

A Thermodynamic Approach to Rheology

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Summary

A continuum theory of deformation and flow is presented, that is based on the principle of conservation of mass, the first and second law of thermodynamics, the concepts of a local thermodynamic state and of a local geometric natural reference state, a principle of determinism and on a postulate concerning the production of entropy. As special cases are considered gases, elastic materials, simple solids and liquids. Stress is in this theory a thermodynamically defined quantity.

Introduction

The mathematical theories of deformation and flow of matter deal essentially with the gross properties of a medium. Addition of heat and performance of mechanical work are considered as distinct means for a change of the state of the medium. The resulting phenomena in any particular material are, however, not unrelated and a thermodynamical treatment of the foundations of the theory of flow and deformation seems the appropriate, and indeed the obvious approach, but then full account should be given of the rate of change of all quantities that determine the thermodynamic state.

A theory of deformation and flow, founded on thermodynamic concepts, should not make use of stress as a primitive concept and of the equations of motion, but the stress concept and the equations of motion should follow as mathematical consequences of the theory. It is to be understood, however, that within the context of a thermodynamic theory the concept of stress is limited by the nature of the state variables, that are being considered. Thus in a theory, in which the effect of changes of geometry on the state of a medium is solely represented by the mass density as a state variable, the concept of stress will only arise as a hydrostatic pressure. One might agree therefore with TRUESDELL's statement, that the equations of mechanics describe a wider range of

phenomena than do the equations of thermodynamics (TRUESDELL 1952), but it should be realized, that the equations of mechanics are lacking in physical content as long as no constitutive equations for the stresses are given.

It is the conviction of the author that stress as a thermodynamically defined quantity is a sufficiently broad concept to cope with the observed phenomena in the deformation and flow of matter, though admittedly in many instances the equations may in an approximation be simplified in a way, that obscures their thermodynamical content. This paper is an attempt to show that a continuum theory of deformation and flow can be based on the principle of conservation of mass, the first and second law of thermodynamics, the concepts of a local thermodynamic state and a local geometric natural reference state, a principle of determinism and on a postulate concerning the production of entropy.

The concept of a local geometric natural reference state in connection with inelastic phenomena was first introduced by ECKART (1948). His use of a reference rate tensor, not subjected to kinematical compatibility equations, has unduly been criticized by TRUESDELL (1952, 1960), because the latter did not recognize the physical content of this concept. The local, generally non-Euclidean metric of the natural reference state is to be considered as a thermodynamic state variable, as it is done for instance by COLEMAN and NOLL (1959), and its rate of change is to be determined by a constitutive equation for the production of entropy.

The principle of determinism put forward in this paper is in the spirit of classical mechanics. It contends that the process of flow and deformation shall be fully determined, if for a body, free in space, at a any initial time the thermodynamic state and, independently of this state, the velocity field inside the body are prescribed. From the arbitrariness of the velocity field with respect to the initial thermodynamic state then follow the equations of motion, while the requirement that interaction between various regions in the body shall be such, that the equation expressing the principle of conservation of energy is identically satisfied, leads to the equation for the local rate of energy dissipation.

For the postulate concerning the production of entropy no other justification can be given than that it may be regarded as another consequence of the principle of determinism if one refuses to complicate the theory further by the addition of other new principles.

It will be shown how the theory, put forward in this paper, reduces the problem of rheological constitutive equations to the determination of scalar functions of state variables, which define the internal energy and the rate of energy dissipation. It should be observed that in this theory, there is no place for pure viscosity, while volume change is

always a purely thermo-elastic phenomenon. It may well be argued however, that this is by no means a limitation of the theory in view of the available data on actual behaviour of materials. The theory leads to the Navier-Stokes equations of viscous flow if the restriction of quasi-stationary flow is introduced. It is this restriction that obscures the thermodynamic nature of the shear stresses in this case.

Also in the case of time-independent plasticity, particularly for the rigid-perfectly plastic model, the thermodynamic content of the equations is obscured by the limiting process, that is to be applied to the equations of the general theory.

Still the author realizes that the thermodynamic approach to rheology, presented in this paper, is open to many questions. In particular the extension of the theory to electro-magnetic phenomena is by no means clear, while further the rigid deterministic approach to rheology may well fail to describe adequately the infinite complexity of actual material behaviour.

Notation

Throughout the paper index notation with summation convention and Kronecker delta is used.

The theory is formulated in terms of rectangular Cartesian coordinates and Cartesian tensors.

We employ the superposed dot for the material time derivative in the moving continuum:

$$\dot{A} = \frac{\partial A}{\partial t} + \frac{\partial A}{\partial x_i} \dot{x}_i.$$

If necessary the extent of application of the dot will be indicated by an overbar, for instance in $\overline{\rho dV}$.

The superposed $^{-1}$ indicates the inverse of a transformation, defined by

$$b_{ix}^{-1} b_{\alpha j} = \delta_{ij}.$$

Orthogonal transformations are indicated by R_{ij} , where

$$R_{ij}^{-1} = R_{ji}.$$

The superposed $\frac{1}{2}$ denotes the square root of a symmetric tensor, defined by

$$C_{\alpha\beta}^{\frac{1}{2}} = \sum_p \sqrt{C^{(p)}} n_\alpha^{(p)} n_\beta^{(p)}.$$

where $C^{(p)}$ is a principal value of the tensor $C_{\alpha\beta}$ and where $n_\alpha^{(p)}$ are the direction cosines of the corresponding principal direction.

Conservation of Mass

In classical mechanics and thermodynamics mass is recognized as an indestructible property of any closed system. The motion of elementary particles of a system can in general not be described by the motion of a continuum, in which each particle occupies a material point. Furthermore the system may consist of different types of particles. If, however, at any instant the probability for a particle to be of a certain type is independent of its location in the system, the average motion of mass inside the system can be represented by the motion $\dot{x}_i = \dot{x}_i(x_1, x_2, x_3, t)$ of a continuum with a mass density $\rho = \rho(x_1, x_2, x_3, t)$. We shall consider only systems for which this continuum approach is permitted and which are of finite extent, with a non-vanishing mass density ρ inside a moving volume V . This volume with constant mass will be denoted as a body.

We shall assume that for the body the velocities $\dot{x}_i$ and the mass density ρ are continuous differentiable functions of the coordinates. The principle of conservation of mass is then expressed by

$$\frac{d}{dt} \int_V \rho dV = \left(\dot{\rho} + \rho \frac{\partial \dot{x}_i}{\partial x_i} \right) dV = 0,$$

or

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x_i} \dot{x}_i + \rho \frac{\partial \dot{x}_i}{\partial x_i} = 0. \quad (1)$$

First Law of Thermodynamics

In classical mechanics and thermodynamics it is asserted that with respect to each of certain preferred coordinate systems, the so-called inertial systems, the quantity energy,

$$U + \frac{1}{2} \int_V \rho \dot{x}_i \dot{x}_i dV,$$

is a second indestructible property of any closed system, where the internal energy U is independent of the average mass velocity $\dot{x}_i$ and is an unique functional of appropriate state variables for the material under consideration. The class of coordinate systems, with respect to which the kinetic energy $\frac{1}{2} \int_V \rho \dot{x}_i \dot{x}_i dV$ is to be defined, is determined

by the group of Galilean transformations

$$x'_i = V_i t + \bar{R}_{ij}(x_j - V_j t), \quad \bar{R}_{ij} \bar{R}_{kj} = \delta_{ik}, \quad (2)$$

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where V_i represents an arbitrary constant velocity and where $\bar{R}_{ij}$ is a constant orthogonal matrix. Since U is to be independent of $\dot{x}_i$, it follows that U must be invariant under the transformation (2).

Second Law of Thermodynamics

Changes of state of a material system can be due to external and internal causes. For a closed system, where the state can only change by internal causes, it is a fact of experience that the system will tend to an equilibrium state, characterized by the vanishing of the time derivatives of all state variables. This concept of irreversibility of the changes of state is by the second law of thermodynamics formulated in terms of a functional of state variables, the entropy S , that for a closed system satisfies the inequality.

$$\dot{S} \geq 0. \quad (3)$$

It may be observed that in an equilibrium state holds $\dot{U} = 0$ and $\dot{S} = 0$, since both U and S are functionals of state variables only.

The Concept of a Local Thermodynamic State

A closed material system may be broken into a number of interacting subsystems. Now it is postulated that, like the kinetic energies, the internal energies as well as the entropies are additive. This implies that the internal energy and the entropy of a subsystem are functionals of state variables, which refer to this subsystem only. It is clear that there will be a limit as to the smallness of a subsystem to which this postulate still applies. The thermodynamic approach is a-priori restricted to systems, where statistical averages are meaningful. However, the definition of a local internal energy u and a local entropy s , both taken per unit mass, for a system in a homogeneous state a mathematical triviality, is a lawful artifice in the description of non-homogeneous states of bodies, where u - and s -distributions may represent the internal energy and the entropy of all subsystems up to the smallest system, that permits a statistical averaging procedure. If furthermore the variation of state variables is small within a region that is large compared to the smallest thermodynamic system, then we may consider the values of u and s in a point as functions of locally defined state variables. However, since the entropy has been introduced to express the irreversibility of the changes of state of a closed system, the entropy per unit mass, s , may itself, without loss of generality, be treated as a parameter specifying the local state, together with other appropriate state variables for which the rate of change is not subjected to any inequality. The

scalar quantity s is invariant under the transformation (2) and the internal energy per unit mass, u , may therefore be any arbitrary function of s .

In order to indicate, that the notion of the smallest thermodynamic system presents under normal circumstances no restriction to the validity of the concept of a local thermodynamic state, it can be observed that the number of particles in air at sealevel amounts to $2 \cdot 7 \cdot 10^{19} \text{ cm}^{-3}$ and in iron to $8 \cdot 6 \cdot 10^{22} \text{ cm}^{-3}$.

According to the second law of thermodynamics for any closed system the rate of change of s must satisfy the inequality (3)

$$\dot{S} = \int_V \rho \dot{s} dV \geq 0.$$

Locally, however, $\dot{s}$ may be negative due to the interaction of various subsystems in the body. Because of the additive property of the entropy we can, besides an entropy production per unit mass $\dot{\bar{s}} \geq 0$, define an entropy flux $\dot{h}_i = \dot{h}_i(x_1, x_2, x_3, t)$, that determines the distribution of entropy, such that

$$\rho \dot{s} = -\frac{\partial \dot{h}_i}{\partial x_i} + \rho \dot{\bar{s}}, \quad \dot{\bar{s}} \geq 0. \quad (4)$$

If the body as a whole is a closed system, its boundary is a surface through which no interaction takes place, and hence on this surface shall hold $\dot{h}_i n_i = 0$, where n_i is the outward unit normal. The inequality for the local rate of entropy production, $\dot{\bar{s}} \geq 0$, ensures that the second law of thermodynamics is satisfied, since

$$\dot{S} = \int_V \left(-\frac{\partial \dot{h}_i}{\partial x_i} + \rho \dot{\bar{s}} \right) dV = -\int_A \dot{h}_i n_i dA + \int_V \rho \dot{\bar{s}} dV.$$

Later on we shall require that the flux of interaction $\dot{h}_i$ is such, that the equation expressing the principle of conservation of energy shall be satisfied identically, thereby establishing the connection between the flux $\dot{h}_i$ and the flux of energy, known as the heatflux. Inequality (4) then becomes equivalent to the Clausius-Duhem inequality of thermodynamics.

Insofar as the rate of change of state variables is not defined in terms of the velocity field of the moving continuum, representing the average mass motion, this rate of change shall be determined by thermodynamic constitutive equations, which are an expression of the properties of the material as a thermodynamic system. They constitute the essence of the theory of irreversible thermodynamics.

The Geometric Natural Reference State

Let the properties of the material under consideration be defined in some reference state. The internal energy u may now be considered as a function of state variables, that define changes with respect to this reference state. Thus in the following s will represent the change of entropy and will be taken equal to zero in the reference state.

It will be assumed that the physical properties of the material in the reference state, that determine the functional dependence of u on the state variables, are preserved in any subsequent process, in particular any anisotropy, that the material may possess. Anisotropic properties can be defined with reference to orthogonal triads in each point of the body, which without rotation are carried along by the motion of the continuum. It is now postulated that the geometrical configuration of the material at any instant in each point of the body is related to the configuration in the reference state by a invertible transformation of line elements

$$da_\alpha = b_{\alpha i} dx_i, \quad \det (b_{\alpha i}) > 0. \quad (5)$$

Here the da_α 's define line elements in the local coordinate system, determined by the orthogonal triads, which, with their fixed directions in space, form a base of reference for the anisotropic properties of the material.

By the theorem on the unique polar decomposition of a tensor with a non-vanishing determinant the above transformation of line elements may be decomposed into a rigid rotation followed by a deformation with a symmetric transformation matrix, as illustrated for the two-dimensional case in Fig. 1. It should be realized that the configuration of the natural reference state in a point of the moving continuum with respect to the orthogonal triads remains always the same, though the identity of the material particles, that make up this configuration, is in general subject to change. This is an allowable concept since the motion of the continuum describes only the average motion of mass, but not the motion of the individual particles. So, if we consider for instance a crystal lattice, in which a process of slip has taken place, then a unit cell can be made up of atoms, that before slip took place belonged with other atoms to different unit cells. The unit cell, illustrated in Fig. 1, in a point of the continuum, covering the lattice, is at any instant the same, but the identity of the atoms, that make up the unit cell, may be subject to change.

It follows from the above that it is in general not permissible to consider the system (5) as exact differentials for the corresponding func-

tions of the coordinate points in the space x_1, x_2, x_3 , because the conditions of integrability will only be satisfied in special cases (i.e. in thermoelasticity). The tensor $b_{\alpha i}$ is a physical concept, like the metric tensor of the natural reference state, as introduced by ECKART (1948), and it is not subject to kinematic compatibility equations derived from the

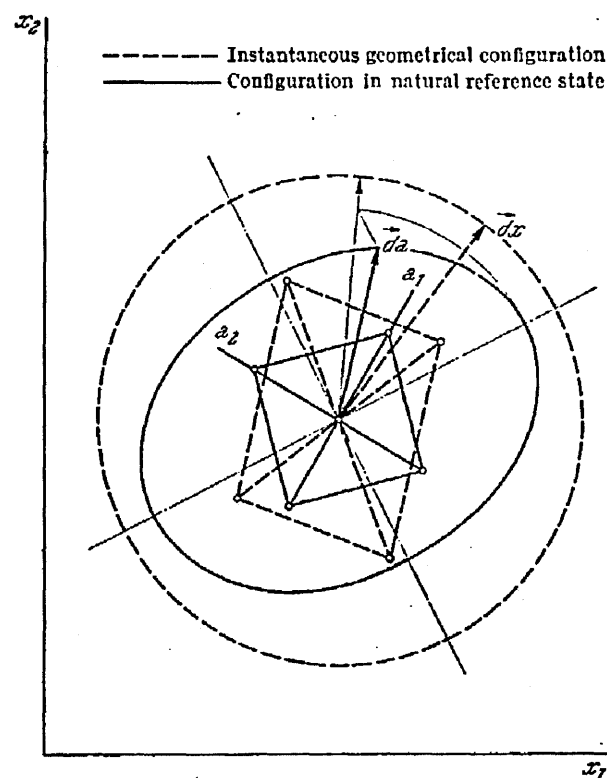


Fig. 1. Two-dimensional illustration of the transformation $da_\alpha = b_{\alpha i} dx_i$

motion of the continuum, which represents only the average motion of mass inside the body.

State variables in the internal energy function u shall, like the internal energy itself, be invariant under the group of Galilean transformation (2). Since the orthogonal triads in each point of the body are connected with the fixed natural reference state, they are not affected by the transformations (2) and hence the da_α 's are invariant under this transformation. It follows that

$$da_\alpha = b_{\alpha i} dx_i = b_{\alpha i} \bar{R}_{ji} dx'_j = b'_{\alpha j} dx'_j,$$

or

$$b_{\alpha i} = b'_{\alpha j} \bar{R}_{ji}. \quad (6)$$

Since the components of the tensor $b_{\alpha i}$ are not invariant under the transformation (2), they are not thermodynamic state variables. They define, however, a tensor $C_{\alpha\beta}$

$$C_{\alpha\beta} = b_{\alpha i} b_{\beta i} = b'_{\alpha j} \bar{R}_{ji} b'_{\beta k} \bar{R}_{ki} = b'_{\alpha j} b'_{\beta j}, \quad (7)$$

which does possess the required property of invariance under the group of Galilean transformations. We shall show in the following that a broad theory of rheology can be based upon an internal energy, that is an unique function of the state variables s and $C_{\alpha\beta}$.

$$u = u(s, C_{\alpha\beta}). \quad (8)$$

The Principle of Determinism

From classical mechanics it is known that if, independently of each other, initial positions and initial velocities of mass points are given, the subsequent motion is determined. It is in the spirit of this principle of determinism, that it is postulated here, that an initial thermodynamic state and an initial velocity field, prescribed independently of each other, shall suffice to determine the subsequent motion and accompanying thermodynamic processes. It follows that to all possible thermodynamic states and to all velocity fields shall correspond definite rates of change of all state variables.

It was pointed out before that insofar as the rate of change of state variables is not defined in terms of the velocity field of the moving continuum, this rate of change shall be determined by the material as a thermodynamic system. However, an element of volume dV , imbedded in the moving continuum, does in general not represent one and the same thermodynamic system at subsequent times, since the velocity field defines only the average motion of mass. This difficulty does not arise, if it is postulated that the thermodynamic processes depend only on the instantaneous values of the state variables, because at any time t an element of volume dV does comprise a thermodynamic system within the limitations imposed by the concept of a local thermodynamic state.

From here on therefore, we shall consider the rate of entropy production $\dot{s}$ and the flux of interaction $\dot{h}_i$ to be at any instant uniquely determined by the thermodynamic state, as characterized by the values of the state variables.

With respect to the geometric natural reference state it can be observed that its rate of change, characterized by $\dot{\bar{d}a_\alpha}$, may be expressed in terms of quantities, determined by a local thermodynamic process through the values of the state variables, as well as in terms of the rate of

change of the tensor $b_{\alpha i}$ and the velocity field of the moving continuum:

$$\frac{d}{dt}a_\alpha = p_{\alpha i} dx_i = \left(\dot{b}_{\alpha i} + b_{\alpha j} \frac{\partial \dot{x}_j}{\partial x_i} \right) dx_i,$$

or

$$\dot{b}_{\alpha i} = p_{\alpha i} - b_{\alpha j} \frac{\partial \dot{x}_j}{\partial x_i}, \quad (9)$$

where the tensor $p_{\alpha i}$ shall now be uniquely determined by the values of the state variables. This concept of a rate of change of the natural reference state determined by a thermodynamic process, independent of the concept of a moving continuum, is due to ECKART (1948); though by him it was formulated in a more restricted sense in terms of a rate of change of the reference metric.

With the aid of (9) the rate of change of the state variables $C_{\alpha\beta}$ can be expressed by

$$\dot{C}_{\alpha\beta} = \dot{b}_{\alpha i} b_{\beta i} + b_{\alpha i} \dot{b}_{\beta i} = p_{\alpha i} b_{\beta i} + b_{\alpha i} p_{\beta i} - 2b_{\alpha i} b_{\beta j} d_{ij}, \quad (10)$$

where d_{ij} is the rate of deformation tensor, defined by

$$d_{ij} = \frac{1}{2} \left(\frac{\partial \dot{x}_i}{\partial x_j} + \frac{\partial \dot{x}_j}{\partial x_i} \right).$$

Now, on the basis of an internal energy function $u = u(s, C_{\alpha\beta})$, a number of conclusions can be drawn from the first law of thermodynamics and the principle of determinism.

The rate of change of u is given by

$$\dot{u} = \frac{\partial u}{\partial C_{\alpha\beta}} \dot{C}_{\alpha\beta} + \frac{\partial u}{\partial s} \dot{s},$$

or, according to expressions (4) and (10), by

$$\rho \dot{u} = 2\rho \frac{\partial u}{\partial C_{\alpha\beta}} b_{\alpha i} p_{\beta i} - 2\rho \frac{\partial u}{\partial C_{\alpha\beta}} b_{\alpha i} b_{\beta j} d_{ij} + \rho \frac{\partial u}{\partial s} \dot{s} - \frac{\partial u}{\partial s} \frac{\partial \dot{h}_i}{\partial x_i}. \quad (11)$$

We shall define the following quantities, which are determined by the thermodynamic state through the internal energy function u :

$$t_{ij} = -2\rho \frac{\partial u}{\partial C_{\alpha\beta}} b_{\alpha i} b_{\beta j}, \quad (12)$$

$$T = \frac{\partial u}{\partial s}. \quad (13)$$

The tensor t_{ij} will be denoted as stress tensor and the quantity T as temperature, because these quantities will appear to possess all the characteristics, usually attributed to quantities with these names.

For a body, that constitutes a closed system, conservation of energy is expressed by

$$\begin{aligned}\dot{U} + \int_V \rho \ddot{x}_i \dot{x}_i dV &= \int_V \rho (\dot{u} + \ddot{x}_i \dot{x}_i) dV \\ &= \int_V \left[t_{ij} d_{ij} - t_{ij} b_{jx}^{-1} p_{\alpha i} + T \rho \dot{s} - T \frac{\partial \dot{h}_i}{\partial x_i} + \rho \ddot{x}_i \dot{x}_i \right] dV = 0. \quad (14)\end{aligned}$$

By means of the divergence theorem, and observing that on the bounding surface of the body as a closed system holds $\dot{h}_i n_i = 0$, we can transform eq. (14) into

$$\begin{aligned}\int_V \left[\left(-\frac{\partial t_{ij}}{\partial x_j} + \rho \ddot{x}_i \right) \dot{x}_i + T \rho \dot{s} + \frac{\partial T}{\partial x_i} \dot{h}_i - t_{ij} b_{jx}^{-1} p_{\alpha i} \right] dV + \\ + \int_A t_{ij} n_j \dot{x}_i dA = 0. \quad (15)\end{aligned}$$

According to the principle of determinism, formulated above, any possible thermodynamic state and any independently chosen velocity field constitute allowable and sufficient initial conditions for the mathematical description of the subsequent motion with the accompanying thermodynamic processes. Therefore eq. (15) must hold for arbitrary velocity fields $\dot{x}_i$, while all other quantities, ρ , $\ddot{x}_i$, and the quantities determined by the thermodynamic state, are independent of $\dot{x}_i$. From the principal theorem of the calculus of variations then follows the important conclusion, that

$$\frac{\partial t_{ij}}{\partial x_j} - \rho \ddot{x}_i = 0 \text{ in } V \quad (16)$$

and

$$t_{ij} n_j = 0 \text{ on } A. \quad (17)$$

Equations (16) are to be identified as the equations of motion of Cauchy, which in our case are obtained without reference to the principle of balance of momentum, be it in the limited sense of a thermodynamically defined stress tensor. Further this stress tensor is symmetric, not by virtue of the principle of balance of moment of momentum, but because of the symmetry of the tensor $C_{\alpha\beta}$ in (12).

By eqs. (16) and (17) eq. (15), expressing the conservation of energy, is reduced to

$$\int_V \left(T \rho \dot{s} + \frac{\partial T}{\partial x_i} \dot{h}_i - t_{ij} b_{jx}^{-1} p_{\alpha i} \right) dV = 0. \quad (18)$$

The flux $\dot{h}_i$ has been introduced to represent the interaction between various regions in the body. So far no restriction has been imposed on this interaction. We shall now require that the flux of interaction $\dot{h}_i$ is such, that the eq. (18) is satisfied identically, i.e.

$$T \varrho \dot{s} + \frac{\partial T}{\partial x_i} \dot{h}_i - t_{ij} b_{jx} p_{\alpha i} = 0. \quad (19)$$

Let us now consider a closed region of volume $V_{\text{int.}}$, bounded by a surface $A_{\text{int.}}$ inside the body. For the rate of change of the energy, contained in the volume $V_{\text{int.}}$, is found

$$\int_{V_{\text{int.}}} \varrho (\dot{u} + \ddot{x}_i \dot{x}_i) dv = \int_{A_{\text{int.}}} (t_{ij} n_j \dot{x}_i - T \dot{h}_i n_i) dA. \quad (20)$$

Hence the interaction between the region $V_{\text{int.}}$ and the rest of the body can be interpreted as a flux of mechanical energy (i.e. defined with the aid of the velocity field of the continuum), $t_{ij} n_j \dot{x}_i$, and a flux of non-mechanical energy, $-T \dot{h}_i n_i$, through the surface $A_{\text{int.}}$. The flux $q_i = T \dot{h}_i$ is then to be identified as the heatflux.

While according to (17) the mechanical interaction vanishes, if the thermodynamic state is such that $t_{ij} n_j = 0$, the non-mechanical interaction by the very definition of $\dot{h}_i$, vanishes only if $\dot{h}_i n_i = 0$. Interaction without energy exchange is beyond the scope of thermodynamics. Hence the temperature T must be unequal to zero for all thermodynamic states, where a non-mechanical interaction is possible. Therefore the scale for T , hitherto left undefined, must satisfy the condition $T \geq 0$; the state with $T = 0$ being defined as the limiting case of a state where any non-mechanical thermodynamic interaction becomes impossible. Inequality (4), after substitution of the heatflux, $q_i = T \dot{h}_i$, with the so-defined absolute temperature, is known as the Clausius-Duhem inequality.

Irreversible Thermodynamics

For the problem of rheology, as it is being considered here, the theory of irreversible thermodynamics pertains to the determination of constitutive equations for the quantities $\dot{s}$, $\dot{h}_i$ and $p_{\alpha i}$, which occur in eq. (19).

First we shall show that the tensor $p_{\alpha i}$ must satisfy a specific condition in order to ensure, that the logical requirement is fulfilled, that the mass density, corresponding to the geometric natural reference state, is constant and equal to a given value ϱ_0 .

The length of a line element in the natural reference state is according to (5) defined by

$$dl_0^2 = da_\alpha da_\alpha = b_{\alpha i} b_{\alpha j} dx_i dx_j. \quad (21)$$

The tensor

$$g_{ij} = b_{\alpha i} b_{\alpha j}, \quad g = \det(g_{ij}) \neq 0, \quad (22)$$

is the metric tensor, that defines the generally non-Euclidean metric of the natural reference state in the x_1, x_2, x_3 space. By virtue of the following equalities

$$\begin{aligned} \frac{\dot{}}{\ln g} &= g_{ij}^{-1} \dot{g}_{ij} = g_{ij}^{-1} \left[\left(p_{\alpha i} - b_{\alpha k} \frac{\partial \dot{x}_k}{\partial x_i} \right) b_{\alpha j} + b_{\alpha i} \left(p_{\alpha j} - b_{\alpha k} \frac{\partial \dot{x}_k}{\partial x_j} \right) \right], \\ \frac{\dot{}}{\ln g} &= g_{ij}^{-1} (p_{\alpha i} b_{\alpha j} + b_{\alpha i} p_{\alpha j}) - 2 \frac{\partial \dot{x}_k}{\partial x_k}, \end{aligned}$$

and with the aid of eq. (1) in the form

$$\frac{\dot{g}}{g} = \ln \frac{\dot{g}}{g_0} = - \frac{\partial \dot{x}_k}{\partial x_k}$$

we arrive at

$$g_{ij}^{-1} (p_{\alpha i} b_{\alpha j} + b_{\alpha i} p_{\alpha j}) = 2 \ln \frac{\dot{g_0} \sqrt{g}}{g}.$$

Since

$$g_{ij} = (b_{\alpha i} b_{\alpha j})^{-1} = b_{i\alpha} b_{j\alpha},$$

we have

$$g_{ij}^{-1} (p_{\alpha i} b_{\alpha j} + b_{\alpha i} p_{\alpha j}) = 2 b_{i\alpha} p_{\alpha i} = 2 \ln \left(\frac{\dot{g_0} \sqrt{g}}{g} \right). \quad (23)$$

Locally the metric tensor g_{ij} defines the relation between a material element of volume dV in the x_1, x_2, x_3 space and the same material element of volume dV_0 in the natural reference state by

$$dV_0 = \sqrt{g} dV.$$

Because the mass content of dV and dV_0 is the same, we have

$$\begin{aligned} \rho_0 dV_0 &= \rho_0 \sqrt{g} dV = \rho dV \\ \frac{\rho_0 \sqrt{g}}{\rho} &= 1. \end{aligned} \quad (24)$$

Hence according to eqs. (23) and (24) the tensor $p_{\alpha i}$ must satisfy the condition

$$2 b_{i\alpha} p_{\alpha i} = 0. \quad (25)$$

If the stress tensor is decomposed into its deviator s_{ij} and its pressure component p ,

$$t_{ij} = s_{ij} - p\delta_{ij}, \quad s_{\alpha\alpha} = 0, \quad (26)$$

we can observe, that because of condition (25), the pressure component does not contribute to the rate of energy dissipation. According to eq. (19)

$$T\dot{\rho}\dot{s} = -\frac{\partial T}{\partial x_i} \dot{h}_i + s_{ij} b_{j\alpha}^{-1} p_{,\alpha i} - p b_{j\alpha}^{-1} p_{,\alpha j},$$

or by (25)

$$T\dot{\rho}\dot{s} = -\frac{\partial T}{\partial x_i} \dot{h}_i + s_{ij} b_{j\alpha}^{-1} p_{,\alpha i}. \quad (27)$$

As all three quantities, T , ρ , and $\dot{s}$, are non-negative, we know from what has been postulated in the preceding paragraphs, that the rate of energy dissipation $T\dot{\rho}\dot{s}$ is a positive, semi-definite function of state variables.

We note that the rate of energy dissipation is always the scalar product of a vector or tensor of quantities, determined by the thermodynamic state, and a dissipation vector or tensor. The relative magnitudes of the components of the dissipation vector or tensor shall depend on the dissipation mechanism. We shall now *postulate* that sufficient information on the dissipation mechanism is contained in the energy dissipation function, such as to ensure that the relative magnitudes of the components of the dissipation vector or tensor depend on the state variables solely through the functional dependence of the energy dissipation function on those state variables, that are associated with the dissipation vector or tensor in the expression for the rate of energy dissipation.

The quantities $\frac{\partial T}{\partial x_i}$ and s_{ij} in eq. (27) are no state variables, since they are not invariant under the transformation (2). We shall show, however, that they are related to state variables through orthogonal transformations.

According to the theorem on the unique polar decomposition of a tensor with a non-vanishing determinant, we have

$$b_{\alpha i} = C_{\alpha\beta}^{1/2} R_{\beta i}, \quad R_{\alpha i} R_{\beta i} = \delta_{\alpha\beta}, \quad (28)$$

where $C_{\alpha\beta}^{1/2}$ is invariant and where $R_{\alpha i}$ obeys the transformation rule

$$R'_{\alpha i} = R_{\alpha j} \bar{R}_{ij}. \quad (29)$$

Hence the quantities

$$t_{ij} R_{\alpha i} R_{\beta j} = -2\varrho \frac{\partial u}{\partial C_{\mu\nu}} C_{\mu\alpha}^{1/2} C_{\nu\beta}^{1/2} \quad (30)$$

are proper state variables.

Further it can be observed that by virtue of the invariance of the quantity

$$\frac{\partial T}{\partial x_i} dx_i = \frac{\partial T}{\partial x_j} \bar{R}_{ji} dx'_j$$

the transformation rule for $\frac{\partial T}{\partial x_i}$ reads

$$\left(\frac{\partial T}{\partial x_i}\right)' = \frac{\partial T}{\partial x_j} \bar{R}_{ij}. \quad (31)$$

Therefore the quantities

$$R_{\alpha i} \frac{\partial T}{\partial x_i} = R_{\alpha j} \bar{R}_{ij} \frac{\partial T}{\partial x_k} \bar{R}_{ik} = \left(R_{\alpha i} \frac{\partial T}{\partial x_i}\right)' \quad (32)$$

are invariant under the transformation (2) and are proper state variables.

The orthogonal transformations applied to t_{ij} and $\frac{\partial T}{\partial x_i}$ in (30) and (32) are of importance in the case of anisotropy. Then the rate of energy dissipation is not a function of the invariants of these quantities and a rotation is necessary to bring the material directions in concordance with the orthogonal triads, specifying the local anisotropy.

We shall now assume that the rate of energy dissipation due to spatial interaction, represented by the first term on the right hand side of eq. (27), is independent of the local rate of energy dissipation, represented by the second term. We then have

$$T\varrho\dot{s} = D_1 + D_2 \quad (33)$$

with

$$D_1 = -\frac{\partial T}{\partial x_i} \dot{h}_i = D_1(p, T, R_{\alpha i} \frac{\partial T}{\partial x_i}) \geq 0, \quad (34)$$

$$D_2 = s_{ij} b_{j\alpha} p_{\alpha i} = D_2(p, T, s_{ij} R_{\alpha i} R_{\beta j}) \geq 0. \quad (35)$$

According to what has been postulated above the vector $\dot{h}_i$, as a dissipation vector in $\frac{\partial T}{\partial x_i}$ -space, is determined by

$$\dot{h}_i = -\lambda_1 \frac{\partial D_1}{\partial \left(\frac{\partial T}{\partial x_i}\right)}, \quad (36)$$

and $b_{j\alpha} p_{\alpha i}$, as a dissipation tensor in s_{ij} -space, by

$$b_{j\alpha} p_{\alpha i} = \lambda_2 \frac{\partial D_2}{\partial s_{ij}},$$

or

$$p_{\alpha i} = b_{\alpha j} b_{j\beta} p_{\beta i} = \lambda_2 b_{\alpha j} \frac{\partial D_2}{\partial s_{ij}}. \quad (37)$$

Thus the directions of the dissipation vector and tensor satisfy the so-called normality condition with respect to surfaces of constant rate of energy dissipation in the $\frac{\partial T}{\partial x_i}$ - and s_{ij} -space respectively. This condition has by ZIEGLER been interpreted as a generalization to the nonlinear case of the Onsager relations (ZIEGLER 1961). Here we have simply postulated this condition on the basis of deterministic reasoning. It leads to constitutive equations of a special nature, which have the advantage that they are sufficiently specific to permit, if experimentally verified, the definition of rheological properties of materials in terms of an empirically determinable scalar function for the rate of energy dissipation.

The material derivative of the tensor $b_{\alpha i}$ and of the state variables $C_{\alpha\beta}$, given by (9) and (10), can now be expressed in terms of the velocity field of the continuum and the function D_2

$$\dot{b}_{\alpha i} = b_{\alpha j} \left[\lambda_2 \frac{\partial D_2}{\partial s_{ij}} - \frac{\partial \dot{x}_j}{\partial x_i} \right], \quad (38)$$

$$\dot{C}_{\alpha\beta} = \lambda_2 \left[b_{\alpha j} \frac{\partial D_2}{\partial s_{ij}} b_{\beta i} + b_{\alpha i} b_{\beta j} \frac{\partial D_2}{\partial s_{ij}} \right] - 2b_{\alpha i} b_{\beta j} d_{ij},$$

or

$$\dot{C}_{\alpha\beta} = 2b_{\alpha i} b_{\beta j} \left(\lambda_2 \frac{\partial D_2}{\partial s_{ij}} - d_{ij} \right). \quad (39)$$

The values of the scalar factors λ_1 and λ_2 , that determine the magnitude of the dissipation quantities, are found by substitution of (36) and (37) into the expressions (34) and (35)

$$\lambda_1 = \left[\frac{\partial T}{\partial x_i} \frac{\partial D_1}{\partial \left(\frac{\partial T}{\partial x_i} \right)} \right]^{-1} D_1, \quad (40)$$

$$\lambda_2 = \left[s_{ij} \frac{\partial D_2}{\partial s_{ij}} \right]^{-1} D_2. \quad (41)$$

The theory is now complete, since the rate of change of all quantities, that have been introduced, is determined as soon as an initial thermo-

dynamic state and an initial velocity field are given. The material properties and the constitutive equations are fully defined in terms of the function for the internal energy, $u = u(C_{\alpha\beta}, s)$, and the functions $D_1 = D_1(p, T, R_{\alpha i} \frac{\partial T}{\partial x_i})$ and $D_2 = D_2(p, T, s_{ij} R_{\alpha i} R_{\beta j})$, that determine the rate energy dissipation in the irreversible thermodynamic processes.

It should be observed that the function $u = u(C_{\alpha\beta}, s)$ need only to define the change of the internal energy per unit mass with respect to some known reference state, characterized by a mass density ρ_0 , an absolute temperature T_0 , and a stress tensor $(t_{ij})_0$. The absolute value of the internal energy per unit mass is irrelevant in the theory of rheology; this in contrast to the absolute values of the dissipation functions D_1 and D_2 , which determine the magnitudes of the dissipation quantities.

Summary of Rheological Equations

The rheological problem, according to the theory that has been formulated in this paper, is described by the following equations:

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x_i} \dot{x}_i + \rho \frac{\partial \dot{x}_i}{\partial x_i} = 0; \quad (1)$$

$$\rho \left(\frac{\partial s}{\partial t} + \frac{\partial s}{\partial x_i} \dot{x}_i \right) = - \frac{\partial \dot{h}_i}{\partial x_i} + \frac{D_1 + D_2}{T}; \quad (4), (33)$$

$$\dot{h}_i = -\lambda_1 \frac{\partial D_1}{\partial \left(\frac{\partial T}{\partial x_i} \right)}; \quad (36)$$

$$\frac{\partial b_{\alpha i}}{\partial t} + \frac{\partial b_{\alpha i}}{\partial x_k} \dot{x}_k = b_{\alpha j} \left(\lambda_2 \frac{\partial D_2}{\partial s_{ij}} - \frac{\partial \dot{x}_j}{\partial x_i} \right); \quad (38)$$

$$\frac{\partial C_{\alpha\beta}}{\partial t} + \frac{\partial C_{\alpha\beta}}{\partial x_i} \dot{x}_i = 2b_{\alpha i} b_{\beta j} \left[\lambda_2 \frac{\partial D_2}{\partial s_{ij}} - \frac{1}{2} \left(\frac{\partial \dot{x}_i}{\partial x_j} + \frac{\partial \dot{x}_j}{\partial x_i} \right) \right]; \quad (39)$$

$$R_{\alpha i} = \bar{C}_{\alpha\beta}^{-1/2} b_{\beta i}; \quad (28)$$

$$t_{ij} = -2\rho \frac{\partial u}{\partial C_{\alpha\beta}} b_{\alpha i} b_{\beta j} = s_{ij} - p\delta_{ij}, \quad p = -\frac{1}{3}t_{ii}; \quad (12)$$

$$T = \frac{\partial u}{\partial s}, \quad T \geq 0; \quad (13)$$

$$\frac{\partial t_{ij}}{\partial x_j} = \rho \ddot{x}_i = \rho \left(\frac{\partial \dot{x}_i}{\partial t} + \frac{\partial \dot{x}_i}{\partial x_k} \dot{x}_k \right); \quad (16)$$

$$u = u(C_{\alpha\beta}, s), \quad u = 0 \quad \text{for} \quad \rho = \rho_0, \quad T = T_0, \quad t_{ij} = (t_{ij})_0; \quad (8)$$

$$D_1 = D_1 \left(p, T, R_{\alpha i} \frac{\partial T}{\partial x_i} \right), \quad \lambda_1 = \left[\frac{\partial T}{\partial x_i} \frac{\partial D_1}{\partial \left(\frac{\partial T}{\partial x_i} \right)} \right]^{-1} D_1; \quad (34), (40)$$

$$D_2 = D_2(p, T, s_{ij} R_{\alpha i} R_{\beta j}), \quad \lambda_2 = \left[s_{ij} \frac{\partial D_2}{\partial s_{ij}} \right]^{-1} D_2. \quad (35), (41)$$

These equations define a system of 30 field equations for the 30 dependent variables ρ , $\dot{x}_i$, s , $\dot{h}_i$, T , $b_{\alpha i}$, $C_{\alpha\beta}$, and t_{ij} . Proper initial conditions for this system are of the form

$$\begin{aligned} t = 0: \quad b_{\alpha i} &= b_{\alpha i}(x_1, x_2, x_3), \\ s &= s(x_1, x_2, x_3), \\ \dot{x}_i &= \dot{x}_i(x_1, x_2, x_3). \end{aligned}$$

The initial mass density follows then from (24)

$$\rho = \rho_0 \sqrt{g}, \quad g = \det(g_{ij}), \quad g_{ij} = b_{\alpha i} b_{\alpha j},$$

while the initial values of $C_{\alpha\beta}$ are determined by $C_{\alpha\beta} = b_{\alpha i} b_{\beta i}$.

For a body that constitutes a closed thermodynamic system, the boundary conditions are given by

$$t_{ij} n_j = 0, \quad \dot{h}_i n_i = 0 \quad \text{on } A.$$

Proper boundary conditions for non-closed thermodynamic systems are

$$t_{ij} n_j = p_i^0 \quad \text{or} \quad \dot{x}_i = \dot{x}_i^0 \quad \text{on } A$$

and

$$T = T^0 \quad \text{or} \quad \dot{h}_i n_i = \dot{h}^0 \quad \text{on } A.$$

Here the super index 0 indicates a prescribed function of time.

It is clear that the boundary conditions impose certain restrictions on the initial conditions in the boundary layer of the body. It should be realized, however, that prescribed initial boundary conditions are an artificial concept in the description of natural phenomena occurring in infinite space, where all systems interact with adjoining systems and where this interaction is never a one-way traffic.

Special Cases

In order to illustrate the theory we shall now consider a number of special constitutive equations, corresponding to special forms for the functions u , D_1 and D_2 .

a) Gases

Let us consider the case that the internal energy per unit mass depends only on the absolute temperature, $u = f(T)$, or more specifically

$$u = c(T - T_0), \quad c = \text{constant.} \quad (42)$$

With the aid of (13) we arrive at the following equation

$$c \frac{\partial u}{\partial s} - u = cT_0,$$

which determines the dependence of u on s

$$u = k \exp\left(\frac{s}{c}\right) - cT_0, \quad k = k(C_{\alpha\beta}). \quad (43)$$

First we shall assume now that the effect of changes of geometry on the state of the medium is solely represented by the mass density. According to (24) we may then put $k = k(g)$. More specifically we shall consider ($u = 0$ for $g = 1$ and $s = 0$)

$$u = cT_0 \left[g^\gamma \exp\left(\frac{s}{c}\right) - 1 \right]. \quad (44)$$

The stress tensor and the temperature are then given by

$$\begin{aligned} t_{ij} &= -2\rho \frac{\partial u}{\partial C_{\alpha\beta}} b_{\alpha i} b_{\beta j} = -2\rho \frac{\partial u}{\partial g} g \delta_{ij} \\ &= -2c\gamma\rho T_0 g^\gamma \exp\left(\frac{s}{c}\right) \delta_{ij}, \end{aligned} \quad (45)$$

$$T = \frac{\partial u}{\partial s} = T_0 g^\gamma \exp\left(\frac{s}{c}\right). \quad (46)$$

Stress arises in this case only as a hydrostatic pressure, which by elimination of the entropy from (46) and (45) is found to obey the equation of state for a perfect gas.:

$$p = 2c\gamma\rho T.$$

The constant c is to be interpreted as the specific heat at constant volume, c_v , while the introduction of the specific heat at constant pressure, c_p , through the enthalpy or heat function h .

$$dh = d\left(u + \frac{p}{\rho}\right) = (c_v + 2c_v\gamma) dT = c_p dT,$$

shows that the constant $2c_v\gamma$ is the gas constant $R = c_p - c_v$.

The simplest example of an equation for u of the type (43), that leads to shear stresses, is offered by

$$u = cT_0 \left[\frac{C_{xx}}{3} \exp\left(\frac{s}{c}\right) - 1 \right]. \quad (47)$$

For the stresses and the temperature follows

$$t_{ij} = -2\rho \frac{\partial u}{\partial C_{\alpha\beta}} b_{\alpha i} b_{\beta j} = -\frac{2}{3} \rho c T_0 \exp\left(\frac{s}{c}\right) g_{ij}, \quad (48)$$

$$T = \frac{\partial u}{\partial s} = \frac{T_0}{3} C_{xx} \exp\left(\frac{s}{c}\right). \quad (49)$$

Since

$$g_{ii} = C_{xx},$$

the expression for the pressure component may, after elimination of s , be written in the form

$$p = -\frac{1}{3} t_{ii} = \frac{2}{9} \rho c T_0 \exp\left(\frac{s}{c}\right) g_{ii} = \frac{2}{3} \rho c T. \quad (50)$$

This is the equation of state for a mono-atomic gas with

$$R = \frac{2}{3} c = c_p - c_v = \frac{2}{3} c_v.$$

For a complete description of the mono-atomic gas the dissipation functions D_1 and D_2 must be specified. We shall examine the simplest forms, that satisfy the conditions $D_1 \geq 0$, $D_2 \geq 0$.

$$D_1 = \alpha \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i}, \quad \alpha = \alpha(p, T) > 0, \quad (51)$$

$$D_2 = \beta s_{ij} s_{ij}, \quad \beta = \beta(p, T) > 0. \quad (52)$$

We then have according to (36) a heatflux $q_i = T \dot{h}_i$, determined by

$$q_i = -\alpha T \frac{\partial T}{\partial x_i}, \quad (53)$$

which is equivalent to Fourier's law of heat conduction. The dissipation function D_2 can be used to determine the stress rate

$$\dot{t}_{ij} = t_{ij} \left(\frac{\dot{s}}{c} + \frac{\dot{\rho}}{\rho} \right) - \frac{2}{3} c T_0 \rho \exp\left(\frac{s}{c}\right) \dot{g}_{ij}$$

or, according to (1) and (38)

$$\dot{t}_{ij} = t_{ik} \frac{\partial \dot{x}_k}{\partial x_j} + t_{kj} \frac{\partial \dot{x}_k}{\partial x_i} + t_{ij} \frac{\partial \dot{x}_k}{\partial x_k} - t_{ij} \frac{\dot{s}}{c} = \beta (t_{ik} s_{kj} + t_{jk} s_{ki}). \quad (54)$$

This rather unwieldy expression may be replaced by a considerably simpler constitutive equation in the case of quasi-stationary, small distortions with respect to the natural reference state.

Small distortions with respect to the natural reference state can be defined with

$$\frac{C_{\alpha\beta}}{g^{\frac{1}{3}}} = \delta_{\alpha\beta} + e_{\alpha\beta}, \quad |e_{\alpha\beta}| \ll 1. \quad (55)$$

We note that eq. (39) can be written in the form

$$\begin{aligned} \frac{\dot{\frac{1}{g^{\frac{1}{3}}}}}{\frac{1}{g^{\frac{1}{3}}}} &= \frac{\dot{\frac{1}{g^{\frac{1}{3}}}}}{\frac{1}{g^{\frac{1}{3}}}} \left(\frac{C_{\alpha\beta}}{\frac{1}{g^{\frac{1}{3}}}} \right) + g^{\frac{1}{3}} \left(\frac{\dot{C}_{\alpha\beta}}{\frac{1}{g^{\frac{1}{3}}}} \right) = \\ &= -\frac{2}{3} g^{\frac{1}{3}} \frac{\partial \dot{x}_k}{\partial x_k} \left(\frac{C_{\alpha\beta}}{\frac{1}{g^{\frac{1}{3}}}} \right) + 2b_{\alpha i} b_{\beta j} \left[\lambda_2 \frac{\partial D_2}{\partial s_{ij}} - d_{ij} + \frac{1}{3} d_{kk} \delta_{ij} \right]. \end{aligned}$$

But according to eqs (1) and (24) we have

$$\frac{\dot{\frac{1}{g^{\frac{1}{3}}}}}{\frac{1}{g^{\frac{1}{3}}}} + \frac{2}{3} g^{\frac{1}{3}} \frac{\partial \dot{x}_k}{\partial x_k} = 0.$$

Hence the rate of distortion is given by

$$\left(\frac{\dot{C}_{\alpha\beta}}{\frac{1}{g^{\frac{1}{3}}}} \right) = \frac{2b_{\alpha i} b_{\beta j}}{\frac{1}{g^{\frac{1}{3}}}} \left[\lambda_2 \frac{\partial D_2}{\partial s_{ij}} - d_{ij} + \frac{1}{3} d_{kk} \delta_{ij} \right], \quad (56)$$

or, after substitution of the expressions (48), (49), (50), and (52)

$$\begin{aligned} \left(\frac{\dot{C}_{\alpha\beta}}{\frac{1}{g^{\frac{1}{3}}}} \right) &= -6p\beta \left(\frac{C_{\alpha\beta}}{\frac{1}{g^{\frac{1}{3}}}} \right) \left(\frac{C_{\beta\gamma} - \frac{1}{3} C_{\delta\delta} \delta_{\beta\gamma}}{C_{xx}} \right) - \\ &\quad - \frac{2b_{\alpha i} b_{\beta j}}{\frac{1}{g^{\frac{1}{3}}}} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right). \end{aligned} \quad (57)$$

Introduction of the tensor $e_{\alpha\beta}$ from (55) leads to

$$\begin{aligned} \left(\frac{\dot{C}_{\alpha\beta}}{\frac{1}{g^{\frac{1}{3}}}} \right) &= \dot{e}_{\alpha\beta} = -2p\beta (\delta_{\alpha\gamma} + e_{\alpha\gamma}) \left(\frac{e_{\beta\gamma} - \frac{1}{3} e_{\delta\delta} \delta_{\beta\gamma}}{1 + \frac{1}{3} e_{xx}} \right) - \\ &\quad - \frac{2b_{\alpha i} b_{\beta j}}{\frac{1}{g^{\frac{1}{3}}}} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right). \end{aligned} \quad (58)$$

If we neglect the tensor $e_{\alpha\gamma}$ with respect to $\delta_{\alpha\gamma}$, because the distortions are assumed to be small, we have

$$\dot{e}_{\alpha\beta} + 2p\beta \left(e_{\alpha\beta} - \frac{1}{3} e_{\gamma\gamma} \delta_{\alpha\beta} \right) \approx - \frac{2b_{\alpha i} b_{\beta j}}{g^{\frac{1}{3}}} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right). \quad (59)$$

It follows from the theory of differential equations that

$$|\dot{e}_{\alpha\beta}| \ll \left| \frac{2b_{\alpha i} b_{\beta j}}{g^{\frac{1}{3}}} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right) \right|, \quad (60)$$

provided in the gas flow the following conditions are satisfied

$$\left| \frac{d^n}{dt^n} \left[\frac{2b_{\alpha i} b_{\beta j}}{g^{\frac{1}{3}}} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right) \right] \right| \ll (2p\beta)^n \left| \frac{2b_{\alpha i} b_{\beta j}}{g^{\frac{1}{3}}} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right) \right|. \quad (61)$$

By virtue of (60) we may then put according to (56)

$$d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \approx \lambda_2 \frac{\partial D_2}{\partial s_{ij}} = \beta s_{ij}. \quad (62)$$

Thus we are led to the equations of viscosity of Navier-Stokes without volume viscosity. The shear stresses are in our case still thermodynamically defined quantities, though their thermodynamic origin is fully obscured in the eqs. (62).

In most gas flows the conditions (61) will be satisfied. Shock waves may be an exception, and it is just in connection with the calculated and measured thickness of shock waves, that the need for the existence of volume viscosity was felt (GILBARG and PAOLUCCI 1953). Perhaps the explanation for the discrepancy between theory and experiment must in this case be sought in the fact, that for shock waves the conditions (61) are not satisfied. The decisive quantity is here the value of

$$2p\beta = \frac{\rho RT}{\mu}, \quad (63)$$

where μ represents the viscosity ($s_{ij} = 2\mu(d_{ij} - \frac{1}{3}d_{kk}\delta_{ij})$).

b) Elastic Materials

An elastic material will be defined here as a material, for which the dissipation tensor $p_{\alpha i}$ (9) vanishes. The geometric natural reference state can then always be defined such that the system (5), $da_x = b_{\alpha i} dx_i$, represents exact differentials for functions $a_x = a_x(x_1, x_2, x_3)$, or

$$b_{\alpha i} = \frac{\partial a_x}{\partial x_i}. \quad (64)$$

Hence the motion of elementary particles in an elastic body can be described by the motion of a continuum, in which each particle occupies a material point. The displacement tensor $\frac{\partial a_\alpha}{\partial x_i}$ describes the change, which the displacement from the state of the body at time t to the reference state induces in the relative position of any two points as these points draw together.

For the material of a body, that as a system free in space will not desintegrate, the stress-free state must correspond to a thermodynamic equilibrium state with non-vanishing mass density. Besides on the temperature, the internal energy function u for such a material will depend on the inter-particle distances, and thereby on $g = (dV_0/dV)^2$. The simplest form of such a function is presented by

$$u = cT + cT_0(g^\gamma - 2)$$

or, according to

$$u - c \frac{\partial u}{\partial s} = cT_0(g^\gamma - 2),$$

by

$$u = cT_0 \left[k(C_{\alpha\beta}) e^{\frac{s}{c}} + g^\gamma - 2 \right]. \quad (65)$$

Let us consider an elastic body for which there exists a state, to be taken as reference state, which is completely stress-free. Any choice for $k(C_{\alpha\beta})$ in the function u , defined with respect to this reference state, must satisfy the following requirements:

- 1^o the stresses t_{ij} vanish for $T = T_0$ and $C_{\alpha\beta} = \delta_{\alpha\beta}$,
- 2^o u is positive definite for all isentropic deformations ($s = 0$) from the stress-free reference state.

If we restrict ourselves to isotropic materials, and if the first invariant of the inverse of $C_{\alpha\beta}$ is denoted by $\bar{C}_{\alpha\alpha}^{-1}$, the following expression for u satisfies the requirements, formulated above.

$$u = cT_0 \left[\frac{1}{3} \left\{ \left(\frac{1}{2} - \beta \right) g^{-\frac{1}{3}} C_{\alpha\alpha} + \left(\frac{1}{2} + \beta \right) g^{\frac{1}{3}} \bar{C}_{\alpha\alpha}^{-1} \right\} \times \right. \\ \left. \times g^\gamma \exp \left(\frac{s}{c} \right) + g^\gamma - 2 \right]. \quad (66)$$

Here c , β , and γ represent material constants with the restriction: $-\frac{1}{2} \leq \beta \leq \frac{1}{2}$.

It can be observed that, since $\text{Det} \left(g^{-\frac{1}{3}} C_{\alpha\beta} \right) = 1$, the tensor $g^{-\frac{1}{3}} C_{\alpha\beta}$ is a measure for distortion at constant volume, while g represents the influence of change of volume.

Expression (66) appears to lead to some of the thermo-elastic effects observed in rubber-like materials, where the "compression modulus", $4\varrho c\gamma^2 T_0$, is large compared to the "shear modulus", $\frac{2}{3}\varrho c T_0$. For $\gamma \rightarrow \infty$ we arrive at the Mooney-Rivlin theory for rubber, in which the pressure component is treated as a thermodynamically undefined quantity and the deformations are subjected to the subsidiary condition $g = 1$.

However, the three material constants in expression (66) prove to be inadequate to cope with the experimental data on rubber-like materials. A better quantitative description is expected from a five constants theory, based on the following expressions for u :

$$u = c(T - T_0) + C_1(g^\gamma - 1) \quad (67)$$

and

$$u = C_2 \left[\frac{1}{3} \left\{ \left(\frac{1}{2} - \beta \right) g^{-\frac{1}{3}} C_{\alpha\alpha} + \left(\frac{1}{2} + \beta \right) g^{\frac{1}{3}} C_{\alpha\alpha}^{-1} \right\} - 1 \right] e^{\frac{s}{c}} + cT_0 \left(e^{\frac{s}{c}} - 1 \right) + C_1 \left[(g^\gamma - 1) e^{\frac{s}{c}} + (g^\gamma - 1) \right]. \quad (68)$$

Here the isothermal bulkmodulus of elasticity, C , the shear modulus of elasticity, G , and the coefficient of cubic thermal expansion, α , all defined with respect to small deviations from the natural reference state, are related to the specific heat at constant volume, c , and to the constants C_1 , C_2 , and γ by

$$C = 8\varrho\gamma^2 C_1 \left[1 - \frac{C_1}{2cT_0} \right], \quad G = \frac{2}{3}\varrho C_2, \\ \alpha = \frac{1}{4\gamma T_0 \left[1 - \frac{C_1}{2cT_0} \right]}. \quad (69)$$

c) Simple Solids

A material will be denoted here as a solid, if the stress-free state corresponds to a thermodynamic equilibrium state. As it already follows from this definition of a solid, and as it will be shown in the following, it may be difficult to distinguish between a solid and a liquid.

The adjective "simple" will be used here to indicate that the same functions u , D_1 and D_2 apply to the material in all points of the body. Unfortunately all real solids are to some extent non-simple solids, as for instance all metals with their polycrystalline structure.

In contrast to an elastic material, in a general solid the dissipation tensor $p_{\alpha i}$ shall vanish only under special conditions of stress and temperature; and hence the system (5), $da_\alpha = b_{\alpha i} dx_i$, after an arbitrary

thermodynamic history from a certain reference time t_0 , will not represent exact differentials for functions $a_x = a_x(x_1, x_2, x_3)$.

For the internal energy function u of a simple solid we could consider expression (68). However, since for most solids, as for instance all metals, only small deviations from the natural reference state can be realised, it usually suffices to consider the theory for this case.

We shall first consider the theory for small deviations from the natural reference state as it is applied in the field of structural analysis. There the theory is usually further restricted by the condition that the deviations of the configuration in the natural reference state from a certain reference configuration of the continuum remain small.

If we denote the coordinates of the material points of the continuum in a certain reference geometry by ξ_1, ξ_2, ξ_3 , then we can define the motion of the continuum by three single-valued functions

$$x_i = x_i(\xi_1, \xi_2, \xi_3, t). \quad (70)$$

We can now write

$$da_x = b_{\alpha i} dx_i = b_{\alpha i} \frac{\partial x_i}{\partial \xi_k} d\xi_k. \quad (71)$$

If we put

$$b_{\alpha i} \frac{\partial x_i}{\partial \xi_k} = \delta_{\alpha k} + \beta_{\alpha k}, \quad (72)$$

then we can express the condition, that the deviations of the configuration in the natural reference state from the reference configuration of the continuum remain small, by

$$|\beta_{\alpha k}| \ll 1. \quad (73)$$

Here it should be observed that we wish the quantities $\beta_{\alpha k}$ to be invariant under the Galilean transformation (2) in order that condition (73) may be fulfilled, irrespective of the choice of the inertial system. The coordinates ξ_1, ξ_2, ξ_3 should then be invariant under the transformation (2), which implies that the axes of the coordinate system ξ_i must concur with fixed material directions in the reference geometry of the body, like the orthogonal triads, that serve as a base for the da_x 's.

If we introduce as a measure of deformation of the continuum the Lagrangian strain tensor

$$E_{ij} = \frac{1}{2} \left(\frac{\partial x_k}{\partial \xi_i} \frac{\partial x_k}{\partial \xi_j} - \delta_{ij} \right), \quad (74)$$

and if we take as geometric state variables the components of an "elastic" strain tensor, defined by

$$E'_{\alpha\beta} = \frac{1}{2} \left(C_{\alpha\beta} - \delta_{\alpha\beta} \right) = \frac{1}{2} \left(b_{ix}^{-1} b_{i\beta}^{-1} - \delta_{\alpha\beta} \right), \quad (75)$$

then we have the equality

$$E'_{\alpha\beta} b_{\alpha i} \frac{\partial x_i}{\partial \xi_k} b_{\beta j} \frac{\partial x_j}{\partial \xi_l} = \frac{1}{2} \left(2E_{kl} + \delta_{kl} - b_{\alpha i} \frac{\partial x_i}{\partial \xi_k} b_{\alpha j} \frac{\partial x_j}{\partial \xi_l} \right).$$

From (72) and (73) we conclude that

$$E_{ij} - E''_{ij} = E'_{\alpha\beta} \delta_{\alpha i} \delta_{\beta j} = E'_{ij}, \quad |E''_{ij}| = \frac{1}{2} |\beta_{\alpha i} \delta_{\alpha j} + \beta_{\alpha j} \delta_{\alpha i} + \beta_{\alpha i} \beta_{\alpha j}| \ll 1, \quad (76)$$

where E''_{ij} is called the inelastic or plastic strain tensor,

The state of the material is now at any time t determined by the variables E'_{ij} and s , while according to (74) and (76) the tensor E'_{ij} is defined in terms of the three functions (70) and the six independent components of the symmetric tensor E''_{ij} . The internal energy per unit mass may then be given by

$$u = u(E'_{ij}, s). \quad (77)$$

If we let the natural reference state at some instant coincide with the reference geometry of the continuum, then the mass density is the same for the natural reference state and for the reference geometry of the continuum and is equal to ϱ_0 . Accordingly, we have

$$\text{Det} \left(b_{\alpha i} \frac{\partial x_i}{\partial \xi_k} b_{\alpha j} \frac{\partial x_j}{\partial \xi_l} \right) = 1, \quad \text{or } E''_{ii} = 0. \quad (78)$$

In this case, by taking ξ_1, ξ_2, ξ_3 as the independent space variables and performing all calculations in the reference geometry of the body, we satisfy the principle of conservation of mass automatically, while the principle of conservation of energy for the body as a closed system is expressed by

$$\begin{aligned} & \int_{V_0} \varrho_0 (\dot{u} + \ddot{x}_i \dot{x}_i) dV \\ &= \int_{V_0} \left[\varrho_0 \frac{\partial u}{\partial E'_{ij}} \dot{E}_{ij} - \varrho_0 \frac{\partial u}{\partial E'_{ij}} \dot{E}''_{ij} + \varrho_0 \frac{\partial u}{\partial s} \dot{s} + \varrho_0 \ddot{x}_i \dot{x}_i \right] dV = 0 \end{aligned}$$

We introduce the temperature T by (13) and, instead of the stress tensor t_{ij} (12) of Cauchy, the pseudo stress tensor of Kirchhoff, σ_{ij}

$$\sigma_{ij} = \varrho_0 \frac{\partial u}{\partial E'_{ij}}. \quad (79)$$

Further we have according to (4) and (70)

$$\varrho_0 \dot{s} = -\frac{\varrho_0}{\varrho} \frac{\partial \dot{h}_i}{\partial \xi_k} \frac{\partial \xi_k}{\partial x_i} + \varrho_0 \dot{\bar{s}}. \quad (80)$$

On the surface of the body as a closed system $\dot{h}_i n_i = 0$ holds. With the aid of the divergence theorem the equation for conservation of energy can now be written in the form

$$\begin{aligned} \int_{V_0} \left[\left\{ -\frac{\partial}{\partial \xi_j} \left(\frac{\partial x_i}{\partial \xi_k} \sigma_{kj} \right) + \varrho_0 \ddot{x}_i \right\} \dot{x}_i + T \varrho_0 \dot{\bar{s}} + \frac{\partial}{\partial \xi_j} \left(\frac{\varrho_0}{\varrho} \frac{\partial \xi_j}{\partial x_i} T \right) \dot{h}_i - \sigma_{ij} \dot{E}_{ij}'' \right] dV + \\ + \int_{A_0} \frac{\partial x_i}{\partial \xi_k} \sigma_{kj} n_j \dot{x}_i dA = 0. \end{aligned} \quad (81)$$

By similar reasoning as applied to eq. (15) we may deduce from eq. (81) the following equations

$$\frac{\partial}{\partial \xi_j} \left(\frac{\partial x_i}{\partial \xi_k} \sigma_{kj} \right) - \varrho_0 \ddot{x}_i = 0 \quad \text{in } V_0, \quad (82)$$

$$T \varrho_0 \dot{\bar{s}} + \frac{\partial}{\partial \xi_j} \left(\frac{\varrho_0}{\varrho} \frac{\partial \xi_j}{\partial x_i} T \right) \dot{h}_i + \sigma_{ij} \dot{E}_{ij}'' = 0 \quad \text{in } V_0, \quad (83)$$

$$\frac{\partial x_i}{\partial \xi_k} \sigma_{kj} n_j = 0 \quad \text{on } A_0. \quad (84)$$

If we rewrite the expression (83) for the rate of energy dissipation in the form

$$T \varrho_0 \dot{\bar{s}} = -\frac{\partial}{\partial \xi_j} \left(\frac{\varrho_0}{\varrho} \frac{\partial \xi_j}{\partial x_i} T \right) \frac{\partial x_i}{\partial \xi_k} \frac{\partial \xi_k}{\partial x_i} \dot{h}_i + \sigma_{ij} \dot{E}_{ij}'',$$

we observe, that the rate of energy dissipation is given by the sum of two scalar products. One is the product of the vector of state variables, invariant under the transformation (2),

$$-\frac{\partial}{\partial \xi_j} \left(\frac{\varrho_0}{\varrho} \frac{\partial \xi_j}{\partial x_i} T \right) \frac{\partial x_i}{\partial \xi_k},$$

and the dissipation vector $\frac{\partial \xi_k}{\partial x_i} \dot{h}_i$. The other is the scalar product of the stress tensor σ_{ij} and the dissipation tensor $\dot{E}_{ij}''$. After introducing

$$s_{ij}^* = \sigma_{ij} + p^* \delta_{ij}, \quad p^* = -\frac{1}{3} \sigma_{\alpha\alpha}, \quad (85)$$

$$\frac{\partial T_{ij}^*}{\partial \xi_j} = \frac{\partial}{\partial \xi_j} \left(\frac{\varrho_0}{\varrho} \frac{\partial \xi_j}{\partial x_i} T \right), \quad (86)$$

and using further the notation and assumptions, underlying (33) through (37), we may write

$$D_1 = -\frac{\partial}{\partial \xi_j} \left(\frac{\rho_0}{\rho} \frac{\partial \xi_j}{\partial x_i} T \right) \dot{h}_i = D_1 \left(p^*, T, \frac{\partial T_{ji}^*}{\partial \xi_j} \frac{\partial x_i}{\partial \xi_k} \right) \geq 0, \quad (87)$$

$$D_2 = \sigma_{ij} \dot{E}_{ij}'' = s_{ij}^* \dot{E}_{ij}'' = D_2(p^*, T, s_{ij}^*) \geq 0, \quad (88)$$

$$\dot{h}_i = -\lambda_1 \frac{\partial D_1}{\partial \left(\frac{\partial T_{ji}^*}{\partial \xi_j} \right)}, \quad \lambda_1 = \left[\frac{\partial T_{ji}^*}{\partial \xi_j} \frac{\partial D_1}{\partial \left(\frac{\partial T_{ki}^*}{\partial \xi_k} \right)} \right]^{-1} D_1, \quad (89)$$

$$\dot{E}_{ij}'' = \lambda_2 \frac{\partial D_2}{\partial s_{ij}^*}, \quad \lambda_2 = \left[s_{ij}^* \frac{\partial D_2}{\partial s_{ij}^*} \right]^{-1} D_2. \quad (90)$$

The rheological problem for a certain material is again reduced to the determination of three scalar functions: the internal energy function, u , and the two dissipation functions D_1 and D_2 . The restriction that the inelastic strains shall remain small, (73), is indeed a natural one in a theory of deformation, where all changes are a priori to be defined with respect to a geometric reference state of a body. The internal energy function can no longer be considered as a function of the Lagrangian strain tensor if the condition $|\beta_{\alpha k}| \ll 1$ is not fulfilled. Consequently the geometric reference state of a body then loses its meaning with respect to the thermodynamic state of the material. A theory for large inelastic strains is a theory of flow rather than of deformation.

It can be shown that for small deviations from the natural reference state of the material $(|E'_{ij}| \ll 1, \left| \frac{s}{c_v} \right| \ll 1)$ the expression for the internal energy for an isotropic material is given by (BESSELING 1960)

$$\begin{aligned} \rho_0 u = T_0 \rho_0 s + \frac{1}{2} C \left(1 + \frac{C \alpha^2 T_0}{\rho_0 c_v} \right) E_{ii}^2 + G \left(E'_{ij} - \frac{1}{3} E_{kk} \delta_{ij} \right) \times \\ \times \left(E'_{ij} - \frac{1}{3} E_{kk} \delta_{ij} \right) - \frac{C \alpha T_0}{c_v} E_{ii} s + \frac{\rho_0 T_0}{2 c_v} s^2. \end{aligned} \quad (91)$$

Here is C the isothermal bulk modulus of elasticity, G the shear modulus of elasticity, α the coefficient of cubic thermal expansion, and c_v the specific heat per unit mass at constant volume.

Though for $|E'_{ij}| \ll 1$ the difference between ρ_0 and ρ may be neglected, the geometric non-linearities due to a deviation of $\frac{\partial x_i}{\partial \xi_j}$ from δ_{ij} play an essential role in the determination of the stability of structures. If we neglect the deviations of $\frac{\partial x_i}{\partial \xi_j}$ from δ_{ij} with respect to δ_{ij} and put $\rho = \rho_0$,

we arrive for the isentropic and the isothermal case with $E''_{ij} = 0$ at the classic linear theory of elasticity.

A non-vanishing dissipation function D_2 leads to a theory of creep, from which the theory of plasticity may be derived by a limiting process, as indicated by ZIEGLER (1962).

From the experimental fact that even for small strains the stresses s_{ij}^* cannot exceed certain values, depending on the material, we may conclude that with increasing stresses s_{ij}^* the rate of energy dissipation, given by D_2 , tends to infinity. As the relation between rate of dissipation and stress is more strongly non-linear, surfaces for equal difference in rate of dissipation will lie closer together in s_{ij}^* -space. In the limit a surface of indefinite rate of energy dissipation may be conceived, that separates the region of rate of dissipation $= 0$ from the region of rate of dissipation $= \infty$. It is the yield surface of the so-called elastic-ideally plastic material. It can be defined by an equation of the form

$$\varphi(p^*, T, s_{ij}^*) = 0. \quad (92)$$

For values of s_{ij}^* inside the yield surface the material is thermo-elastic ($\dot{E}''_{ij} = 0$). At the yield surface, as a surface of indefinite rate of energy dissipation, the rate of inelastic strain is given by

$$\dot{E}''_{ij} = \lambda_2 \frac{\partial \varphi}{\partial s_{ij}^*}. \quad (93)$$

The positive scalar λ_2 , which determines the magnitude of the rate of energy dissipation, now depends on the rate of total deformation, $\dot{E}_{ij}$, or follows from the rate of stress. In order that the state of stress does not leave the yield surface, which would imply $\dot{E}''_{ij} = 0$, the following condition must be satisfied.

$$\dot{\varphi} = \frac{\partial \varphi}{\partial s_{ij}^*} \dot{s}_{ij}^* + \frac{\partial \varphi}{\partial p^*} \dot{p}^* + \frac{\partial \varphi}{\partial T} \dot{T} = 0 \quad (94)$$

or

$$\dot{\varphi} = \frac{\partial \varphi}{\partial s_{ij}^*} 2G \left[\dot{E}_{ij} - \frac{1}{3} \dot{E}_{kk} \delta_{ij} - \dot{E}''_{ij} \right] + \frac{\partial \varphi}{\partial p^*} \dot{p}^* + \frac{\partial \varphi}{\partial T} \dot{T} = 0. \quad (95)$$

By substitution of (93) into eq. (95) we arrive at the following expression for λ_2

$$\lambda_2 = \left[2G \frac{\partial \varphi}{\partial s_{ij}^*} \frac{\partial \varphi}{\partial s_{ij}^*} \right]^{-1} \left[\frac{\partial \varphi}{\partial s_{ij}^*} 2G \left(\dot{E}_{ij} - \frac{1}{3} \dot{E}_{kk} \delta_{ij} \right) + \frac{\partial \varphi}{\partial p^*} \dot{p}^* + \frac{\partial \varphi}{\partial T} \dot{T} \right], \quad (96)$$

subject to the condition $\lambda_2 \geq 0$.

If the thermal effects, and the influence of the hydrostatic component of stress, p^* , on the yield condition, may be neglected, the plasticity equations given above are equivalent to the Prandtl-Reuss theory of plasticity (PRANDTL 1924; REUSS 1930).

In the mechanics of metal-forming we have to deal with large inelastic strains and, as it has already been pointed out above, the theory will then be a theory of flow rather than a theory of deformation. In principle the general rheological equations, derived in this paper, present such a theory of flow. They are, however, so complicated that rigorous solutions of practical problems seem to be out of the question, even if the deviations from the natural reference state remain small. If, however, the latter condition is combined with the condition of isotropy of the material, a simplified version of the theory can be formulated.

We consider as a measure of deviation from the natural reference state the quantities.

$$e'_{ij} = \frac{1}{2} (\delta_{ij} - g_{ij}), \quad (97)$$

which we subject to the condition

$$|e'_{ij}| \ll 1. \quad (98)$$

Because of (24) and (98) we may neglect the quantity $\frac{\rho - \rho_0}{\rho_0}$ with respect to unity.

Though the components of e'_{ij} are not invariant under the transformation (2) and are, therefore, themselves not state variables, the invariants of e'_{ij} do possess the required invariance properties of state variables for an isotropic material.

If we introduce the deviator of the tensor e'_{ij} ,

$$e'_{ij} = e_{ij} - \frac{1}{3} e'_{kk} \delta_{ij}, \quad (99)$$

and if for small deviations from the natural reference state ($|e'_{ij}| \ll 1$, $|\frac{s}{c_v}| \ll 1$) the expression for the internal energy is limited to terms quadratic in e'_{ij} and $\frac{s}{c_v}$, we arrive for an isotropic material at the following result

$$\rho u = T_0 \rho s + \frac{1}{2} C \left(1 + \frac{C \alpha^2 T_0}{\rho c_v} \right) e'_{ii}{}^2 + G e'_{ij} e'_{ij} - \frac{C \alpha T_0}{c_v} e'_{ii} s + \frac{\rho T_0}{2 c_v} s^2. \quad (100)$$

Here again C is the isothermal bulk modulus of elasticity, G the shear modulus of elasticity, α the coefficient of cubic thermal expansion, and c_v the specific heat per unit mass at constant volume. It should be ob-

served that $\frac{C}{\rho}$ and $\frac{G}{\rho}$ are the proper material constants, but since $\frac{\rho - \rho_0}{\rho_0} \ll 1$, C and G are themselves nearly constant.

We observe that, because of (98), ϵ'_{ij} may be neglected with respect to δ_{ij} . Consequently we have

$$t_{ij} = -2\rho \frac{\partial u}{\partial C_{\alpha\beta}} b_{\alpha i} b_{\beta j} = \rho \frac{\partial u}{\partial \epsilon'_{kl}} g_{kl} g_{ij} \approx \rho \frac{\partial u}{\partial \epsilon'_{ij}}.$$

The expressions for the stresses and the temperature, that can be deduced from (100), read then as follows

$$t_{ij} = \rho \frac{\partial u}{\partial \epsilon'_{ij}} = 2G\epsilon'_{ij} + C \left(1 + \frac{C\alpha^2 T_0}{\rho c_v} \right) \epsilon'_{kk} \delta_{ij} - \frac{C\alpha T_0}{c_v} s \delta_{ij}, \quad (101)$$

$$T = \frac{\partial u}{\partial s} = T_0 - \frac{C\alpha T_0}{\rho c_v} \epsilon'_{ii} + \frac{T_0}{c_v} s. \quad (102)$$

The rate of change of the tensor ϵ'_{ij} is according to eqs. (22) and (38) determined by

$$\begin{aligned} \dot{\epsilon}'_{ij} &= -\frac{1}{2} \dot{g}_{ij} = -\frac{1}{2} (\dot{b}_{\alpha i} b_{\alpha j} + b_{\alpha i} \dot{b}_{\alpha j}), \\ \dot{\epsilon}'_{ij} &= -\frac{1}{2} g_{kj} \left(\lambda_2 \frac{\partial D_2}{\partial s_{ik}} - d_{ik} \right) - \frac{1}{2} g_{ik} \left(\lambda_2 \frac{\partial D_2}{\partial s_{kj}} - d_{kj} \right) - \\ &\quad - \frac{1}{2} g_{kj} \frac{1}{2} \left(\frac{\partial \dot{x}_i}{\partial x_k} - \frac{\partial \dot{x}_k}{\partial x_i} \right) + \frac{1}{2} g_{ik} \frac{1}{2} \left(\frac{\partial \dot{x}_k}{\partial x_j} - \frac{\partial \dot{x}_j}{\partial x_k} \right), \end{aligned}$$

or, since ϵ'_{ij} may be neglected with respect to δ_{ij} ,

$$\dot{\epsilon}'_{ij} = d_{ij} - \lambda_2 \frac{\partial D_2}{\partial s_{ij}} + \epsilon'_{kj} \frac{1}{2} \left(\frac{\partial \dot{x}_i}{\partial x_k} - \frac{\partial \dot{x}_k}{\partial x_i} \right) - \epsilon'_{ik} \frac{1}{2} \left(\frac{\partial \dot{x}_k}{\partial x_j} - \frac{\partial \dot{x}_j}{\partial x_k} \right). \quad (103)$$

The skew-symmetric tensor

$$\omega_{ij} = \frac{1}{2} \left(\frac{\partial \dot{x}_i}{\partial x_j} - \frac{\partial \dot{x}_j}{\partial x_i} \right) \quad (104)$$

is known as the spin tensor. We can now rewrite eqs. (103) as follows

$$\dot{\epsilon}'_{ii} = d_{ii}. \quad (105a)$$

$$\dot{\epsilon}'_{ij} - \epsilon'_{kj} \omega_{ik} + \epsilon'_{ik} \omega_{kj} = d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} - \lambda_2 \frac{\partial D_2}{\partial s_{ij}}. \quad (105b)$$

The left-hand side of eq. (105b) represents the so-called Jaumann derivative (JAUMANN 1911) of the tensor ϵ'_{ij} . It differs from the ordinary

material derivative only in case $|\omega_{ij}|$ is by an order of magnitude larger than $\left| d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} - \lambda_2 \frac{\partial D_2}{\partial s_{ij}} \right|$.

In order to complete the theory of flow with small deviations from the natural reference state expressions should be given for the dissipation functions D_1 and D_2 . Since the material must be isotropic we have

$$D_1 = D_1\left(p, T, \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i}\right), \quad (106)$$

$$D_2 = D_2(p, T, s_{ij}s_{ij}, s_{ij}s_{jk}s_{ki}). \quad (107)$$

An expression of the form (51) leads again to Fourier's heat conduction law, while $D_2 = D_2(T, s_{ij}s_{ij})$ furnishes the creep equations, proposed by ODQVIST (1936). When we consider time-independent plasticity again as a limiting case of creep, a yield surface

$$\varphi(T, s_{ij}s_{ij}) = 0 \quad (108)$$

leads to equations of the form

$$\dot{e}'_{ij} - e'_{kj}\omega_{ik} + e'_{ik}\omega_{kj} = d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} - \lambda s_{ij}, \quad \lambda \geq 0, \quad (109)$$

which are a generalization of the Prandtl-Reuss theory of plasticity.

In view of the difficulties, encountered when we try to solve in practical plasticity problems the equations for small deviations from the natural reference state, the theory is often simplified further by neglecting these deviations from the natural reference state altogether. The constitutive equations are then reduced to

$$d_{ii} = 0,$$

$$d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} = \lambda s_{ij}, \quad (110)$$

where

$$\lambda \geq 0 \text{ if } \varphi = 0, \dot{\varphi} = 0,$$

$$\lambda = 0 \text{ if } \varphi < 0 \text{ or } \varphi = 0 \text{ and } \dot{\varphi} < 0. \quad (111)$$

In this theory for the rigid-ideally plastic model the thermodynamic origin of the stresses is fully obscured. The pressure component is an undefined quantity, subjected only to boundary conditions and the equations of motion for the stresses (16), while the deviator components of stress have to satisfy the boundary conditions and the equations of motion, as well as the flow eqs. (110) in those regions, where the yield condition (108) is satisfied.

d) Liquids

Liquids are usually defined as materials in which shear stresses are necessarily accompanied by motion of the continuum. However every material with a dissipation function D_2 , that vanishes only for $s_{ij} = 0$, complies with this definition, in particular those materials, which we have called simple solids, if they are subject to creep for non-vanishing s_{ij} . The distinction between a solid and a liquid thus can only be a quantitative one in terms of the time constant in the dissipation function D_2 .

Since liquids offer great resistance against compression, while shear stresses remain small, a theory of flow for liquids, based upon the assumption that the deviations from the natural reference state remain small, will usually be adequate. For the internal energy, the stresses and the temperature we may then employ the expressions (100), (101) and (102), as liquids will generally be isotropic. In many flow problems the constitutive eqs. (105) can for liquids be simplified considerably, however.

If we consider a dissipation function of the type

$$D_2 = \beta s_{ij} s_{ij},$$

then we have according to (56) the equation

$$\overline{\left(\frac{C_{\alpha\beta}}{g^{\frac{1}{3}}}\right)} = \frac{2b_{\alpha i} b_{\beta j}}{g^{\frac{1}{3}}} \left[\beta s_{ij} - d_{ij} + \frac{1}{3} d_{kk} \delta_{ij} \right].$$

From the equality

$$(C_{\alpha\beta} - \delta_{\alpha\beta}) R_{\alpha i} R_{\beta j} = -2e'_{ij}$$

and the condition (98) we can conclude that

$$|C_{\alpha\beta} - \delta_{\alpha\beta}| \ll 1,$$

and

$$e_{\alpha\beta} R_{\alpha i} R_{\beta j} \approx -2e'_{ij}.$$

Hence, according to $s_{ij} = 2Ge'_{ij}$ and (28)

$$\dot{e}_{\alpha\beta} \approx -2G_{\beta} \frac{C_{\alpha\gamma} C_{\beta\delta}}{g^{\frac{1}{3}}} e_{\gamma\delta} - 2 \frac{C_{\alpha\gamma} R_{\gamma i} C_{\beta\delta} R_{\delta j}}{g^{\frac{1}{3}}} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right)$$

or, if $C_{\alpha\beta} - \delta_{\alpha\beta}$ is neglected with respect to $\delta_{\alpha\beta}$,

$$\dot{e}_{\alpha\beta} + 2G_{\beta} e_{\alpha\beta} \approx -2R_{\alpha i} R_{\beta j} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right). \quad (112)$$

If the flow is such, that the following condition is satisfied

$$\left| \frac{d^n}{dt^n} \left[2R_{\alpha i} R_{\beta j} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right) \right] \right| \ll (2G\beta)^n \left| 2R_{\alpha i} R_{\beta j} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right) \right|, \quad (113)$$

then it follows from the theory of differential equations that

$$|\dot{e}_{\alpha\beta}| \ll \left| 2R_{\alpha i} R_{\beta j} \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right) \right|. \quad (114)$$

In that case the eqs. (109) may be replaced by

$$-G\beta e_{\alpha\beta} R_{\alpha i} R_{\beta j} = \beta s_{ij} = d_{ij} - \frac{1}{3} d_{kk} \delta_{ij}. \quad (115)$$

These are the usual constitutive equations for shear viscosity of an isotropic liquid, in which the thermodynamic origin of the stresses is fully obscured.

Whether a flow problem may be treated as a problem of liquid flow with the aid of eqs. (115) or should be treated as flow of a solid with the aid of eqs. (105b) will depend on whether or not in the solution of the problem the conditions (113) are satisfied. However, in the decisive quantity

$$2G\beta = \frac{G}{\mu},$$

where μ is the viscosity $\left(s_{ij} = 2\mu \left(d_{ij} - \frac{1}{3} d_{kk} \delta_{ij} \right) \right)$, appears the shear modulus of elasticity, which does not lend itself to a direct measurement for liquids with a small value of μ , just because for such liquids the conditions (113) will be satisfied in practically all flow phenomena.

Concluding Remarks

Whether stress as a thermodynamically defined quantity, subjected to equations of motion as a consequence of the principle of determinism, is a sufficiently broad concept in the theory of rheology, should ultimately be decided by experiments. Mathematical abstractions in physical theories can only find their justification in so far as they provide a basis for the correlation of observable phenomena.

In author's opinion a sharp distinction should be made between theories, in which distribution of stress vectors is introduced as the action of the material outside upon the material inside a closed surface, and theories in which a description is given of a material as a thermodynamic system. Since the response of the material will in general depend on the history of the external action, in theories of the first kind materials

have to be characterized by a response functional. On the other hand in theories of the second kind the state of the material is at any moment supposed to be fully determined by the values of the state variables and the response of the material will be known as soon as the internal energy function is known and constitutive equations are given for the rate of change of the state variables, where these equations are independent of the history of the process, if the set of thermodynamic state variables is complete for the phenomena under consideration.

In some special cases the theories of the first and second kind are equivalent. Such is the case in the theory for ideal creep and ideal plasticity of an isotropic material with small deviations from the natural thermodynamic reference state. Then the thermodynamic state is assumed to be fully determined by the temperature and the state of stress (BESSELING 1966). The constitutive equations of the theory of the second kind may then be interpreted as response functions in a theory of the first kind. The theory of elasticity on the other hand must be considered as a theory of the second kind, if it is based upon GREEN's concept of a natural state of the continuum (TRUEDEL 1952). Recent papers on materials with fading memory (TRUEDEL 1965) deal again with theories of the first kind. Though they present a perfectly valid approach of the rheological problem, it must be doubted, whether it will ever be possible to determine for a specific material by laboratory experiments the tensorial functionals, that appear in these theories.

In author's opinion a more promising approach is offered by theories of the second kind, in which new state variables are introduced as the need for them arises, as for instance in the case of non-simple solids. Though in principle one could try to treat a polycrystalline metal as a conglomeration of differently orientated anisotropic bodies of a simple solid, where the physical properties might even vary from one body to another, this approach is only feasible if the configuration of the various bodies is simplified to such an extent, that it becomes doubtful, whether the analysis has some bearing on the behaviour of the actual material. Author prefers a representation of the non-simple solid, in which the internal energy distribution is the weighted sum of a small number of distributions, each depending on its own set of state variables and representative for a portion of the material imbedded in the moving continuum together with all other portions. By assigning different dissipation functions to the various portions we can obtain a description of phenomena like primary creep, creep-recovery, anisotropic strain hardening and Bauschinger effect (BESSELING 1953, 1958).

There remains the difficult and laborious task of the experimentalist to show which is the proper theory for the analysis of rheological problems for real materials.

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Discussion

ONAT: The number of state variables $C_{\alpha\beta}$ which you have in your theory is six?

BESSELING: Six, because you eliminate three rotations. But the three rotations are always there because you have to return to the natural reference state. So there are really nine quantities geometrically and one for the thermodynamics.

ONAT: It seems to me that at least in linear viscoelasticity six would be too small a number for state variables.

BESSELING: I agree, of course. This is just the simplest case and it leads only to the theory of secondary creep and ideal plasticity. But you can improve on the representation by taking more state variables.

NAGHDI: If I understood you correctly, you defined the stress tensor in terms of internal energy as partial derivative of . . .

BESSELING: Yes.

NAGHDI: That is a constitutive assumption. It is the same point as discussed yesterday that constitutive equations should be separated from the basic field equations.

BESSELING: I only look at it differently. You start out from an a-priori concept of stress.

NAGHDI: The stress tensor is introduced (in the usual way) through the stress vector which acts across a surface of the body.

BESSELING: I do not introduce this stress vector.

NAGHDI: But you use it!

BESSELING: I call it stress tensor. That is just a quantity that appears in my equations but I nowhere introduce the equation of balance of momentum or something like that where you have to introduce the a-priori concept of stress.

NAGHDI: In your energy equation you have to state what is the rate of work done by surface forces.

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BESSELING: No, I have no surface forces, I consider a closed system in an empty universe. And of course, inside this closed system I can then turn to a non-closed system. It would be more usual to introduce the stress at the surface but then, at a later point, you find the stress in terms of the internal energy and somewhere you have used two definitions of stress, I think.

NAGHDI: No.

BESSELING: Maybe you can say I have not introduced the more general concept of stress. I consider a special case, in which the stress is related to the internal energy.

NAGHDI: The constitutive assumption for the stress tensor is separate from the basic field equations.

BESSELING: Yes, you may introduce stress as separate from the basic theory — but I don't see any real objections against not doing that.

KESTIN: Perhaps it is worth remarking here that the derivation of Cauchy's equations of motion from the assumptions on the slides was achieved about three years ago by GREEN and RIVLIN. The assumption of the invariance with respect to a Galilean transformation together with the additivity of internal and kinetic energy yields the equations of motion. It is also worth mentioning, I think, that the argument can be inverted and is normally inverted to state that the use of the equations of motion together with the principle of invariance with respect to Galilean transformation yields the statement that internal energy is additive to kinetic energy.

BESSELING: With respect to the paper mentioned I think there is a difference. GREEN and RIVLIN introduce stress as a stress vector at the surface. Then, from that the stress tensor inside is derived. I think, in that argument you are not allowed to do the step which is done in the paper to say that the equations shall be satisfied for any volume and therefore also for a volume dV . I think, in order to have these arguments you should really introduce stress as a quantity, determined by the internal state, and not as some kind of abstract a-priori concept.

NAGHDI: GREEN and RIVLIN start with a balance of energy together with invariance requirements under superposed rigid body motions. Then, they derive Cauchy's equations of motion and the equation for conservation of mass. You objected to the introduction of the idea of the stress vector. The stress vector is introduced as part of the balance of energy and the arguments they use about the integrand are the usual arguments based on the continuity of the functions. This time it is applied to the balance of energy.

BESSELING: You have introduced the internal energy and you have not stated what things this internal energy depends on.

NAGHDI: It does not matter, as long as they state that it is invariant under superposed rigid body motions. This is precisely an argument that one would use in the construction of any type of constitutive equations.

BESSELING: I think, we should talk about it in private.

KLUITENBERG: You do not derive the entropy production but you suggest it. Can you generalize this idea, so that you have also volume-viscosity?

BESSELING: No. In this approach there is no place for volume-viscosity. But I am still wondering whether there are convincing experimental data that there is volume-viscosity. As long as this is not settled I don't see why we should complicate things by introducing it. Now, of course, I know of some instances where you can get better correspondence between theory and experiments by introducing volume-viscosity. But on the other hand maybe you may equally improve on the correspondence by introducing the kind of relaxation effects that are associated with highly non-stationary states. As long as this point is not settled I would like to consider volume-viscosity as not existent.

KLUITENBERG: I think, there is a paper by KARIM and ROSENHEAD¹ where they agree, that volume-viscosity does exist.

ONAT: But certainly there is relaxation phenomena observed in linear visco-elastic solids in the presence of pure volume changes.

BESSELING: Of course, you can get relaxation effects by the thermodynamic phenomena of heat conduction and convection.

KESTIN: It can be shown that if a system performs work in a reversible way which is described by the pressure multiplied into the total derivative of volume and does not possess internal variables of state then the bulk-viscosity is zero. This is the normal assumption that we make when we study gases. In the case of liquids the statement carries through but it becomes somewhat trivial by the fact that in liquids we normally also introduce the assumption that the density remains constant. Now, in a solid, in a viscoelastic solid, we have the case where internal variables operate and under those conditions bulk-viscosity has a non-vanishing value.

BESSELING: I agree that by introducing certain internal variables it will be possible to obtain a non-vanishing bulk-viscosity.

¹ L. M. KARIM and L. ROSENHEAD, Rev. Mod. Phys. 24 (1952), 108.