrictions.

Finally, the last condition follows from the vanishing coefficient of $\operatorname{Grad} \mathbf{G}$ and it has the form

$$H_T + \Lambda^\varepsilon K = 0, \quad J_T = 0. \tag{633}$$

Inspection of the results (629), (631) for thermal coefficients yields

$$\Lambda^{\varepsilon} = \Lambda^{\varepsilon}(T) \quad \Rightarrow \quad \Lambda^{\varepsilon} = \frac{1}{T}, \quad \text{i.e.} \quad H_T = -\frac{K}{T}, \tag{634}$$

where the ideal wall argument has been used.

It is not quite clear what limitations on partial stress tensors are imposed by conditions (628), (630). Derivatives of partial stresses with respect to the mass density ρ^F as well as with respect to the deformation gradient $\mathbf{F}^S$ seem to restrict elastic properties of the system in equilibrium. This does not seem very plausible. Hence we assume that the coefficient $\mathfrak{y}$ vanishes, i.e.

$$\mathfrak{y} = 0. \tag{635}$$

Then the multipliers of momentum equations vanish as well. As the consequence of (611), (613), (621), (627) we obtain

$$-\rho^0_{12} = \varepsilon_d - T\eta_d = const. \quad \Rightarrow \quad \varepsilon_d = const., \ \eta_d = 0. \tag{636}$$

It is convenient to introduce the following notation

$$\begin{aligned} \psi &:= \varepsilon - T\eta, \\ \rho\psi_0 &:= \rho\psi - \tfrac{1}{2}\varepsilon_d \left(\mathbf{F}^S \acute{\mathbf{X}}^F\right) \cdot \left(\mathbf{F}^S \acute{\mathbf{X}}^F\right). \end{aligned} \tag{637}$$

Then, for Lagrange multipliers we have

$$\Lambda^{\rho^F} = -\frac{1}{T}\frac{\partial \rho\psi_0}{\partial \rho^F} = \Lambda_0^{\rho^F}, \quad \mathbf{\Lambda}^F = -\frac{1}{T}\frac{\partial \rho\psi_0}{\partial \mathbf{F}^S}, \quad \Lambda^n = -\frac{1}{T}\frac{\partial \rho\psi_0}{\partial \Delta_n} = \lambda^n \Delta_n, \tag{638}$$

and the relation (611) implies the following classical formula for the internal energy

$$\varepsilon = \psi - T\frac{\partial \psi}{\partial T}. \tag{639}$$

Simultaneously the relations (628), (630) yield

$$\begin{aligned} &\frac{\partial H_V}{\partial \rho^F} - \Lambda^{\varepsilon}\frac{\partial Q_V}{\partial \rho^F} - \Lambda^{\rho^F} = 0, \quad \frac{\partial \Phi}{\partial \rho^F} = 0, \\ &2III\left(\frac{\partial H_V}{\partial III} - \Lambda^{\varepsilon}\frac{\partial Q_V}{\partial III}\right) + \rho^F \Lambda^{\rho^F} - \left(H_V - \Lambda^{\varepsilon} Q_V\right) = 0, \end{aligned} \tag{640}$$

$$2III\frac{\partial \Phi}{\partial III} - \Phi = 0 \quad \Rightarrow \quad \Phi = J^S \Phi_0, \quad \Phi_0 = const. \tag{641}$$

These relations yield the following integrability condition for the multiplier Λ^{ρ^F}

$$\rho^F \frac{\partial \Lambda^{\rho^F}}{\partial \rho^F} + J^S \frac{\partial \Lambda^{\rho^F}}{\partial J^S} = 0 \quad \Rightarrow \quad \Lambda^{\rho^F} = \Lambda^{\rho^F}\left(T, \rho_t^F\right), \quad \rho_t^F := J^{S-1}\rho^F. \tag{642}$$

Consequently, integration of $(638)_1$ leads to the following additive splitting of the free energy ψ

$$\begin{aligned} \rho\psi &= \rho^F\psi^F + \rho^S\psi^S - \frac{1}{2}\lambda^n T\Delta_n^2 + \frac{1}{2}\varepsilon_d \left(\mathbf{F}^S\acute{\mathbf{X}}^F\right)\cdot\left(\mathbf{F}^S\acute{\mathbf{X}}^F\right), \\ \psi^F &= \psi^F\left(T,\rho_t^F\right), \quad \psi^S = \psi^S\left(T,\mathbf{F}^S\right). \end{aligned} \tag{643}$$

The above separation property is characteristic for the so-called **simple mixtures**. It means that the choice of constitutive variables (597) rules out the coupling of components through deformations: changes of the current mass density ρ_t^F do not have influence on ψ^S and deformations $\mathbf{F}^S$ of the skeleton do not have influence on ψ^F.

In addition, integration in $(640)_1$ yields

$$H_V - \frac{Q_V}{T} = -\frac{\rho^F\psi^F}{T}, \quad \text{i.e.} \quad \mathbf{H} = \frac{1}{T}\left(\mathbf{Q} - \rho^F\psi^F\acute{\mathbf{X}}^F\right), \tag{644}$$

where we have accounted for the relations (633) and (634).

Inspection of relations (636), (622) and (626) leads immediately to the following identification of constitutive coefficients coupled to the relative acceleration

$$\varepsilon_d = -\rho_{12}^0, \quad \sigma^S = -2\mathfrak{z}\rho_{12}^0, \quad \sigma^F = -2\left(1-\mathfrak{z}\right)\rho_{12}^0. \tag{645}$$

Simultaneously, relation (619) with (637), (638), (643) and (644) for partial stresses $\mathbf{P}_0^S$ and relation (624) for partial stresses $\mathbf{P}_0^F$ yield

$$\begin{aligned} \mathbf{P}^S &= \frac{\partial\rho^S\psi^S}{\partial\mathbf{F}^S} + \beta\Delta_n J^S\mathbf{F}^{S-T} - \mathfrak{z}\rho_{12}^0\mathbf{F}^S\acute{\mathbf{X}}^S\otimes\acute{\mathbf{X}}^S, \quad \beta := T\lambda^n\Phi_0 J^{S-1}, \\ \mathbf{P}^F &= -\rho_t^{F2}\frac{\partial\psi^F}{\partial\rho_t^F}J^S\mathbf{F}^{S-T} - \beta\Delta_n J^S\mathbf{F}^{S-T} - \left(1-\mathfrak{z}\right)\rho_{12}^0\mathbf{F}^S\acute{\mathbf{X}}^S\otimes\acute{\mathbf{X}}^S. \end{aligned} \tag{646}$$

Hence, as mentioned in the introduction, the partial stresses do not possess a coupling term characteristic for Biot's model and this fallacy of the model can be removed by additional constitutive variables.

For practical purposes it is convenient to transform equations of the model to Eulerian coordinates. We write them in an arbitrary noninertial reference system. The set of balance equations (590) has then the form

– mass balance for the fluid component

$$\frac{\partial\rho_t^F}{\partial t} + \operatorname{div}\left(\rho_t^F\mathbf{v}^F\right) = 0, \tag{647}$$

– momentum balance for the skeleton

$$\begin{aligned} &\rho_t^S\left(\frac{\partial\mathbf{v}^S}{\partial t} + \mathbf{v}^S\cdot\operatorname{grad}\mathbf{v}^S\right) = \operatorname{div}\mathbf{T}^S + \rho_t^S\mathbf{b}^S + J^{S-1}\Pi_T\operatorname{grad}\mathbf{T} + \pi\left(\mathbf{v}^F-\mathbf{v}^S\right) - \\ &-\rho_{12}\left[\frac{\partial}{\partial t}\left(\mathbf{v}^F-\mathbf{v}^S\right) - \left(1-\mathfrak{z}\right)\left(\mathbf{v}^F-\mathbf{v}^S\right)\cdot\operatorname{grad}\mathbf{v}^F - \mathfrak{z}\left(\mathbf{v}^F-\mathbf{v}^S\right)\cdot\operatorname{grad}\mathbf{v}^S\right], \end{aligned} \tag{648}$$

– momentum balance for the fluid

$$\rho_t^F\left(\frac{\partial\mathbf{v}^F}{\partial t} + \mathbf{v}^F\cdot\operatorname{grad}\mathbf{v}^F\right) = \operatorname{div}\mathbf{T}^F + \rho_t^F\mathbf{b}^F - J^{S-1}\Pi_T\operatorname{grad}\mathbf{T} - \pi\left(\mathbf{v}^F-\mathbf{v}^S\right) +$$

$$+\rho_{12}\left[\frac{\partial}{\partial t}\left(\mathbf{v}^F-\mathbf{v}^S\right)-(1-\mathfrak{z})\left(\mathbf{v}^F-\mathbf{v}^S\right)\cdot\operatorname{grad}\mathbf{v}^F-\mathfrak{z}\left(\mathbf{v}^F-\mathbf{v}^S\right)\cdot\operatorname{grad}\mathbf{v}^S\right],\qquad(649)$$

– energy balance

$$\frac{\partial\rho_t\varepsilon}{\partial t}+\operatorname{div}\left(\rho_t\varepsilon\mathbf{v}^S+\mathbf{q}\right)-\mathbf{T}^S\cdot\operatorname{grad}\mathbf{v}^S-\mathbf{T}^F\cdot\operatorname{grad}\mathbf{v}^F-\qquad(650)$$

$$-\left(\mathbf{v}^F-\mathbf{v}^S\right)\cdot\left\{\pi\left(\mathbf{v}^F-\mathbf{v}^S\right)+J^{S-1}\Pi_T\operatorname{grad}T-\right.$$

$$\left.-\rho_{12}\left[\frac{\partial}{\partial t}\left(\mathbf{v}^F-\mathbf{v}^S\right)-(1-\mathfrak{z})\left(\mathbf{v}^F-\mathbf{v}^S\right)\cdot\operatorname{grad}\mathbf{v}^F-\mathfrak{z}\left(\mathbf{v}^F-\mathbf{v}^S\right)\cdot\operatorname{grad}\mathbf{v}^S\right]\right\},$$

– porosity balance

$$\frac{\partial J^{S-1}\Delta_n}{\partial t}+\operatorname{div}\left(J^{S-1}\Delta_n\mathbf{v}^S+\mathbf{j}\right)+\frac{J^{S-1}\Delta_n}{\tau}=0.\qquad(651)$$

The external forces $\rho_t^S\mathbf{b}^S, \rho_t^F\mathbf{b}_t^F$, called *apparent body forces*, contributing to momentum balance equations have the following structure

$$\begin{aligned}
&\rho_t^S\mathbf{b}^S=\rho_t^S\left(\mathbf{b}_b^S+\mathbf{i}^S\right),\quad \rho_t^F\mathbf{b}^F=\rho_t^F\left(\mathbf{b}_b^F+\mathbf{i}^F\right),\\
&\mathbf{i}^S:=\ddot{\mathbf{c}}+2\mathbf{\Omega}\left(\mathbf{v}^S-\dot{\mathbf{c}}\right)+\left(\dot{\mathbf{\Omega}}-\mathbf{\Omega}^2\right)(\mathbf{x}-\mathbf{c}),\\
&\mathbf{i}^F:=\ddot{\mathbf{c}}+2\mathbf{\Omega}\left(\mathbf{v}^F-\dot{\mathbf{c}}\right)+\left(\dot{\mathbf{\Omega}}-\mathbf{\Omega}^2\right)(\mathbf{x}-\mathbf{c}),\quad \mathbf{\Omega}:=\dot{\mathbf{O}}\mathbf{O}^T\equiv-\mathbf{\Omega}^T,
\end{aligned}\qquad(652)$$

where $\rho_t^S\mathbf{b}_b^S, \rho_t^F\mathbf{b}_b^F$ are true (e.g. gravitational) body forces, and $\rho_t^S\mathbf{i}^S, \rho_t^F\mathbf{i}^F$ are *inertial body forces*. In order of appearance in the above relations, they consist of the inertial force of relative translation, Coriolis force, Euler force, centrifugal force. They depend on the matrix of angular velocity $\mathbf{\Omega}$ of the noninertial system with respect to an inertial one. Certainly, the inertial body forces vanish in an inertial reference system. It should be mentioned that the partial accelerations appearing in the above partial momentum balance equations combined with apparent body forces are objective, i.e. invariant with respect to the Euclidean transformation.

The remaining notation used above is as follows

$$\rho_t^S=\rho^S J^{S-1},\quad \rho_t=\rho_t^S+\rho_t^F,\quad \rho_{12}=\rho_{12}^0J^{S-1},\quad \pi=\Pi_V J^{S-1},\qquad(653)$$

while the Cauchy stress tensors $\mathbf{T}^S, \mathbf{T}^F$ are given by the following constitutive relations

$$\mathbf{T}^S=J^{S-1}\mathbf{P}^S\mathbf{F}^{ST}=2\rho_t^S\left[\frac{\partial\psi^S}{\partial I}\mathbf{B}^S+\frac{\partial\psi^S}{\partial II}\left(I\mathbf{1}-\mathbf{B}^S\right)\mathbf{B}^S+\frac{\partial\psi^S}{\partial III}III\mathbf{1}\right]+\qquad(654)$$

$$+\beta\Delta_n\mathbf{1}-\mathfrak{z}\rho_{12}\left(\mathbf{v}^F-\mathbf{v}^S\right)\otimes\left(\mathbf{v}^F-\mathbf{v}^S\right),\quad \mathbf{B}^S=\mathbf{F}^S\mathbf{F}^{ST},$$

$$\begin{aligned}
\mathbf{T}^F&=J^{S-1}\mathbf{P}^F\mathbf{F}^{ST}=-p^F\mathbf{1}-\beta\Delta_n\mathbf{1}-(1-\mathfrak{z})\rho_{12}\left(\mathbf{v}^F-\mathbf{v}^S\right)\otimes\left(\mathbf{v}^F-\mathbf{v}^S\right)\\
p^F&=\rho_t^{F2}\frac{\partial\psi^F}{\partial\rho_t^F},
\end{aligned}\qquad(655)$$

with the free energy given by

$$\rho_t\psi = \rho_t^S\psi^S\left(T, I, II, III\right) + \rho_t^F\psi^F\left(T, \rho_t^F\right) - \rho_{12}\left(\mathbf{v}^F - \mathbf{v}^S\right)\cdot\left(\mathbf{v}^F - \mathbf{v}^S\right). \tag{656}$$

The energy ε and the energy flux vector $\mathbf{q}$ are given by

$$\varepsilon = \psi - T\frac{\partial\psi}{\partial T}, \quad \mathbf{q} = J^{S-1}\mathbf{F}^S\mathbf{Q} = J^{S-1}Q_V\left(\mathbf{v}^F - \mathbf{v}^S\right) - J^{S-1}K\operatorname{grad}T, \tag{657}$$

and the porosity flux has the form

$$\mathbf{j} = J^{S-1}\mathbf{F}^S\mathbf{J} = \Phi_0\left(\mathbf{v}^F - \mathbf{v}^S\right). \tag{658}$$

There remains the question of practical estimation of additional parameters ρ_{12}^0 and $\mathfrak{z}$. The added mass coefficient ρ_{12}^0 has been extensively studied in literature concerning Biot's model. The parameter $\mathfrak{z}$ is new. There seem to exist various possibilities for its estimation connected to the fact that it appears in contributions which may be time independent. As an example let us consider a stationary isothermal process in which, in a chosen inertial frame of reference, the skeleton does not move (i.e. $\mathbf{v}^S = 0$). Such a flow of the fluid through a porous material is described by the mass balance and by the momentum balance for the fluid. For simplicity we neglect changes of porosity. Then we have

$$\operatorname{div}\left(\rho_t^F\mathbf{v}^F\right) = 0, \tag{659}$$

$$\begin{aligned}\left[\rho_t^F + 2\left(1-\mathfrak{z}\right)\rho_{12}\right]\mathbf{v}^F\cdot\operatorname{grad}\mathbf{v}^F &= -\operatorname{grad}p^F - \left[\pi + \left(1-\mathfrak{z}\right)\rho_{12}\operatorname{div}\mathbf{v}^F\right]\mathbf{v}^F,\\ p^F &= p^F\left(\rho_t^F\right).\end{aligned}$$

The correction of the permeability coefficient π driven by volume changes of the fluid $\operatorname{div}\mathbf{v}^F$ seems to be very small. However the correction of mass density appearing on the left-hand side of this equation may be essential and measurable. For instance, in an irrotational flow ($\operatorname{rot}\mathbf{v}^F = 0$) we have approximately

$$\operatorname{grad}\left[n_0\left(p - p_0\right) + \frac{1}{2}\left(\rho_t^F + 2\left(1-\mathfrak{z}\right)\rho_{12}\right)\mathbf{v}^F\cdot\mathbf{v}^F\right] + \pi\mathbf{v}^F = 0, \tag{660}$$

where $p = p^F/n$ is the pore pressure and p_0 its constant reference value. If the pressure increment is of the order of, say, 10 kPa the velocity of the fluid must be of the order of 1 m/s to make both contributions of the similar order. Practically measurable would be the influence of $\mathfrak{z}$ for much smaller velocities which seem to be plausible at least for rocks.

We proceed to present basic results for the model which yields couplings not appearing in simple mixtures. As we have seen (Lecture 9), in order to obtain expected couplings between components the thermodynamics of miscible mixtures requires a dependence on gradients of mass densities. This indicates that such couplings are related to weak nonlocal interactions which are described in the simplest case by the second gradients of deformation[21]. In the case of porous materials it is sufficient to incorporate a dependence

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[21] Current partial mass densities ρ_t^α are described by volume changes, say for small deformations $\left(\rho_0^\alpha - \rho_t^\alpha\right)/\rho_0^\alpha$ which, in turn, are given by deformation gradients. Consequently, gradients of current mass densities describe a dependence on **second** gradients of deformation.

on the gradient of porosity. This does not mean that models with other second gradients are not meaningful but, of course, they are much more difficult to handle. For the purpose of construction of a linear model of Biot's type it is sufficient to add the variable $\mathbf{N} = \operatorname{Grad} n$. The set of unknown fields given by (589) remains the same, i.e.

$$\mathcal{V} := \left\{\rho^F, \acute{\mathbf{x}}^S, \acute{\mathbf{x}}^F, \mathbf{F}^S, T, n\right\} \quad \text{for} \quad (\mathbf{X}, t) \in \mathcal{B}_0 \times \mathcal{T}. \tag{661}$$

Also the set of balance equations (590)-(594) and the set of constitutive quantities $\mathcal{F}$ (596) do not change. There is a change in the set of constitutive variables in which we leave out the relative acceleration $\mathbf{a}_r$ but add $\mathbf{N}$. Hence, we have

$$\begin{aligned} \mathcal{C} \quad &: \;= \left\{\rho^F, \mathbf{F}^S, \acute{\mathbf{X}}^F, \Delta_n, T, \mathbf{G}, \mathbf{N}\right\}, \quad \mathbf{G} := \operatorname{Grad} T, \quad \mathbf{N} := \operatorname{Grad} n, \\ \mathcal{F} \quad &= \; \mathcal{F}(\mathcal{C}). \end{aligned} \tag{662}$$

We have to modify as well the simplifying assumptions. We replace the assumptions 5° and 6° by the following ones

5'° The dependence on the gradient of porosity $\mathbf{N}$ is linear.

6'° Higher order combinations of variables $\mathbf{G}, \acute{\mathbf{X}}^F, \Delta_n, \mathbf{N}$ can be neglected.

The analysis of the second law of thermodynamics reveals that the thermodynamical equilibrium is again defined by the relations

$$\mathbf{G}|_E = 0, \quad \acute{\mathbf{X}}^F\Big|_E = 0, \quad \boldsymbol{\Delta}_n|_E = 0. \tag{663}$$

Vector fluxes, instead of (604), and momentum sources, instead of (605), must have the form

$$\begin{aligned} \mathbf{Q} &= Q_V \acute{\mathbf{X}}^F - K\mathbf{G} + Q_N \mathbf{N}, \\ \mathbf{H} &= H_V \acute{\mathbf{X}}^F + H_T \mathbf{G} + H_N \mathbf{N}, \\ \mathbf{J} &= \Phi \acute{\mathbf{X}}^F + J_T \mathbf{G} + J_N \mathbf{N}, \end{aligned} \tag{664}$$

$$\mathbf{F}^{ST}\hat{\mathbf{p}} = \Pi_V \acute{\mathbf{X}}^F + \Pi_T \mathbf{G} + \Pi_N \mathbf{N}, \tag{665}$$

where the coefficients may be functions of the reduced set of constitutive variables

$$\mathcal{C}' := \left\{\mathbf{F}^S, T, \Delta_n\right\}. \tag{666}$$

The variables $\mathbf{F}^S, T$ characterize equilibrium processes (ρ^F in equilibrium is not independent due to the vanishing relative velocity $\acute{\mathbf{X}}^F\Big|_E = 0$). The dependence on the nonequilibrium variable Δ_n must be treated separately due to its scalar character.

The rest of the analysis is similar to this presented in the previous case. We skip it and present here only some final results for isotropic materials.

The Helmholtz free energy for this model has the following form

$$\rho\psi = \rho^S \psi^S + \rho^F \psi^F, \tag{667}$$

$$\psi^S = \psi^S\left(I, II, J^S, \rho_t^F, T, \Delta_n\right), \quad \psi^F = \psi^F\left(J^S, \rho_t^F, T, \Delta_n\right), \quad \rho_t^F = \rho^F J^{S-1}.$$

The partial Piola-Kirchhoff stress tensors are given by the relations

$$\begin{aligned}\mathbf{P}^F &= -\rho_t^{F2}\frac{\partial\psi^F}{\partial\rho_t^F}J^S\mathbf{F}^{S-T} - \Phi_0\rho\frac{\partial\psi^F}{\partial\Delta_n}J^S\mathbf{F}^{S-T}, \qquad (668)\\ \mathbf{P}^S &= \rho^S\frac{\partial\psi^S}{\partial\mathbf{F}^S} + \Phi_0\rho\frac{\partial\psi^F}{\partial\Delta_n}J^S\mathbf{F}^{S-T},\end{aligned}$$

while fluxes and sources satisfy the following constitutive relations

$$\begin{aligned}\mathbf{H} &= \frac{1}{T}\left(\mathbf{Q} - \boldsymbol{\rho}^F\psi^F\acute{\mathbf{X}}^F\right), \quad \mathbf{J} = \Phi_0 J^S\acute{\mathbf{X}}^F, \quad \Phi_0 = const.,\\ \hat{\mathbf{p}} &= \pi\mathbf{F}^S\acute{\mathbf{X}}^F - N\mathbf{F}^{S-1}\,\mathrm{Grad}\,n, \quad \hat{n} = -\frac{\Delta_n}{\tau}. \qquad (669)\end{aligned}$$

Consequently, in this model there exist equilibrium couplings of partial stresses through volume changes of components described by J^S and ρ_t^F as well as nonequilibrium couplings described by the dependence on Δ_n. In addition, there are couplings through the momentum source which are due to the diffusion velocity $\acute{\mathbf{X}}^F$ as well as the gradient of porosity $\mathrm{Grad}\,n$. In the next Lecture we show that linearization of this model leads to an extension of the classical Biot model of saturated porous materials.

Lecture 13: Linear models of saturated poroelastic materials

Linear modeling of two-component porous materials was primarily initiated by works in the field of soil mechanics. These were investigations of H. Darcy (1803-1858), K. Terzaghi (1883-1963), P. Fillunger (1883-1937), Y. I. Frenkel (1894-1952), M. A. Biot (1905-1985) and many others. The aim was to construct a description of the coupling between mechanical response of skeleton and flows of fluids through the channels of porous and granular materials. Early models were linear and quasistatic but at the end of 1930ies the problem of propagation of acoustic waves began to be investigated as well.

These linear models, in particular the so-called Biot model, describe the behavior of the following fields

1. Current *partial* mass densities, ρ_t^S, ρ_t^F or current *real* mass densities, ρ_t^{SR}, ρ_t^{FR}. The subscript t indicating the reference to the current location is usually dropped as in the linear model there is no distinction between Eulerian and Lagrangian description. Descriptions by either set of densities are equivalent if the porosity field n is incorporated: $\rho_t^S = (1-n)\,\rho_t^{SR}$, $\rho_t^F = n\rho_t^{FR}$.

2. The displacement of the skeleton, $\mathbf{u}^S$. Its derivative with respect to $\mathbf{x}$ defines the deformation tensor. In the linear theory this is Almansi-Hamel deformation tensor $\mathbf{e}^S$. The time derivative gives the velocity of the skeleton, $\mathbf{v}^S$. Volume changes are specified by the first invariant of Almansi-Hamel tensor, $e = \operatorname{tr}\mathbf{e}^S$. If there is no mass exchange between components this, in turn, determines uniquely changes of the partial mass density and the field of mass density ρ_t^S becomes superfluous

$$e = \frac{\rho_0^S - \rho_t^S}{\rho_0^S}, \quad |e| \ll 1, \tag{670}$$

where ρ_0^S is the initial value of the partial mass density, corresponding to $\mathbf{e}^S = 0$. This relation follows from the following identity (integrability condition)

$$\frac{\partial \mathbf{e}^S}{\partial t} = \operatorname{sym}\operatorname{grad}\mathbf{v}^S \quad \text{i.e.} \quad \frac{\partial e}{\partial t} = \operatorname{div}\mathbf{v}^S. \tag{671}$$

Therefore the mass balance equation yields

$$\frac{\partial \rho_t^S}{\partial t} + \operatorname{div}\left(\rho_t^S \mathbf{v}^S\right) \approx \frac{\partial \rho_t^S}{\partial t} + \rho_0^S \operatorname{div}\mathbf{v}^S = \frac{\partial}{\partial t}\left(\rho_t^S + \rho_0^S e\right) = 0. \tag{672}$$

Easy integration leads to (670).

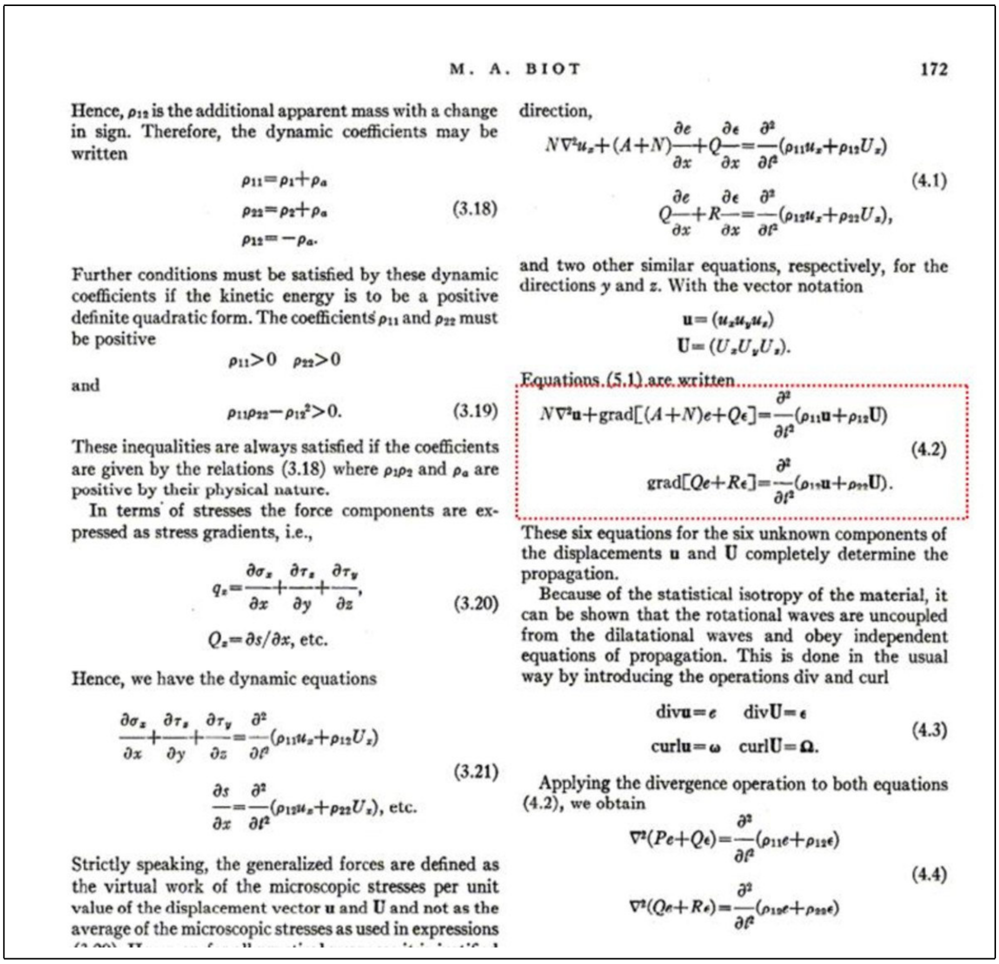
3. The velocity of the fluid, $\mathbf{v}^F$. It is customary in Biot's model to work with the displacement of the fluid, $\mathbf{U}$. However, as in the fluid mechanics in general, this quantity does not have any physical meaning and it is not sought in solving boundary value problems. It plays only an auxiliary role in the model and defines the velocity of the fluid $\mathbf{v}^F = \partial\mathbf{U}/\partial t$ as well as its volume

changes, $\varepsilon = \operatorname{div} \mathbf{U}$. As in the case of the skeleton, through the partial mass balance equation the latter determines uniquely changes of the partial mass density, ρ_t^F, if there is no mass exchange between components

$$\varepsilon = \frac{\rho_0^F - \rho_t^F}{\rho_0^F}, \quad \frac{\partial \varepsilon}{\partial t} = \operatorname{div} \mathbf{v}^F, \quad |\varepsilon| \ll 1, \tag{673}$$

where ρ_0^F is the initial value of the fluid partial mass density. Derivation is analogous to that presented above for the skeleton.

4. The porosity n (denoted by ϕ in many works on Biot's model). In Biot's model this quantity does not appear in the explicit form. However, its changes can be calculated in terms of volume changes of both components and material parameters (compressibilities) appearing in the model. Hence, even though not constant, the porosity is not listed among fields of Biot's model.



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Hence, ρ_{12} is the additional apparent mass with a change in sign. Therefore, the dynamic coefficients may be written

$$\begin{aligned} \rho_{11} &= \rho_1 + \rho_a \\ \rho_{22} &= \rho_2 + \rho_a \\ \rho_{12} &= -\rho_a. \end{aligned} \tag{3.18}$$

Further conditions must be satisfied by these dynamic coefficients if the kinetic energy is to be a positive definite quadratic form. The coefficients ρ_{11} and ρ_{22} must be positive

$$\rho_{11} > 0 \quad \rho_{22} > 0$$

and

$$\rho_{11}\rho_{22} - \rho_{12}^2 > 0. \tag{3.19}$$

These inequalities are always satisfied if the coefficients are given by the relations (3.18) where $\rho_1 \rho_2$ and ρ_a are positive by their physical nature.

In terms of stresses the force components are expressed as stress gradients, i.e.,

$$\begin{aligned} q_x &= \frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau_z}{\partial y} + \frac{\partial \tau_y}{\partial z}, \\ Q_x &= \partial s / \partial x, \text{ etc.} \end{aligned} \tag{3.20}$$

Hence, we have the dynamic equations

$$\begin{aligned} \frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau_z}{\partial y} + \frac{\partial \tau_y}{\partial z} &= \frac{\partial^2}{\partial t^2}(\rho_{11} u_x + \rho_{12} U_x) \\ \frac{\partial s}{\partial x} &= \frac{\partial^2}{\partial t^2}(\rho_{12} u_x + \rho_{22} U_x), \text{ etc.} \end{aligned} \tag{3.21}$$

Strictly speaking, the generalized forces are defined as the virtual work of the microscopic stresses per unit value of the displacement vector **u** and **U** and not as the average of the microscopic stresses as used in expressions

direction,

$$\begin{aligned} N \nabla^2 u_x + (A+N) \frac{\partial e}{\partial x} + Q \frac{\partial \epsilon}{\partial x} &= \frac{\partial^2}{\partial t^2}(\rho_{11} u_x + \rho_{12} U_x) \\ Q \frac{\partial e}{\partial x} + R \frac{\partial \epsilon}{\partial x} &= \frac{\partial^2}{\partial t^2}(\rho_{12} u_x + \rho_{22} U_x), \end{aligned} \tag{4.1}$$

and two other similar equations, respectively, for the directions y and z. With the vector notation

$$\begin{aligned} \mathbf{u} &= (u_x u_y u_z) \\ \mathbf{U} &= (U_x U_y U_z). \end{aligned}$$

Equations (5.1) are written

$$\begin{aligned} N \nabla^2 \mathbf{u} + \operatorname{grad}[(A+N)e + Q\epsilon] &= \frac{\partial^2}{\partial t^2}(\rho_{11} \mathbf{u} + \rho_{12} \mathbf{U}) \\ \operatorname{grad}[Qe + R\epsilon] &= \frac{\partial^2}{\partial t^2}(\rho_{12} \mathbf{u} + \rho_{22} \mathbf{U}). \end{aligned} \tag{4.2}$$

These six equations for the six unknown components of the displacements **u** and **U** completely determine the propagation.

Because of the statistical isotropy of the material, it can be shown that the rotational waves are uncoupled from the dilatational waves and obey independent equations of propagation. This is done in the usual way by introducing the operations div and curl

$$\begin{aligned} \operatorname{div} \mathbf{u} = e &\quad \operatorname{div} \mathbf{U} = \epsilon \\ \operatorname{curl} \mathbf{u} = \boldsymbol{\omega} &\quad \operatorname{curl} \mathbf{U} = \boldsymbol{\Omega}. \end{aligned} \tag{4.3}$$

Applying the divergence operation to both equations (4.2), we obtain

$$\begin{aligned} \nabla^2(Pe + Q\epsilon) &= \frac{\partial^2}{\partial t^2}(\rho_{11} e + \rho_{12} \epsilon) \\ \nabla^2(Qe + R\epsilon) &= \frac{\partial^2}{\partial t^2}(\rho_{12} e + \rho_{22} \epsilon) \end{aligned} \tag{4.4}$$

Fig.13: *Quotation from the paper of* M. A. Biot*: Theory of Propagation of Elastic Waves in a Fluid-Saturated Porous Solid. I. Low-Frequency Range,* JASA, **28**, 168-178, 1956.

5. The temperature T does not appear in Biot's model. Processes are assumed to be isothermal. This assumption may be a good approximation in description

> of soils and rocks saturated by water, oil or other similar fluids. However, it does not seem to be appropriate for acoustics of porous materials saturated by a gas in which sound propagates rather in adiabatic conditions. This is, for instance, the case in foams damping the noise.

M. A. Biot wrote equations of his model in the form of an extension of displacement equations of the classical theory of isotropic elasticity. In Figure 13, we reproduce the page of the paper of M. A. Biot from 1956 in which the governing equations (4.2) of his model appear.

Biot himself was frequently changing the notation. In the version presented in the Figure, the model contains the constant material parameters A, N $(= \mu^S$ – shear modulus) which describe effective (macroscopic, depending on an initial porosity n_0) elastic properties of the skeleton (solid component), and related to, for instance, Lamé coefficients, λ, μ, the parameter R describes the effective (macroscopic) compressibility of the fluid, Q is the effective coupling parameter, characteristic for Biot's model, and ρ_{12} describes the coupling through the relative accelerations and it is usually attributed to the so-called added mass effect. The Biot model in this form is until today the most frequently used model for the investigation of acoustic properties of porous materials.

In some of his works M. Biot uses also the *increment of fluid contents,* ζ, as a field replacing volume changes of the fluid, ε. This field is defined in the following way

$$\zeta = n_0 \left(e - \varepsilon \right) \equiv n_0 \operatorname{div} \left(\mathbf{u} - \mathbf{U} \right). \qquad (674)$$

The latter relation yields an important conclusion

$$\frac{\partial \zeta}{\partial t} = n_0 \operatorname{div} \left(\mathbf{v}^S - \mathbf{v}^F \right). \qquad (675)$$

Hence the field ζ cannot change without diffusion: there must be a relative motion of components in order to change the fluid contents. However, it means as well that changes of fluid contents cannot appear in thermodynamical equilibrium processes. This conclusion has the paramount consequences for the applicability of variational methods in the theory of poroelastic materials. It indicates that, in spite of such frequent statements in the literature, the true variational principle for porous materials cannot be introduced and only the so-called pseudovariational method can be applied. This means that the so-called action functional does not exist and one may only construct variations as nonintegrable differential forms.

We proceed to derive field equations of the linear model on the basis of nonlinear models discussed in the previous Lecture. As usual we follow the thermodynamical strategy and construct these equations on the basis of balance equations.

In an inertial reference system the partial momentum balance equations have the following linearized form

$$\rho_0^S \frac{\partial \mathbf{v}^S}{\partial t} = \operatorname{div} \mathbf{T}^S + \rho_0^S \mathbf{b}^S + \hat{\mathbf{p}}, \quad \rho_0^F \frac{\partial \mathbf{v}^F}{\partial t} = - \operatorname{grad} p^F + \rho_0^F \mathbf{b}^F - \hat{\mathbf{p}}, \qquad (676)$$

where the current mass densities are replaced by their reference values, convective parts of momentum fluxes (i.e. div $\left(\rho^S \mathbf{v}^S \otimes \mathbf{v}^S \right)$ and div $\left(\rho^F \mathbf{v}^F \otimes \mathbf{v}^F \right)$, respectively) are neglected and it is assumed that the partial stress tensor in the fluid reduces to the partial pressure p^F. This coincides with the nonlinear result (668) under constitutive assumptions presented in the previous Lecture.

The first two simplifications follow from the linearization, while the last one means that we consider the fluid component to be ideal on the macroscopic level of description. This does not have to be the case for the true fluid whose viscosity appears in the microstructural relation for momentum source $\hat{\mathbf{p}}$. We return further to this relation.

The quantities $\rho_0^S \mathbf{b}^S, \rho_0^F \mathbf{b}^F$ are partial external body forces per unit volume.

Frequently the partial description of momentum is replaced by the bulk momentum and only one of the partial momenta. It is usually the partial momentum balance for the fluid because in some cases of practical bearing the inertial force of the fluid can be neglected and this momentum balance yields then a generalization of Darcy's law. The bulk momentum balance which is the sum of partial equations has the form

$$\rho_0 \frac{\partial \mathbf{v}}{\partial t} = \operatorname{div} \mathbf{T} + \rho_0 \mathbf{b}, \tag{677}$$

where

$$\begin{aligned} \mathbf{T} &\approx \mathbf{T}^S - p^F \mathbf{1}, \quad \rho_0 = \rho_0^S + \rho_0^F, \\ \rho_0 \mathbf{v} &= \rho_0^S \mathbf{v}^S + \rho_0^F \mathbf{v}^F, \quad \rho_0 \mathbf{b} = \rho_0^S \mathbf{b}^S + \rho_0^F \mathbf{b}^F. \end{aligned} \tag{678}$$

Obviously, $\mathbf{T}$ denotes the bulk stress tensor and $\mathbf{v}$ is the so-called barycentric velocity. The latter is not a very useful field because it does not have any global physical interpretation: Diffusion separates particles of components after a finite time so much that one cannot define any reasonable collection of centers of gravity. However, in some quasistatic problems the bulk momentum balance equation may be very useful. It appears, for instance, in the theory of plastic deformations of soils in which the bulk stress tensor plays an important role.

The above structure of momentum balance shows that the partial stress tensor in the skeleton cannot be usually identified with the so-called effective stresses introduced to soil mechanics by Terzaghi. The partial pressure in the fluid p^F is in many cases related to the so-called *pore pressure*, p, by the relation $p^F = np$, where n is the current porosity.

The balance equation of porosity in the simplest case of large relaxation times ($\tau \longrightarrow \infty$, i.e. $\hat{n} = -\frac{\Delta_n}{\tau} \longrightarrow 0$) for linear isotropic case has the following form

$$\frac{\partial \Delta_n}{\partial t} + \Phi \operatorname{div}\left(\mathbf{v}^F - \mathbf{v}^S\right) = 0, \quad \Delta_n = n - n_E, \quad n_E = n_0\left(1 + \delta e\right), \tag{679}$$

where δ, Φ are material parameters dependent on n_0. The lack of relaxation properties of porosity is the common assumption in geotechnical applications. It is not so obvious in applications to biomechanics, description of tissues, etc.

The above equation has the following solution

$$n = n_0 \left[1 + \delta e + \frac{\Phi}{n_0}\left(e - \varepsilon\right)\right], \tag{680}$$

Such changes of porosity are always present in Biot's model but not stated explicitly. The reason is that porosity in Biot's model is not an *independent* field. According to (680), it is given in terms of volumetric strains of both components, e, ε, and the material parameters required by the above equation, δ, Φ, follow from material parameters present in the model (no additional material parameters for porosity!).

In order to construct field equations by means of the above balance equations we need in general constitutive relations for the following *constitutive quantities*

$$\left\{\mathbf{T}^S, \mathbf{T}^F, \hat{\mathbf{p}}, \mathbf{J}, n_E, \hat{n}\right\}. \tag{681}$$

We have indicated already some simplifications in this set. Instead of the tensor $\mathbf{T}^F$ we need a constitutive relation only for the partial pressure p^F. For the flux of porosity $\mathbf{J}$ and the equilibrium porosity n_E the constitutive assumptions are already incorporated in the porosity balance equation (679). Consequently, in order to close the system we need constitutive relations of the form

$$\begin{aligned} \mathbf{T}^S &= \mathbf{T}^S\left(\mathbf{e}^S, \varepsilon, \Delta_n, \mathbf{v}^F - \mathbf{v}^S, \mathbf{a}_r, \operatorname{grad} n\right), \\ p^F &= p^F\left(\mathbf{e}^S, \varepsilon, \Delta_n, \mathbf{v}^F - \mathbf{v}^S, \mathbf{a}_r, \operatorname{grad} n\right), \end{aligned} \tag{682}$$

and for the momentum source which we present in a linear form with respect to vectorial variables (comp. the combination of (605), (669) in the nonlinear isothermal case)

$$\hat{\mathbf{p}} = \hat{\mathbf{p}}_{diff} - N \operatorname{grad} n - \rho_{12}\mathbf{a}_r, \tag{683}$$

where $\hat{\mathbf{p}}_{diff}$ is the part determined by the relative velocity $\mathbf{v}^F - \mathbf{v}^S$, N is a material parameter. In the simplest case $\hat{\mathbf{p}}_{diff} = \pi\left(\mathbf{v}^F - \mathbf{v}^S\right)$, where π is the constant permeability coefficient.

For the purpose of construction of Biot's model we can leave out the dependence on Δ_n. This assumption is not necessary for the linearity of the model and some wave problems have been already investigated with an influence of Δ_n. It has been found that this influence is indeed very small. The lack of dependence on $\operatorname{grad} n$ would yield the following result (see: (654), (655) & (656))

$$\mathbf{T}^S = \mathbf{T}^S\left(\mathbf{e}^S\right), \quad p^F = p^F(\varepsilon). \tag{684}$$

This is the *simple mixture* model whose linearization yields Biot's constitutive relations for stresses with $Q = 0$. As shown in the previous Lecture for the nonlinear model this fault of the model can be removed. Essential is the constitutive dependence on $\operatorname{grad} n$ which yields the possibility of coupling proposed by Biot.

In the linear model which follows from (682) and (683) we obtain the following relations for partial stresses

$$\begin{aligned} \mathbf{T}^S &= \mathbf{T}_0^S + \lambda^S e\mathbf{1} + 2\mu^S\mathbf{e}^S + Q\varepsilon\mathbf{1} - N(n - n_0)\mathbf{1}, \\ p^F &= p_0^F - \rho_0^F\kappa\varepsilon - Qe - N(n - n_0), \end{aligned} \tag{685}$$

where n_0 is a constant reference value of porosity, $\lambda^S, \mu^S, \kappa, Q, N$ are material parameters which depend on the reference value of porosity, n_0. We have incorporated in stresses the contribution of $\operatorname{grad} n$ appearing in the momentum source $\hat{\mathbf{p}}$. This is possible for a constant coefficient N which is the case in the linear model.

Bearing the above relations in mind we see that the set of balance equations (671), (673), (676), (679), i.e. two scalar, two vector and one tensor equations form the set of field equations for the fields $\left\{\mathbf{e}^S, \varepsilon, n, \mathbf{v}^S, \mathbf{v}^F\right\}$. Clearly, if we introduce the displacement vector $\mathbf{u}^S$ then we can skip the tensor equation for $\mathbf{e}^S$ and the momentum balance equation for the skeleton becomes the second order equation for this displacement.

Consequently, the model is determined by the following set of material parameters

$$\left\{\lambda^S, \mu^S, \rho_0^F \kappa, Q, \delta, \Phi, n_0; N, \pi, \rho_{12}\right\}. \tag{686}$$

The second group contains the parameter N which is additional to the set proposed by Biot and two parameters π, ρ_{12} which describe an influence of relative motion of components.

This set may be still reduced to a smaller and more fundamental set and we present further a procedure which yields this reduction. We should also mention that the constant permeability coefficient π has been found not appropriate in the description of acoustic waves. Measurements for monochromatic waves indicate that it should be frequency-dependent. Such a dependence has been already suggested by Biot who proposed a correction following from a microstructural estimates. The problem is that the correction of equations by introducing the frequency dependent complex permeability as suggested by Biot and many others, say in the form $\pi F(\omega)$, is mathematically nonsensical. After such a correction solutions of the equations of motion would have to be complex. In addition, functions appearing in these equations are defined on different spaces: some of them are time-dependent and some other frequency-dependent and this is, of course, mathematically not correct. Papers concerning this subject avoid the problem by writing Fourier transforms in which the variable of Fourier transformation is identified with the frequency appearing in F.

The above remarks indicate the necessity of a correction in the formulation of the problem and this, as a matter of fact, was already suggested by Biot himself. Namely, the influence of relative velocities in the macroscopic model should have a form reflecting viscous-like effects following from obstacles for the motion of the real fluid in channels. It means that, similarly to viscoelastic materials, one should expect a kind of hereditary integral describing the momentum source.

In spite of their practical importance explicit relations for the bulk permeability π are not needed in the macroscopic construction of such a model. They may be adjusted to experiments or selected by means of some analysis of microstructure in particular problems. It is only essential in the linear model to account for their changes in time as a dynamic process goes on. This can be done in the same way as it is done for viscoelastic properties of solids. We proceed to construct such a model of momentum sources.

First of all, as it was pointed out, the second law of thermodynamics indicates the following dissipation inequality

$$\hat{\mathbf{p}}_{diff} \cdot \mathbf{w} \geq 0, \quad \mathbf{w} := \mathbf{v}^F - \mathbf{v}^S. \tag{687}$$

Consequently, $\hat{\mathbf{p}}_{diff}$ must be odd in the relative velocity. Within a linear model of isotropic materials it has then the following form for a *constant* relative velocity $\mathbf{w}$

$$\hat{\mathbf{p}}_{diff}(\mathbf{w}, t) = \pi(t)\, \mathbf{w}, \tag{688}$$

which indicates a smallness of the relative velocity. Knowledge of this single-step response function $\pi(t)$ is sufficient to predict an output $\hat{\mathbf{p}}_{diff}$ for an arbitrary constant input $\mathbf{w}$. Let us note that the time dependence of the permeability coefficient π should be invariant with respect to the translation of the origin of time axis. This means that t is the time lag since application of the constant relative velocity $\mathbf{w}$. An input $\mathbf{w}(t) = \mathbf{w}_0 H(t - t_0)$, where $H(t - t_0)$ is the Heaviside function would lead to the output $\hat{\mathbf{p}}_{diff} = \boldsymbol{\pi}(t - t_0)\mathbf{w}_0$. Consequently, for the two-step history

$$\mathbf{w}(t) = H(t - t_1)\Delta\mathbf{w}_1 + H(t - t_2)\Delta\mathbf{w}_2, \tag{689}$$

the output must have the following form

$$\hat{\mathbf{p}}_{diff}(t) = \pi_1(t, t_1, t_2)\Delta\mathbf{w}_1 + \pi_2(t, t_1, t_2)\Delta\mathbf{w}_2. \tag{690}$$

This expression is valid for all constant increments of the relative velocity. Hence, it holds in particular for $\Delta\mathbf{w}_2 = 0$. Then the momentum source must be $\pi(t - t_1)\Delta\mathbf{w}_1$. In the same way we identify the second contribution and it follows

$$\mathbf{w}(t) = \sum_{\alpha=1}^{2} H(t - t_\alpha)\Delta\mathbf{w}_\alpha \quad \Longrightarrow \quad \hat{\mathbf{p}}_{diff}(t) = \sum_{\alpha=1}^{2} \pi_\alpha(t - t_\alpha)\Delta\mathbf{w}_\alpha. \tag{691}$$

Certainly, the same argument applies for an arbitrary number of steps. In rheology this is called *Boltzmann's superposition principle*. By means of some continuity assumptions which are similar to these of the theory of viscoelasticity we can approximate by step history the response to an arbitrary integrable history of the relative velocity. We have then

$$\mathbf{w}(t) = \int_{-\infty}^{t} H(t - s)\, d\mathbf{w}(s) \quad \Longrightarrow \quad \hat{\mathbf{p}}_{diff}(t) = \int_{-\infty}^{t} \pi(t - s)\, d\mathbf{w}(s). \tag{692}$$

As we assume the invariance with respect to the translation the initial point of the relative motion can be chosen arbitrarily. Therefore it is convenient to set the lower limit of integration at $-\infty$.

Integration by parts and the change of variables yields

$$\hat{\mathbf{p}}_{diff}(t) = \pi(0)\mathbf{w}(t) + \int_{0}^{\infty} \dot{\pi}(s)\mathbf{w}(t - s)\, ds, \quad \dot{\pi}(s) := \frac{\partial \pi}{\partial s}. \tag{693}$$

This constitutive relation contains the memory functional typical for viscous effect. The instantaneous reaction is characterized by the initial permeability $\pi(0)$. We demonstrate here only some simple properties of the above relation but it is obvious that the relation for the momentum source can be easily extended on nonlinear models. Such extensions are known for memory materials and we shall not present any details in this Lecture.

Let us write the relation (693) for the harmonic disturbance of the frequency ω. We obtain immediately

$$\begin{aligned} \mathbf{w} \quad &= \quad \mathbf{w}^*(\mathbf{x})\, e^{-i\omega t}, \quad \hat{\mathbf{p}}_{diff} = \hat{\mathbf{p}}^*_{diff}(\mathbf{x})\, e^{-i\omega t} \quad \Longrightarrow \\ &\Longrightarrow \quad \hat{\mathbf{p}}^*_{diff} = \left(-i\omega \frac{1}{\pi(0)} \int_0^\infty \pi(s)\, e^{i\omega s} ds\right) \pi(0)\, \mathbf{w}^*. \end{aligned} \tag{694}$$

The transform of permeability coefficient in the parenthesis can be now identified with the relation $F(\omega)\pi(0)$ proposed for the permeability as a function of frequency. This contribution appears in Fourier transformed momentum balance equations rather than in the original momentum balance equations which hold for an arbitrary time dependent input.

The above hereditary form of the momentum source is, as already indicated, attributed to viscosity of the true fluid and to the tortuosity. However, the influence of tortuosity is assumed to lead also to the added mass effect and, consequently, to the nondiagonal form of the matrix of mass densities. This yields contributions of the relative accelerations which were discussed in the previous Lecture. We return to this interpretation of the added mass in the next Lecture on monochromatic waves.

This completes the general remarks on the construction of a two-component model for poroelastic materials. However, we demonstrate here additionally a procedure of identification of some effective materials parameters for linear poroelastic materials which seems to be rather unique in the transition from semimacroscopic to macroscopic description. This procedure has been initiated by works of Gassmann in 1951 and developed by M. A. Biot and D. G. Willis in 1957.

Before we proceed to discuss this procedure we quote here another form of Biot's constitutive relations which possesses a particular practical bearing. First of all, we can use the variable ζ, the increment of fluid contents, instead of the volume change of fluid, ε. Then the relations for the bulk stress $\mathbf{T}$ and the pore pressure p have the form

$$\mathbf{T} \approx \mathbf{T}^S + \mathbf{T}^F = \mathbf{T}_0 + \left(\lambda^S + \rho_0^F \kappa + 2Q\right) e\mathbf{1} + 2\mu^S \mathbf{e}^S - \frac{Q + \rho_0^F \kappa}{n_0}\zeta\mathbf{1},$$

$$\mathbf{T}_0 = \mathbf{T}_0^S - p_0^F \mathbf{1},$$

$$p = \frac{1}{n}p^F \approx \frac{1}{n_0}\left(1 - \frac{n-n_0}{n_0}\right)\left[n_0 p_0 - \left(Q + \rho_0^F\kappa\right)e + \frac{\rho_0^F\kappa}{n_0}\zeta\right], \quad p_0 = \frac{p_0^F}{n_0}, \tag{695}$$

and changes of porosity are given by the following relation

$$\frac{n-n_0}{n_0} = \delta e + \frac{\Phi}{n_0^2}\zeta. \tag{696}$$

If the initial pore pressure p_0 is much smaller than material parameters $\frac{Q+\rho_0^F\kappa}{n_0}, \frac{\rho_0^F\kappa}{n_0^2}$ then we can neglect the contribution following from changes of porosity. We obtain finally

$$\mathbf{T} = \mathbf{T}_0 + Ke\mathbf{1} + 2G\,\mathrm{dev}\,\mathbf{e}^S - C\zeta\mathbf{1}, \quad \mathrm{dev}\,\mathbf{e}^S = \mathbf{e}^S - \tfrac{1}{3}e\mathbf{1}, \tag{697}$$

$$K = \lambda^S + \tfrac{2}{3}\mu^S + \rho_0^F\kappa + 2Q, \quad C = \frac{Q+\rho_0^F\kappa}{n_0}, \quad G = \mu^S,$$

$$p = p_0 - Ce + M\zeta, \quad M = \frac{\rho_0^F\kappa}{n_0^2}. \tag{698}$$

This form shows clearly that stresses consist of equilibrium parts given by the deformation $\mathbf{e}^S$ and nonequilibrium parts containing ζ. The set of parameters

$$\{K, G, M, C, \delta, \Phi, n_0; N, \pi, \rho_{12}\} \tag{699}$$

replaces the set (686).

We apply these relations to some simple static processes in granular materials. These processes yield solely purely volumetric deformations. For such processes we introduce a procedure stemming from the averaging method over a representative elementary volume

(REV) which yields relations between $\lambda^S + \frac{2}{3}\mu^S$ or K, $\rho_0^F\kappa$, or M, Q or C, and N, δ, Φ on the one hand-side and true compressibilities of substances, K_s, K_f of the solid frame and fluid components, respectively, the initial porosity, n_0 and the undrained compressibility modulus K_d on the other hand. Certainly, any other combination of macroscopic parameters can be then also easily calculated. The compressibilities K_s, K_f are measured in experiments on the substance of the skeleton and on the fluid outside porous materials and they are, of course, independent of any particular morphology of the porous material. Simultaneously, the modulus K_d is measured in very simple undrained compression experiments and is used in soil mechanics on the equal footing with the true compressibilities.

Description of granular materials by means of a macroscopic model is particularly easy when a deformation is homogeneous, spherically symmetric and the mechanical reactions of the system reduce to pressures. Such a system will be now considered.

For such a deformation, we have

$$\mathbf{e}^S = \tfrac{1}{3}e\mathbf{1}, \quad p^S = -\tfrac{1}{3}\operatorname{tr}\mathbf{T}^S, \quad p^F = -\tfrac{1}{3}\operatorname{tr}\mathbf{T}^F, \tag{700}$$

and the *macroscopic constitutive relations* for partial pressures are as follows (comp. (685))

$$\begin{aligned} p^S - p_0^S &= -\left(\lambda^S + \tfrac{2}{3}\mu^S\right)e - Q\varepsilon + N\left(n - n_0\right), \\ p^F - p_0^F &= -\rho_0^F\kappa\varepsilon - Qe - N\left(n - n_0\right). \end{aligned} \tag{701}$$

For porosity changes we have (see: (680))

$$\frac{n - n_0}{n_0} = \delta e + \frac{\Phi}{n_0}\left(e - \varepsilon\right), \tag{702}$$

Momentum balance equations are in the homogeneous equilibrium identically satisfied. External loading is applied through the boundary. Hence, in the static case we have the *equilibrium condition of* the full pressure change with a given excess (external) pressure Δp, i.e.

$$\Delta p = \left(p^S - p_0^S\right) + \left(p^F - p_0^F\right). \tag{703}$$

In order to solve the problem, i.e. to find five quantities $e, \varepsilon, p^S - p_0^S, p^F - p_0^F, n$ for a given excess pressure Δp we need, in addition to the above four equations (701), (702), (703), another boundary condition. This will be specified later for three different problems which we call *gedankenexperiments.*

However, this simple linear problem can be also formulated in terms of semimacroscopic quantities e^R, ε^R, $p^{SR} - p_0^{SR}$, $p^{FR} - p_0^{FR}$ and n. The first two quantities describe real volume changes of the solid material and of the fluid, respectively, and they are related to the real mass densities ρ^{SR}, ρ^{FR} by relations analogous to (670) and (673), i.e.

$$e^R = \frac{\rho_0^{SR} - \rho^{SR}}{\rho_0^{SR}}, \quad \varepsilon^R = \frac{\rho_0^{FR} - \rho^{FR}}{\rho_0^{FR}}. \tag{704}$$

The constitutive relations on this level are very simple

$$p^{SR} - p_0^{SR} = -K_s e^R, \quad p^{FR} - p_0^{FR} = -K_f \varepsilon^R. \tag{705}$$

The construction of the boundary condition requires an assumption which we justify in the next Lecture. Namely, it must be assumed that surface contributions of components to the common traction is given by the porosity. We have then

$$\begin{aligned} p^S &= (1-n)\,p^{SR}, \quad p_0^S = (1-n_0)\,p_0^{SR}, \\ p^F &= np^{FR}, \quad p_0^F = n_0 p_0^{FR}, \end{aligned} \tag{706}$$

i.e.

$$\begin{aligned} p^S - p_0^S &= (1-n_0)\left(p^{SR} - p_0^{SR}\right) - \frac{n-n_0}{n_0} n_0 p_0^{SR} \approx (1-n_0)\left(p^{SR} - p_0^{SR}\right), \\ p^F - p_0^F &= n_0\left(p^{FR} - p_0^{FR}\right) + \frac{n-n_0}{n_0} n_0 p_0^{FR} \approx n_0\left(p^{FR} - p_0^{FR}\right). \end{aligned} \tag{707}$$

Then the condition (703) becomes

$$\begin{aligned} \Delta p &= \left((1-n)\,p^{SR} - (1-n_0)\,p_0^{SR}\right) + \left(np^{FR} - n_0 p_0^{FR}\right) = \\ &= (1-n)\left(p^{SR} - p_0^{SR}\right) + n\left(p^{FR} - p_0^{FR}\right) - (n-n_0)\left(p_0^{SR} - p_0^{FR}\right). \end{aligned} \tag{708}$$

The last contribution vanishes if we assume that the initial state is self-equilibrated on the semimacroscopic level, i.e. $p_0^{SR} = p_0^{FR}$. The unknown five quantities of the semimacroscopic description $e^R, \varepsilon^R, p^{SR} - p_0^{SR}, p^{FR} - p_0^{FR}, n$ can be determined from (702), (705), (708), provided, as in the macroscopic description, we formulate an additional boundary condition.

However, we still have at the disposal relations between macroscopic and semimacroscopic description. These are two dynamical compatibility relations (707) and the following geometrical compatibility relations

$$\begin{aligned} e &= \frac{\rho_0^S - \rho^S}{\rho_0^S} = \frac{(1-n_0)\,\rho_0^{SR} - (1-n)\,\rho^{SR}}{(1-n_0)\,\rho_0^{SR}} \approx e^R + \frac{n-n_0}{1-n_0}, \\ \varepsilon &= \frac{\rho_0^F - \rho^F}{\rho_0^F} = \frac{n_0\rho_0^{FR} - n\rho^{FR}}{n_0\rho_0^{FR}} \approx \varepsilon^R - \frac{n-n_0}{n_0}. \end{aligned} \tag{709}$$

If we collect all above equations, we obtain 1 equilibrium condition (703), 1 equation for porosity (702), two macroscopic constitutive relations (701), two semimacroscopic constitutive relations (705), two dynamical compatibility conditions (707) and two geometrical compatibility conditions (709). Additionally, we expect one additional boundary condition for each gedankenexperiment we construct. We shall see that there are three such experiments in the model we are considering. Consequently, we have 13 equations. We assume as well that material parameters K_s, K_f, K_d are given.

Simultaneously, we have five geometrical unknowns, $e, \varepsilon, e^R, \varepsilon^R, n,$ four dynamical unknowns, $p^S - p_0^S, p^F - p_0^F, p^{SR} - p_0^{SR}, p^{FR} - p_0^{FR}$ and the following six macroscopic material parameters: K, M, C, N, δ, Φ. All together these are 15 quantities. This means that we can find solutions of all three problems in terms of the excess pressure Δp and, additionally, if we eliminate Δp we obtain relations between the set of six material parameters and three known parameters K_s, K_f, K_d and the initial porosity n_0.

Three gedankenexperiments were described by Biot and Willis. They are called: 1^0 *jacketed undrained,* 2^0 *jacketed drained* and 3^0 *unjacketed* and they are schematically shown in Figure 14.

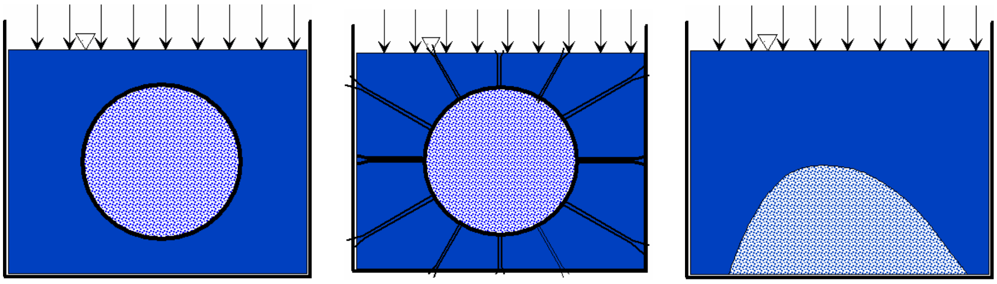

Fig. 14: *Schemes of Gedankenexperiments: 1) jacketed undrained, 2) jacketed drained, 3) unjacketed.*

In experiment 1), the granular material is contained in the impermeable spherical jacket which is assumed to be ideal, i.e. it does not contribute to the balance of forces in the system. In experiment 2), the jacket is permeable, i.e. the pipes may supply or drain the fluid from the sample. In experiment 3) a heap of the granular material is in contact with the fluid in the container.

These experiments are called *gedankenexperiments* (*ger.* =thought experiment) because they are in principle possible but in their evaluation we have to neglect many effects such as saturation and surface tension, nonisothermal character, boundary layers, flows and viscosity, etc.

The conditions which describe them are as follows:

$$1^0 : \zeta = 0, \quad 2^0 : p^{FR} = p_0^{FR}, \quad 3^0 : p^{FR} - p_0^{FR} = \Delta p. \tag{710}$$

We shall not present here the full analysis of the problem. It can be shown that it has two distinct real solutions. One of them possesses $N \neq 0$, in the other one $N = 0$. In the latter case we can construct the solution in the closed form. The formulae for the material parameters are then called the *Gassmann relations* and they have the following form

$$K = \frac{(K_s - K_d)^2}{\frac{K_s^2}{K_W} - K_d} + K_d, \quad C = \frac{K_s (K_s - K_d)}{\frac{K_s^2}{K_W} - K_d}, \quad M = \frac{K_s^2}{\frac{K_s^2}{K_W} - K_d}. \tag{711}$$

where

$$\frac{1}{K_W} := \frac{1 - n_0}{K_s} + \frac{n_0}{K_f}. \tag{712}$$

Simultaneously, for parameters describing changes of porosity it follows

$$\delta = \frac{K_V - K}{n_0 (K_s - K_f)}, \quad \Phi = \frac{n_0 C - n_0 K_f}{K_s - K_f}, \tag{713}$$

where

$$K_V := (1 - n_0) K_s + n_0 K_f, \tag{714}$$

and K and C are given by (711).

Below we present the numerical results for the relations between material parameters. We show in Figures 15 and 16 the macroscopic parameters as functions of the porosity n_0. The following relations were used in these calculations

$$K_s = 48 \times 10^9 Pa, \quad K_f = 2.25 \times 10^9 Pa, \quad K_d = \frac{K_s}{1 + g n_0}. \tag{715}$$

The values of compressibilities K_s and K_f are typical – the first one for the sandstone, the second one for water. The last relation is called the *Geertsma equation* and it specifies K_d in function of the empirical parameter g. The typical value of g for rocks is 50.

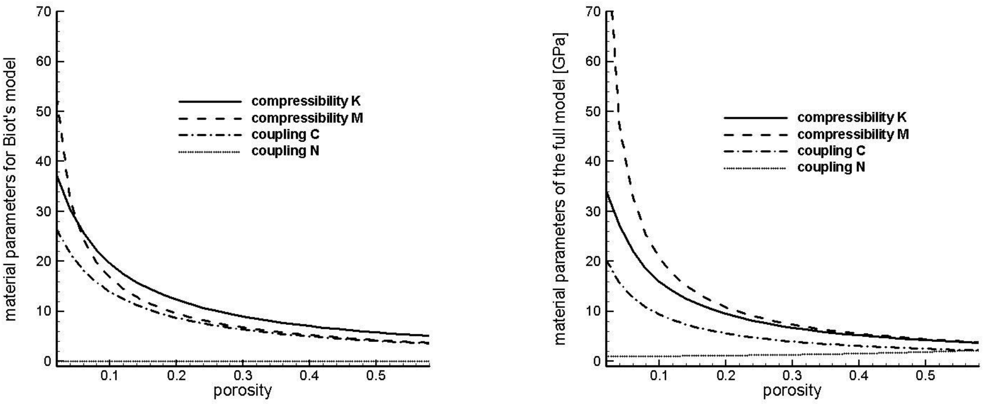

Fig. 15: *Comparison of material parameters for Biot's model (the left panel) and the full model with the porosity gradient (the right panel) with Geertsma parameter* $g = 50$.

It is seen that the compressibility $K = \lambda^S + \frac{2}{3}\mu^S + \rho_0^F \kappa + 2Q$ is a decaying function of n_0 and the results for the Biot model ($N = 0$) and for the full model coincide quantitatively. The compressibility coefficient of the fluid $M = \rho_0^F \kappa / n_0^2$ behaves in the similar way but there exists a quantitative difference between the models in the range of small porosities. The coupling coefficient $C = \left(Q + \rho_0^F \kappa\right) / n_0$ is stronger in the Biot model than in the full model and this is the result of an additional coupling through changes of porosity in the full model. Finally, it is seen that values of the parameter N in the full model are much smaller than values of other parameters. Obviously, in the Biot model this parameter is equal to zero.

In Figure 16, we demonstrate the behavior of the coupling parameter Q for both models. Clearly the values for Biot's model are almost twice as big as these for the full model. This is the indication that interactions between components are in the same range of values because the values of N in the full model are almost identical as these for Q in this model which means that the full interaction term is also identical in both models. This Figure shows as well an instability of the full model for large values of porosity. This may be the indication of a structural instability of granular materials for porosities bigger than app. 0.58 and indicated in some structural works on this subject. This problem has not been investigated any further.

The above results have a very important bearing in the nondestructive testing of soils which we indicate in the next Lecture.

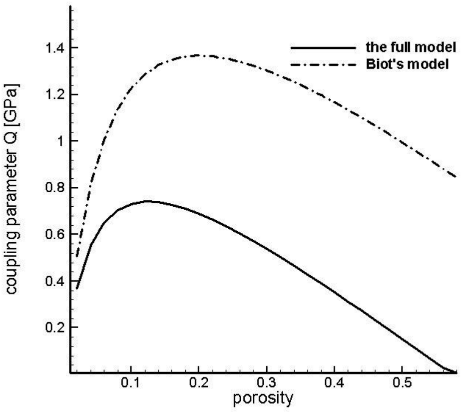

Fig. 16: *Comparison of the coupling parameter Q (right) for the full model and Biot's model with Geertsma parameter* $g = 50$.

Unfortunately the remaining material parameters $G = \mu^S$, π and ρ_{12} do not follow from such simple considerations and require real experiments on porous materials.

Lecture 14: Waves in poroelastic materials

Due to its practical bearing continuous modeling of waves is one of the most important subjects of continuum thermodynamics. Such wave phenomena as propagation of acoustic waves (sound), surface waves (Rayleigh, Stoneley, Love, water waves), shock waves (collision with meteorites, underground nuclear explosions, avalanches, landslides), solitons (nonlinear water waves, porosity waves in granular materials) are commonly appearing and require modeling for practical purposes. They are also used in laboratory and *in situ* investigations of material properties of systems. Speeds of propagation and attenuations of acoustic waves, decay and growth of amplitudes, transmissions and reflections on boundaries, mode couplings, transitions from weak to strong discontinuity waves, propagation of shock and solitons, all these features can be measured and deliver information on material and transient properties of continua. In most cases of practical bearing mathematical models of waves are formed by hyperbolic systems of partial differential equations. Description by such systems motivated the creation of extended thermodynamics which we presented in Lectures 6, 7 and 8.

The purpose of this Lecture is threefold. First, we show on the example of the two-component linear poroelastic materials how the propagation of acoustic fronts can be investigated. Then we demonstrate very briefly on the same example of the model the method of spectral analysis for acoustic waves. Finally, we illustrate typical boundary conditions for porous materials by investigating some surface waves. Due to the lack of time we limit our attention to a purely mechanical modeling and leave out heat conduction and other thermodynamical effects. Still processes described in this Lecture are irreversible. This is due to diffusion processes described by the permeability and this yields to attenuation of waves.

We begin with the analysis of propagation of weak discontinuity waves and investigate the propagation of the front. The front of such a wave is defined as a smooth moving surface on which the fields are continuous but their derivatives may have finite discontinuities. This means in the case of the two-component poroelastic materials that the following jump conditions are satisfied

$$\begin{gathered}\left[\left[\mathbf{v}^S\right]\right]=0, \quad \left[\left[\mathbf{v}^F\right]\right]=0, \quad \left[\left[\mathbf{e}^S\right]\right]=0, \quad [[\varepsilon]]=0, \\ \mathbf{a}^S:=\left[\left[\frac{\partial \mathbf{v}^S}{\partial t}\right]\right]\neq 0, \quad \mathbf{a}^F:=\left[\left[\frac{\partial \mathbf{v}^F}{\partial t}\right]\right]\neq 0,\end{gathered} \tag{716}$$

where the double bracket denotes the jump through the surface $[[\cdots]]:=(\cdots)^+-(\cdots)^-$, the quantities on the right hand side are limits of the quantities on the positive and negative side of the surface, respectively.

The fields satisfying the above conditions must fulfil the Maxwell kinematic compatibility conditions on the front which follow from the general so-called Hadamard conditions. They have the form

$$\begin{aligned}\left[\left[\operatorname{grad}\mathbf{v}^S\right]\right] &= -\frac{1}{c}\mathbf{a}^S\otimes\mathbf{n}, \quad \left[\left[\operatorname{grad}\mathbf{v}^F\right]\right]=-\frac{1}{c}\mathbf{a}^F\otimes\mathbf{n}, \\ \left[\left[\operatorname{grad}\mathbf{e}^S\right]\right] &= -\frac{1}{c}\left[\left[\frac{\partial \mathbf{e}^S}{\partial t}\right]\right]\otimes\mathbf{n}, \quad [[\operatorname{grad}\varepsilon]]=-\frac{1}{c}\left[\left[\frac{\partial\varepsilon}{\partial t}\right]\right]\mathbf{n},\end{aligned} \tag{717}$$

where c is the *speed of propagation* of the front and $\mathbf{n}$ is the unit vector perpendicular to the front.

Bearing the integrability conditions in mind

$$\frac{\partial \mathbf{e}^S}{\partial t} = \frac{1}{2}\left[\operatorname{grad} \mathbf{v}^S + \left(\operatorname{grad} \mathbf{v}^S\right)^T\right], \quad \frac{\partial \varepsilon}{\partial t} = \operatorname{div} \mathbf{v}^F, \tag{718}$$

we obtain immediately

$$\begin{aligned} \left[\left[\frac{\partial \mathbf{e}^S}{\partial t}\right]\right] &= -\frac{1}{2c}\left(\mathbf{a}^S \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{a}^S\right), \quad \left[\left[\operatorname{grad} \mathbf{e}^S\right]\right] = \frac{1}{2c^2}\left(\mathbf{a}^S \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{a}^S\right) \otimes \mathbf{n}, \\ \left[\left[\frac{\partial \varepsilon}{\partial t}\right]\right] &= -\frac{1}{c}\mathbf{a}^F \cdot \mathbf{n}, \quad [[\operatorname{grad} \varepsilon]] = \frac{1}{c^2}\mathbf{a}^F \cdot \mathbf{n}\mathbf{n}. \end{aligned} \tag{719}$$

Now we form the jump of field equations on the front. These follow from the balance equations

$$\begin{aligned} \rho_0^S \frac{\partial \mathbf{v}^S}{\partial t} &= \operatorname{div} \mathbf{T}^S + \hat{\mathbf{p}}, \\ \rho_0^F \frac{\partial \mathbf{v}^F}{\partial t} &= \operatorname{div} \mathbf{T}^F - \hat{\mathbf{p}}, \end{aligned} \tag{720}$$

and constitutive relations

$$\begin{aligned} &\mathbf{T}^S = \mathbf{T}_0^S + \lambda^S e \mathbf{1} + 2\mu^S \mathbf{e}^S + Q\varepsilon \mathbf{1} - N(n - n_0)\mathbf{1}, \\ &\mathbf{T}^F = \mathbf{T}_0^F + \rho_0^F \kappa \varepsilon \mathbf{1} + Q e \mathbf{1} + N(n - n_0)\mathbf{1}, \\ &\hat{\mathbf{p}} = \pi\left(\mathbf{v}^F - \mathbf{v}^S\right), \quad n - n_0 = n_0 \delta e + \Phi(e - \varepsilon). \end{aligned} \tag{721}$$

After easy calculations it follows

$$\begin{aligned} &\left\{\rho_0^S c^2 \mathbf{1} - \lambda^S \mathbf{n} \otimes \mathbf{n} - \mu^S(\mathbf{1} + \mathbf{n} \otimes \mathbf{n}) + N(n_0\delta + \Phi)\mathbf{n} \otimes \mathbf{n}\right\}\mathbf{a}^S - \\ &- \{Q\mathbf{n} \otimes \mathbf{n} + N\Phi \mathbf{n} \otimes \mathbf{n}\}\mathbf{a}^F = 0, \end{aligned} \tag{722}$$

$$-\{Q\mathbf{n} \otimes \mathbf{n} + N(n_0\delta + \Phi)\mathbf{n} \otimes \mathbf{n}\}\mathbf{a}^S + \left\{\rho_0^F c^2 \mathbf{1} - \rho_0^F \kappa \mathbf{n} \otimes \mathbf{n} + N\Phi \mathbf{n} \otimes \mathbf{n}\right\}\mathbf{a}^F = 0. \tag{723}$$

This is an eigenvalue problem. We split it into the normal part parallel to $\mathbf{n}$ and the transversal part perpendicular to $\mathbf{n}$.

In the first case we obtain

$$\begin{aligned} \left\{\rho_0^S c^2 - \left(\lambda^S + 2\mu^S\right) + N(n_0\delta + \Phi)\right\} a_n^S - \{Q + N\Phi\} a_n^F &= 0, \\ -\{Q + N(n_0\delta + \Phi)\} a_n^S + \left\{\rho_0^F c^2 - \rho_0^F \kappa + N\Phi\right\} a_n^F &= 0, \end{aligned} \tag{724}$$

$$a_n^S := \mathbf{a}^S \cdot \mathbf{n}, \quad a_n^F := \mathbf{a}^F \cdot \mathbf{n},$$

This homogeneous set of equations possesses a nontrivial solution if the determinant vanishes. We obtain the following *propagation condition*

$$c^4 - c^2\left\{\frac{\lambda^S + 2\mu^S - N(n_0\delta + \Phi)}{\rho_0^S} + \frac{\rho_0^F \kappa - N\Phi}{\rho_0^F}\right\} +$$

$$+\left\{\frac{\left(\lambda^S+2\mu^S\right)-N\left(n_0\delta+\Phi\right)}{\rho_0^S}\right\}\left\{\frac{\rho_0^F\kappa-N\Phi}{\rho_0^F}\right\}-$$

$$-\frac{1}{\rho_0^S\rho_0^F}\left\{Q+N\Phi\right\}\left\{Q+N\left(n_0\delta+\Phi\right)\right\}=0. \tag{725}$$

This biquadratic equation for c has two positive and two negative solutions which define two *longitudinal waves*: P1-wave and P2-wave (Biot's wave). Namely

$$c^2=\frac{1}{2}\left\{\frac{\lambda^S+2\mu^S-N\left(n_0\delta+\Phi\right)}{\rho_0^S}+\frac{\rho_0^F\kappa-N\Phi}{\rho_0^F}\pm\sqrt{\Delta}\right\}, \tag{726}$$

$$\Delta:=\left\{\frac{\lambda^S+2\mu^S-N\left(n_0\delta+\Phi\right)}{\rho_0^S}-\frac{\rho_0^F\kappa-N\Phi}{\rho_0^F}\right\}^2+4\frac{\left\{Q+N\Phi\right\}\left\{Q+N\left(n_0\delta+\Phi\right)\right\}}{\rho_0^S\rho_0^F}.$$

In the second case we multiply equations (722), (723) by a unit vector $\mathbf{n}_\perp$ perpendicular to $\mathbf{n}$. We obtain

$$\left\{\rho_0^S c^2-\mu^S\right\}a_\perp^S=0,\quad a_\perp^F=0, \tag{727}$$

$$a_\perp^S:=\mathbf{a}^S\cdot\mathbf{n}_\perp,\quad a_\perp^F:=\mathbf{a}^F\cdot\mathbf{n}_\perp.$$

Hence

$$c=\sqrt{\frac{\mu^S}{\rho_0^S}}. \tag{728}$$

This is the velocity of propagation of the *transversal wave*. It looks like the corresponding formula in the classical elasticity.

Let us mention that all these modes are attenuated due to the diffusion. This property cannot be demonstrated by means of such simple arguments for the jumps on the front.

Instead of a simple but cumbersome analytical investigation of the above solutions we present a numerical example. For this analysis we choose the following numerical data typical for sand and water

$$\begin{aligned}\rho_0^{SR}&=2500\,\frac{kg}{m^3},\quad \rho_0^{FR}=1000\,\frac{kg}{m^3},\\ K_s&=48\,GPa,\quad K_f=2.25\,GPa,\quad \pi=n_0\times10^7\,\frac{kg}{m^3s},\end{aligned} \tag{729}$$

which we use in the evaluation of macroscopic material parameters. The value of the permeability coefficient π corresponds to the hydraulic conductivity $\mathrm{K}=10^{-3}\,\frac{m}{s}=0.1\,darcy$[22]. We present the results in dependence on varying porosity n_0 and varying Poisson's ratio ν.

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[22] These two parameters are related in the following way

$$\pi=n_0\frac{\rho_0^{FR}g_{earth}}{\mathrm{K}}.$$

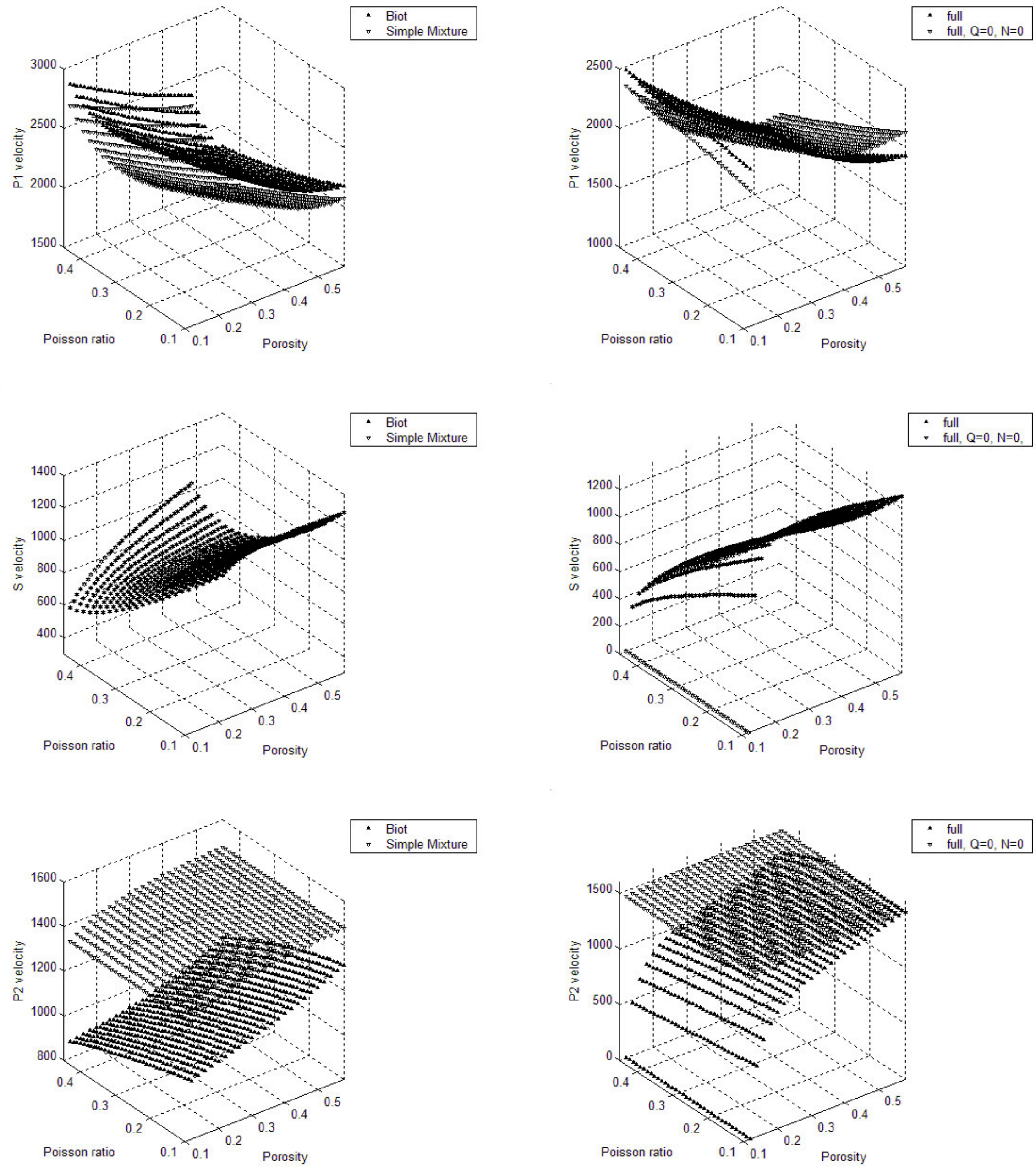

Figure 17: *Front velocities of P1-, S-, and P2-waves*
Left panel: Biot's model and "simple mixture" model $(Q = 0, N = 0)$
Right panel: The full model and the simplified full model

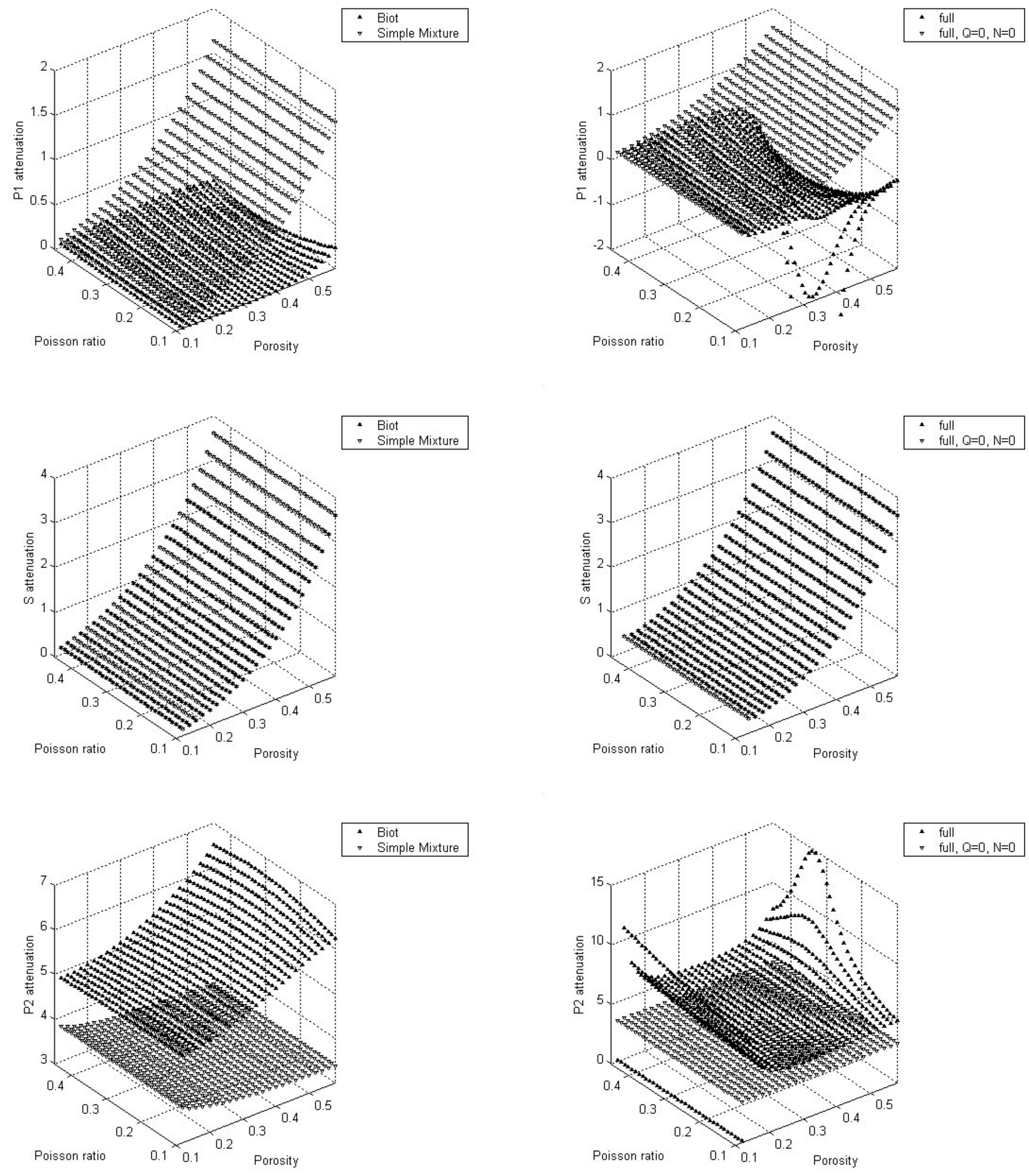

Figure 18: *Attenuation of fronts of P1-, S-, and P2-waves*
Left panel: Biot's model and "simple mixture" model $(Q = 0, N = 0)$
Right panel: The full model and the simplified full model

In Figure 17 we show the behavior of velocities of propagation of fronts of P1-, S-, and P2-waves. These three-dimensional plots illustrate the general qualitative character of the dependence on the initial porosity n_0 and on the Poisson's ratio ν.

In order to show whole surfaces in these 3D-pictures we collected the points in bars in the direction of the ν-axis. Separation of these bars reflects the steps of numerical evaluation – for n_0 this is 0.02, and for ν – 0.01.

First of all let us point out certain general features of these plots. They were calculated by means of the relation (726), with Gassmann-like relations presented in the previous Lecture. In both cases we have used a classical relation between the shear modulus μ^S and the Poisson's ratio ν.

Values of porosity vary between 0.1 and 0.58. This range has been chosen due to the applicability of the full model. As already mentioned in the previous Lecture micro-macro relations for this model yield instabilities below $n_0 = 0.1$ and above the value $n_0 \approx 0.58$. Instabilities in the first region, for $n_0 < 0.1$, follow from negative values of the shear modulus for $N \neq 0$.

Clearly, all above restrictions of the full model are related to the extension of Gassmann relations and, consequently, to the applicability of the full model to a certain limited class of granular materials for which we can claim Gassmann relations to hold. They may not fully apply to modeling of rocks, concrete and similar materials with a compact skeleton.

Plots in the left panel follow for Biot's model and for its simplification which we call "simple mixture" $(Q = 0, N = 0)$. For the latter model all material parameters except Q are identical with those of Biot's model. As we see the velocity of propagation of the front of P1-waves has a similar shape for both models but it is lower for the simple mixture model than for Biot's model. The difference is app. 10%. It is the opposite for P2-waves where fronts propagate faster for the simple mixture model than for Biot's model and the difference is app. 20%. Certainly, velocities of P2-waves decay to zero in both models as n_0 approaches zero.

The plot for velocities of S-waves is identical for both models.

These plots indicate already the important conclusion that the qualitative behavior of Biot's model and the simple mixture model is the same and quantitative differences are small enough to be accepted in practical applications.

Plots for the full model and its simplification with the same values of material parameters except of $Q = 0$ and $N = 0$ are shown in the right panel. For medium values of porosities and Poisson's ratio the behavior of these models is similar to Biot's model and the simple mixture model. Large deviations appear for P1-waves for small values of porosity where a dependence on the Poisson's ratio is different from Biot's model. Also for P2-waves substantial qualitative differences appear for small values of porosity and small values of the Poisson's ratio. In particular, below $n_0 \approx 0.14$ the velocity of the P2-wave within the full model decays more rapidly than within other models.

Again the velocity of the S-wave is almost identical for both models but it behaves differently from the Biot's model and simple mixture model for small porosities where it is decaying rather than growing and it possesses inflection points at app. $n_0 \approx 0.25$.

All these qualitative differences of both full models may be attributed to the singular behavior of the shear modulus μ^S. They would not appear if values of the parameter N were smaller than these predicted by Gassmann relations.

The attenuation of waves cannot be discussed by means of the simple analysis of propagation of fronts. For completeness we show in Figure 18 the numerical results following from the evaluation of *dispersion relations* for monochromatic waves in the limit of infinite frequencies, $\omega \to \infty$.

In spite of qualitative similarity in the whole range of parameters, quantitative differences between attenuations calculated for different models are much larger than the differences between velocities. For instance, the attenuation of the P1-wave as given by Biot's model is a few times smaller than in the simple mixture model (the left panel, the upper picture). It is the other way around for P2-waves which are much stronger attenuated according to Biot's model than to the simple mixture model. However, these differences become much smaller for medium values of parameters.

Again the attenuation of transversal waves is the same for both models – Biot's model and the simple mixture model.

For the full model the attenuation of P1-waves becomes negative in the case of large porosities and small Poisson's ratio. The range of instability is approximately limited by the line: $n_0 = \nu$.

The attenuation of P2-waves becomes also much bigger than in Biot's model for small values of porosity.

In contrast to a singular behavior near the limits of n_0 and ν results seem to agree well in practically relevant medium values of porosity and of Poisson's ratio.

We do not discuss in this Lecture any details of the analysis of monochromatic waves. They are described by the following relations for fields

$$\begin{aligned} &\mathbf{v}^S = \mathbf{V}^S \mathcal{E}, \quad \mathbf{v}^F = \mathbf{V}^F \mathcal{E}, \quad , \mathbf{e}^S = \mathbf{E}^S \mathcal{E}, \quad \varepsilon = E^F \mathcal{E}, \\ &\mathcal{E} := \exp\left[i\left(k\mathbf{n}\cdot\mathbf{x} - \omega t\right)\right], \end{aligned} \tag{730}$$

where ω is a given frequency, k is the so-called *wave number* and it may be complex, $\mathbf{n}$ is the unit vector in the direction of propagation. $\mathbf{V}^S, \mathbf{V}^F, \mathbf{E}^S, E^F$ are constant *amplitudes*. Field equations determine the so-called *dispersion relation* $k = k(\omega)$ which, in turn, determines *phase and group speeds* of propagation, $c_{ph} = \omega / \operatorname{Re} k$, $c_g = \left(d \operatorname{Re} k / d\omega\right)^{-1}$, respectively, and *attenuation* of waves, $\operatorname{Im} k$. However, it is worth mentioning that a simple analysis of the dispersion relation yields some important conclusions concerning parameters of the model. Two of them, Q and ρ_{12} have a particular bearing. As we know from the previous Lecture the coupling parameter Q can be calculated by means of Gassmann relations. Parameter ρ_{12} interpreted as the tortuosity coefficient is used in soil mechanics in a transformed form proposed by Berryman

$$\rho_{12} = \rho_0^F (1 - a), \quad a = \frac{1}{2}\left(\frac{1}{n_0} + 1\right) \quad \text{i.e.} \quad a \geq 1, \quad \rho_{12} \leq 0, \tag{731}$$

where a is called the *tortuosity.* Let us apply the monochromatic wave analysis to the Biot model and some of its simplifications. The constitutive relations (721) are now replaced by the following ones

$$\begin{aligned} &\mathbf{T}^S = \mathbf{T}_0^S + \lambda^S e\mathbf{1} + 2\mu^S \mathbf{e}^S + Q\varepsilon\mathbf{1}, \\ &\mathbf{T}^F = \mathbf{T}_0^F + \rho_0^F \kappa\varepsilon\mathbf{1} + Qe\mathbf{1}, \\ &\hat{\mathbf{p}} = \pi\left(\mathbf{v}^F - \mathbf{v}^S\right) - \rho_{12}\left(\frac{\partial \mathbf{v}^F}{\partial t} - \frac{\partial \mathbf{v}^S}{\partial t}\right), \quad n - n_0 = n_0 \delta e + \Phi\left(e - \varepsilon\right), \end{aligned} \tag{732}$$

i.e. $N = 0$ and we account for the influence of the relative acceleration.

We present numerical results for the fastest bulk wave, P1-wave, in dependence on these parameters. We choose the data which practically coincide with those used for the previous diagrams. In order to expose better the damping the permeability π has been chosen to be bigger than before.

$$\begin{aligned} c_{P1} &= \sqrt{\frac{\lambda^S + 2\mu^S}{\rho_0^S}} = 2500\ \tfrac{m}{s}, \quad c_{P2} = \sqrt{\kappa} = 1000\ \tfrac{m}{s}, \quad c_S = \sqrt{\frac{\mu^S}{\rho_0^S}} = 1500\ \tfrac{m}{s}, \\ \rho_0^S &= 2500\ \tfrac{kg}{m^3}, \quad r = \frac{\rho_0^F}{\rho_0^S} = 0.1, \quad \pi = 10^8\ \tfrac{kg}{m^3 s}, \qquad (733) \\ Q &= 0.8\, GPa, \quad n_0 = 0.4, \quad a = 1.75. \end{aligned}$$

Four particular cases are considered. In the full Biot model both Q and ρ_{12} are different from zero, i.e. a is different from one. In the so-called simple mixture model $Q = 0$ and $a = 1$. In the remaining two cases either $Q = 0$ or $a = 1$. These two cases were investigated in order to clear what is the influence of each of these parameters.

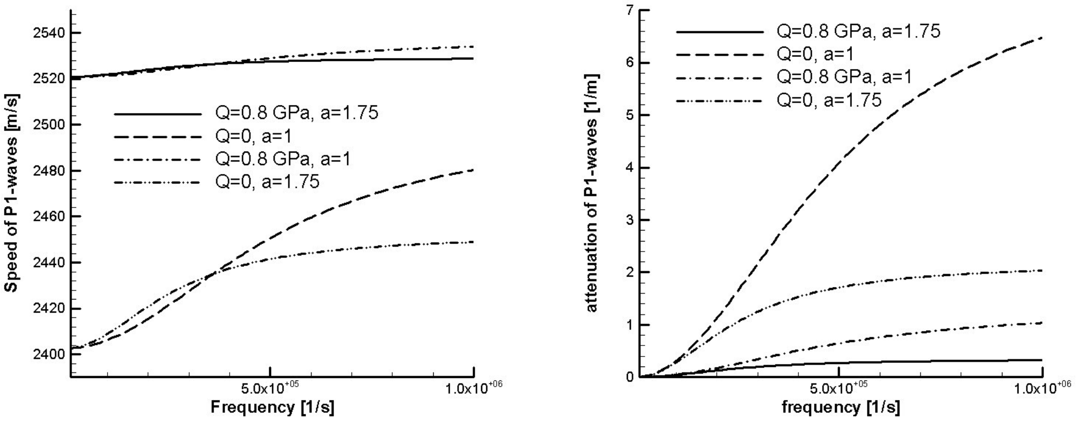

Fig. 19: *Speeds and attenuations of monochromatic P1-waves for four different models.*

In the left panel of Figure 19 we present speeds of propagation of monochromatic P1-waves as functions of the frequency. The simple mixture model ($Q = 0, a = 1$) leads to the biggest difference in the speed between two limits of the frequency $\omega \to 0$ and $\omega \to \infty$. This difference is approximately 100 m/s and it was indeed observed in experiments on soils. The both models with $Q = 0.8\ GPa$ yield almost no difference between these limits. This may indicate that values of the coupling coefficient Q given by Gassmann's relation are too large. Even worse is the influence of tortuosity a. It is seen in diagrams of the right panel. For a moderate value of $a = 1.75$ the attenuation of waves decays more than 10 times. We expect the influence of tortuosity, i.e. complicated shapes of channels of the porous materials to have the exactly opposite effect. Such curvy channels must scatter waves much stronger than straight channels and, consequently, increase rather than decrease the attenuation. Consequently, in spite of numerous papers with such a claim the added mass coefficient ρ_{12} does not seem to have much to do with the tortuosity. The latter has, of course, a strong influence on values of the permeability and, therefore, it seems to be physically justified to prescribe the influence of tortuosity only to the hereditary character of the diffusion contribution. It should be stressed that this issue is still very controversial.

The propagation conditions change dramatically if a boundary appears. It is known from the simplest elastic model that due to the boundary condition on an elastic half-space in addition to the normal longitudinal and transversal bulk waves the so-called Rayleigh surface wave appears which propagates along the boundary with the speed smaller than both speeds of bulk waves.

Similar effects are observed for all boundaries. These waves have a very big practical bearing. Their spatial dispersion is much smaller than this of bulk waves because the latter have spherical and the former cylindrical character. This is the reason, for instance, that damages in earthquakes are caused by surface and not by bulk waves.

Before we discuss some properties of surface waves in saturated porous materials we have to formulate boundary conditions for such media.

The construction of boundary value problems for porous materials requires a definition of the boundary. In the macroscopic description which we presented in previous Lectures it is a smooth orientable surface $\partial\mathcal{B}_0$ of the reference domain $\mathcal{B}_0$ of the skeleton. It means that its current image $\partial\mathcal{B}_t$ moves with the velocity $\mathbf{v}^S$ of particles of the skeleton. This definition does not relate the boundary to fluxes of fluid components and does not specify any properties related to its morphology like, for instance, a fraction of the area of channels approaching the boundary *(surface porosity)*. These properties are essential for the formulation of boundary conditions. The problem with the transition from the real morphology of porous materials to the macroscopic description is demonstrated in Figure 20. It is clear that there are infinitely many possibilities to envelope a porous or granular material in a smooth surface which models the boundary. Variations of the geometry, if they are sufficiently small in comparison with dimensions of REV, do not have any influence on the macroscopic geometry. However, it is easy to see that these small changes may lead to large variations of the surface porosity, i.e. the fraction of the area of openings of channels on a chosen surface to the total area within REV.

From the physical point of view the only reasonable way to define a smooth macroscopic surface modeling the boundary is to locate it somewhere in the layer encompassing boundary solid elements and whose thickness is not larger than the characteristic linear dimension of REV. This choice should be random. Then it was proved A. Delesse in 1848 that the surface and volume porosities are equal. Certainly, it means that the boundary surface cannot be tangent to elements of the skeleton on the boundary but it rather cuts the material and leaves some parts of the real skeleton beyond the domain of continuous model of the porous material. This indicates the existence of boundary layers which have to be incorporated in boundary conditions. Similar remarks concern interfaces between two different porous materials, a porous material and a fluid, etc.

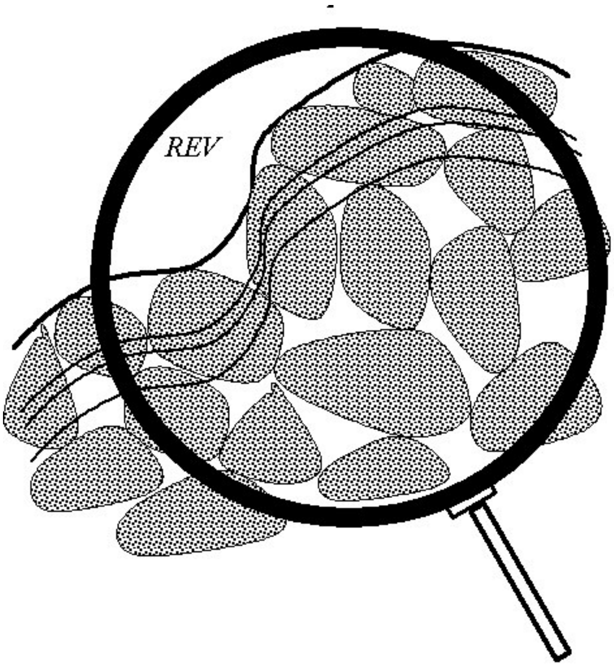

Fig. 20: *On the definition of the boundary of porous materials*

One of the consequences of the equal porosities is the condition (706) $p^S = (1-n)\, p^{SR}$, $p^F = np^{FR}$, etc. which describes equilibrium properties on the boundary without flow effects, i.e. without an influence of boundary layer effects.

Now we are in the position to introduce conditions on $\mathcal{B}_t$ which yield boundary conditions. As mentioned above, the boundary $\partial\mathcal{B}_t$ is assumed to be material with respect to the skeleton. Then partial mass balance equation for the skeleton does not give rise to any conditions and the flow of the fluid must satisfy the following jump condition

$$m^F := \rho_t^{F-} \left(\mathbf{v}^{F-} - \mathbf{v}^S\right) \cdot \mathbf{n} = \rho_t^{F+} \left(\mathbf{v}^{F+} - \mathbf{v}^S\right) \cdot \mathbf{n}. \tag{734}$$

Obviously, ρ_t^{F-} is the current partial mass density of the fluid in the porous material (the negative side of the boundary by the outward orientation of the normal vector $\mathbf{n}$) and ρ_t^{F+} is the partial mass density of the fluid outside the porous material. If this is vacuum this quantity is zero and the condition implies that normal components of velocities of both components are equal. If the material outside is the fluid flowing from the porous material then $\rho_t^{F+} = \rho_t^{FR}$. Other possibilities are obvious.

One cannot require a continuity of partial tractions in porous materials. Terzaghi has constructed an instructive *gedankenexperiment* in which he has shown that the external load is divided between components in a time dependent manner following from the flow of the fluid through the surface. We can require only the continuity of the momentum flux for the mixture, i.e.

$$\left(\mathbf{T}^{S-} - p^{F-}\mathbf{1}\right) \mathbf{n} = \mathbf{t}_{ext}, \tag{735}$$

where $\mathbf{t}_{ext}$ is the full traction applied from exterior to the unit surface.

It means that we have to replace the second vectorial condition by some other conditions. One of them reflects the existence of the boundary layer indicated in the above discussion. Namely we assume that the amount of mass of the fluid which is transported through a unit area of permeable boundary in a unit time is driven by the difference of real pressures in the fluid on both sides of the boundary. Hence, in general,

$$m^F = \alpha' \left(\frac{p^{F-}}{n^-} - \frac{p^{F+}}{n^+} \right), \tag{736}$$

where $p^{F\pm}$ are partial pressures in the fluid on both sides of the boundary and $n^\pm$ denotes the porosity on both sides of the boundary. In the case of the porous materials only on the negative side of the boundary, i.e. for $n^+ = 1$ we have

$$m^F = \alpha \left(p^{F-} - n^- p^{FR+} \right), \quad \alpha := \frac{\alpha'}{n^-}. \tag{737}$$

Obviously, coefficients α', α describe material properties of the boundary. The coefficient α, in some works denoted as $1/T$, is called the *surface permeability.* It has been introduced to the theory of surface waves in porous materials by H. Deresiewicz in 1961. In reflects jointly all properties of the boundary layer. In the particular case of the impermeable boundary $\alpha = 0$ and conditions (734) and (737) coincide. However, the boundary value problem does not degenerate because we do not have to solve the exterior problem. Another particular case of an ideal permeable boundary $\alpha \to \infty$ yields the condition of continuity of pressure: $p^{F-} = n^- p^{FR+}$ commonly used by mathematicians in the theory of diffusion.

In addition to this scalar condition, we have to introduce two other conditions. As (737) reflects only the behavior of the normal velocity $\left(\mathbf{v}^{F-} - \mathbf{v}^S \right) \cdot \mathbf{n}$ they are supposed to describe the behavior of the tangent component of the relative velocity. It has been shown by D. Joseph that, for macroscopically viscous fluids, this components of the velocity have to satisfy a condition similar to Deresiewicz condition. In the case of ideal fluids which we discuss in these Lectures the tangent part must be continuous. In the case of fluid outside porous material this condition has the form

$$\left(\mathbf{v}^{F-} - \mathbf{v}^S \right) - \left[\left(\mathbf{v}^{F-} - \mathbf{v}^S \right) \cdot \mathbf{n} \right] \mathbf{n} = 0. \tag{738}$$

We are ready to formulate the problem of surface waves. In the classical two-dimensional case, we have to solve the field equations for the semiinfinite medium (720), (721) under the condition that the solution decays with the depth and it moves as a wave in the direction of the boundary.

It is convenient to introduce the displacement vector $\mathbf{u}^S$ for the skeleton, and, formally, the displacement vector $\mathbf{u}^F$ for the fluid. The latter is introduced only for the technical symmetry of considerations and it does not have any physical bearing. Then

$$\begin{aligned} \mathbf{u}^S &= \operatorname{grad} \varphi^S + \operatorname{rot} \boldsymbol{\psi}^S, \quad \mathbf{v}^S = \frac{\partial \mathbf{u}^S}{\partial t}, \quad \mathbf{e}^S = \operatorname{sym} \operatorname{grad} \mathbf{u}^S, \\ \mathbf{u}^F &= \operatorname{grad} \varphi^F + \operatorname{rot} \boldsymbol{\psi}^F, \quad \mathbf{v}^F = \frac{\partial \mathbf{u}^F}{\partial t}, \end{aligned} \tag{739}$$

where $\varphi^S, \boldsymbol{\psi}^S, \varphi^F, \boldsymbol{\psi}^F$ are two pairs of potentials analogous to those appearing in the classical elasticity.

We choose the axes with the downward orientation of the z-axis and the x-axis in the direction of propagation of the wave. As the problem is assumed to be two-dimensional we make the following ansatz for solutions

$$\begin{aligned} \varphi^S &= A^S(z)\exp[i(kx-\omega t)], \quad \varphi^F = A^F(z)\exp[i(kx-\omega t)], \\ \psi_y^S &= B^S(z)\exp[i(kx-\omega t)], \quad \psi_y^F = B^F(z)\exp[i(kx-\omega t)], \\ \psi_x^S &= \psi_z^S = \psi_x^F = \psi_z^F = 0, \end{aligned} \tag{740}$$

and

$$\begin{aligned} \rho^S - \rho_0^S &= A_\rho^S(z)\exp[i(kx-\omega t)], \quad \rho^F - \rho_0^F = A_\rho^F(z)\exp[i(kx-\omega t)], \\ n - n_0 &= A^\Delta \exp[i(kx-\omega t)]. \end{aligned} \tag{741}$$

Substitution in the field equations yields relations for the amplitudes which, in the case under considerations, have the exponential form $\exp(-\gamma z)$, where γ is different for each amplitude. However, these exponents should have the common feature to be positive. We know that this is indeed the case in the classical elasticity and, as the result, we obtain Rayleigh waves. For porous materials, the problem is very complicated and only some solutions possess indeed this property of surface waves. In some cases, such solutions do not exist, in some other one obtains the so-called pseudosurface or *leaky* waves.

In addition, boundary conditions yield the dispersion relation $k = k(\omega)$ which specifies the speeds and attenuations of surface waves. Due to the diffusion surface waves in porous materials are always attenuated. Only in the limit $\omega \to 0$ attenuation becomes very small and some surface waves in porous materials remind, for instance, classical Rayleigh or Stoneley waves. In the case of the model with $N = 0, Q = 0, \rho_{12} = 0$ (the simple mixture model) the following dispersion relation follows in this limit of frequencies

$$\left(\frac{\omega}{k}\right)\left\{\left(2-\frac{r+1}{c_s^2}\left(\frac{\omega}{k}\right)^2\right)^2 - 4\sqrt{1-\frac{r+1}{c_s^2}\left(\frac{\omega}{k}\right)^2}\sqrt{1-\frac{r+1}{rc_f^2+1}\left(\frac{\omega}{k}\right)^2}\right\} + \tag{742}$$

$$+O\left(\sqrt{\omega}\right) = 0.$$

It shows the existence of the single surface mode – Rayleigh-like wave. All other modes characteristic for porous materials do not propagate.

We have shown the above example to illustrate technical problems which must be overcome in the wave analysis in porous materials. Simultaneously, it is of the paramount importance for many practical applications and one can expect an extensive research in this field in the near future.

Final remarks

The course on Continuum Thermodynamics presented in these Lecture notes was designed to be delivered in 42 lecture hours. This extent is, obviously, not large enough to cover even the main topics of the subject. For this reason, I have chosen a material according to my own taste and related to my own research without any pretense to the indication of importance or objective judgement of correctness of different approaches. Apart from some practical purposes I have hoped to make clear that the subject of modern thermodynamics is still very attractive for the research. This concerns in particular the thermodynamical strategy of constructing macroscopic models of complex materials, in particular – materials with microstructure.

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