ON THE THERMODYNAMIC THEORY OF DEFORMATION AND FLOW

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Introduction

In the last decades there were many efforts to create an exact basement of rheology. The most successful attempts have the common feature of not approaching to the viscoelasticity on the usual way, with the starting point in the elasticity, but dealing with it as an essentially irreversible process using the methods of nonequilibrium thermodynamics.

It will be shown how the thermodinamical methods are effectual on the field of viscoelasticity, moreover, how to get the general theory of visco-elasticity by means of a few simple ideas. The continuous media studied here are expected not to change their chemical composition so they can be characterized in equilibrium by the mass density, the specific internal energy and by the state of deformation. Supposing the same parameters to be necessary to define the macroscopic state of the moving medium completely as in equilibrium, it can be shown that the medium must be a Kelvin-body or a Newtonian fluid [1, 3, 16]. The behaviour of a real viscoelastic medium can be more complicated. Hence, it seems obvious that the viscoelastic bodies do not remain in the state of local equilibrium when moving, and their thermo-dynamical state cannot be defined by the equilibrium parameters, i.e. the number of the thermodynamical variables of a moving medium is greater than in equilibrium.

There are different methods enlarging the number of the thermodynam-ical parameters. In the non-linear continuum mechanics, the new variables constitute a functional space and are identified with the histories of the deformation [4—8]. Other researchers prefer introducing distinct parameters as this way leads to equivalent results when increasing the number of state variables and the use of the difficult methods of nonlinear functional analysis can be avoided [9—15].

It appears that the thermodynamic theory of relaxations [17, 18] is one of the most succesful methods in the field of deformation and flow. The methods used by us are in close connexion with those of thermodynamic relaxation theory. It must be mentioned that the thermodynamic theory of deformation and flow can answer a lot of questions known as typical non-linear problems, e.g. it can survey the non-Newtonian fluids and the streaming birefringence [15].

Before setting out to develop the linear thermodynamic theory of viscoelasticity, the basic thermodynamical and mechanical methods used in the followings will be outlined (details cf. [1—6]).

1. Kinematical preliminaries

Consider a medium and a point of it P_0 moving in a Cartesian frame. The position of the point P_0 at the reference time t_0 is denoted by $\mathbf{R}'$. This way the different points of the body are depicted as different vectors $\mathbf{R}'$. The motion

$$\mathbf{r} = \mathbf{r}(\mathbf{R}', t), \tag{1.1}$$

may be supposed differentiable so it can be approximated in linear order as

$$\mathbf{r} = \mathbf{r}_0 + \mathbf{x} \cdot (\mathbf{R}' - \mathbf{R}'_0), \tag{1.2}$$

where $\mathbf{x}$ is the deformation gradient. To separate the deformation from the rotation the polar decomposition theorem of Cauchy

$$\mathbf{x} = \mathbf{d} \cdot \mathbf{R} = \mathbf{R} \cdot \mathbf{D} \text{ so, as } \mathbf{d} = \mathbf{d}^T,\ \mathbf{D} = \mathbf{D}^T,\ \mathbf{R}^T = \mathbf{R}^{-1} \tag{1.3}$$

will be used, where $\mathbf{d}$ is the symmetric tensor describing the deformation and $\mathbf{R}$ is the orthogonal tensor describing the rotation. ($\mathbf{d}^T$, $\mathbf{D}^T$ and $\mathbf{R}^T$ stand for the adjoints of the tensors $\mathbf{d}$, $\mathbf{D}$ and $\mathbf{R}$ respectively.) As it is seen from (1.3), the motion of the body can be described in two ways. By the first, the rotation precedes the deformation, the latter is given by $\mathbf{d}$, while in the other way, the case is the opposite and the deformation is given by $\mathbf{D}$. The tensor $\mathbf{D}$ does not change while the body is rotating after deformation. This cannot be said about the tensor $\mathbf{d}$. For this reason, the tensor $\mathbf{D}$ is considered as describing the deformation in the frame corotating with the body.

2. Thermodynamical balances

The balance equations play fundamental role in irreversible thermodynamics and a number of them are important in the theory of viscoelasticity as well. The mass balance

$$\frac{d\varrho}{dt} + \varrho \operatorname{div} \mathbf{v} = 0 \tag{2.1}$$

(ϱ is the density of the medium and $\mathbf{v}$ its velocity) and the momentum balance

$$\varrho \frac{d\mathbf{v}}{dt} + \operatorname{Div} \mathbf{t} = \varrho \mathbf{f} \tag{2.2}$$

— $\mathbf{t}$ is Cauchy's stress tensor and $\mathbf{f}$ is the body force per unit mass — are particularly important. The law of conservation of angular momentum will be used as the source of the symmetry of Cauchy's stress tensor [1, 4, 5]. The balance equation for the kinetic energy is

$$\varrho \frac{d}{dt}\left(\frac{\mathbf{v}^2}{2}\right) - \operatorname{div}(\mathbf{v}\cdot\mathbf{t}) = \varrho \mathbf{f}\mathbf{v} - \mathbf{t} : (\operatorname{Grad} \mathbf{v})^+ \tag{2.3}$$

and similarly, the balance equation for the internal energy [1]:

$$\varrho \frac{du}{dt} + \operatorname{div} \mathbf{J}_q = \mathbf{t} : (\operatorname{Grad} \mathbf{v})^+ \tag{2.4}$$

(u is the specific internal energy, $\mathbf{J}_q$ is the heat current density and $(\operatorname{Grad} \mathbf{v})^+$ is the symmetric part of the gradient of velocity. The notation: ":" stands for the interior product of two tensors.)

3. Thermodynamical treatment of the viscoelasticity

For the sake of simplicity, we suppose that our medium is isotropic and that no part of it changes its volume during the motion. Furthermore, it is also supposed that the thermodynamical state of the moving body can be caracterized by some internal variables which are symmetric tensors of second order. Remarkable enough, the theory does not require any a priori knowledge of the physical meaning of these variables.

Some of these tensors may be even with respect to time inversion (type α), others may be odd (type β) [1, 2, 3]. According to our suppositions the specific energy of the medium u can be given as

$$u = u\,(s,\ \mathbf{D},\ \alpha_1^*,\ \alpha_2^*, \ldots\ \beta_1^*,\ \beta_2^* \ldots) \tag{3.1}$$

where s is the specific entropy and $\alpha_1^*, \alpha_2^*, \ldots \beta_1^*, \beta_2^*$ are the internal tensorial variables. For the substantial time derivative of the internal energy in the sense of the Gibbs relation, we have

$$\dot{u} = T\dot{s} + \frac{\partial u}{\partial \mathbf{D}} : \dot{\mathbf{D}} + \sum_i \frac{\partial u}{\partial \alpha_i^*} : \dot{\alpha}_i^* + \sum_j \frac{\partial u}{\partial \beta_j^*} : \dot{\beta}_j^* \tag{3.2}$$

It is convenient to choose the tensors α^* and β^* in a special way. Remembering that these tensors are unnecessary in equilibrium states, the tensors α^* and β^* can be chosen to zero in equilibrium.

In the following we confine ourselves to the case where the quantities $\frac{\partial u}{\partial \alpha_i^*}$ and $\frac{\partial u}{\partial \beta_j^*}$ in (3.2) may be regarded as linear functions of α_i^* and β_j^*. These functions are homogeneous linear because of the maximum property of the entropy. Since $\dot{u}$ is odd with respect to time inversion, the quantities $\frac{\partial u}{\partial \alpha_i^*}$ don't depend on the variables β_j^* in linear order, and for the same reason the quantities $\frac{\partial u}{\partial \beta_j^*}$ don't depend on the variables α_i^*. Thus, we can conclude that the parameters α_i^* and β_j^* may be chosen in such a way that the last terms in (3.2) are the derivatives of positive definite quadratic forms transformed into diagonal ones.

The equations became more simple if the units of the variables α_i^* and β_j^* are chosen suitably. In this manner the formula (3.2) simplifies to

$$\dot{u} = T\dot{s} + \frac{\partial u}{\partial \mathbf{D}} : \dot{\mathbf{D}} + \frac{1}{\varrho} \sum_i \alpha_i^* : \dot{\alpha}_i^* + \frac{1}{\varrho} \sum_j \beta_j^* : \dot{\beta}_j^* \tag{3.3}$$

By using (3.3) and (2.4) we obtain the actual form of the balance equation of entropy [1—3]:

$$\varrho \dot{s} + \operatorname{div} \frac{\mathbf{J}_q}{T} = \sigma_s \tag{3.4}$$

where the entropy production is given by

$$\sigma_s = \mathbf{J}_q \cdot \operatorname{grad} \frac{1}{T} + \frac{1}{T} \left\{ \mathbf{t} : (\operatorname{Grad} \mathbf{v})^* - \varrho \frac{\partial u}{\partial \mathbf{D}} : \dot{\mathbf{D}} - \sum_i \alpha_i^* : \dot{\alpha}_i^* - \sum_j \beta_j^* : \dot{\beta}_j^* \right\} . \tag{3.5}$$

The formula obtained is written down in a hybrid representation. To eliminate the hybrid character of (3.5) let us introduce the quantities $\mathbf{d}$ and α_i, β_j, $\mathring{\mathbf{d}}$, $\mathring{\alpha}_i$ and $\mathring{\beta}_j$ defined as

$$\alpha_i = \mathbf{R} \cdot \alpha_i^* \cdot \mathbf{R}^T \tag{3.5.a.}$$

$$\beta_j = \mathbf{R} \cdot \beta_j^* \cdot \mathbf{R}^T \tag{3.5.b.}$$

$$\mathring{\mathbf{d}} = \mathbf{R} \cdot \dot{\mathbf{D}} \cdot \mathbf{R}^T = \dot{\mathbf{d}} + \mathbf{d} \cdot \omega - \omega \cdot \mathbf{d} \tag{3.5.c.}$$

$$\mathring{\alpha}_i = \mathbf{R} \cdot \dot{\alpha}_i^* \, \mathbf{R}^T = \dot{\alpha}_i + \alpha_i \cdot \omega - \omega \cdot \alpha_i \tag{3.5.d.}$$

$$\overset{\circ}{\beta}_j = \mathbf{R} \cdot \dot{\beta}_j^* \cdot \mathbf{R}^T = \dot{\beta}_j + \beta_j \cdot \omega - \omega \cdot \beta_j \tag{3.5.e.}$$

where

$$\omega = \dot{\mathbf{R}} \cdot \mathbf{R}^T = -\mathbf{R} \cdot \dot{\mathbf{R}}^T \tag{3.5.f.}$$

is the spin tensor. The tensors α_i, β_j, $\overset{\circ}{\mathbf{d}}$, $\overset{\circ}{\alpha}_i$, $\overset{\circ}{\beta}_j$ are the equivalents of the tensors α_i^*, β_j^*, $\dot{\mathbf{D}}$, $\dot{\alpha}_i^*$, $\dot{\beta}_j^*$ respectively. Making use of these quantities we find for the entropy production:

$$\sigma_s = -\mathbf{J}_q \cdot \operatorname{grad} \frac{1}{T} + \frac{1}{T} \left\{ \left(\frac{\mathbf{d}^{-1}\mathbf{t} + \mathbf{t}\mathbf{d}^{-1}}{2} - \varrho \frac{\partial u}{\partial \mathbf{d}} \right) : \overset{\circ}{\mathbf{d}} - - \sum_i \alpha_i : \overset{\circ}{\alpha}_i - \sum_j \beta_j : \overset{\circ}{\beta}_j \right\} \tag{3.6}$$

Meantime, the formulae (1.2) and (1.3) were used as well.

According to the second law of thermodynamics the entropy production is nonnegative and it can be zero only in the case of equilibrium. The same is valid for the dissipation of energy, which can be obtained from σ_s by multiplying it by the absolute temperature T, that is:

$$T\sigma_s = -J_q \cdot \frac{\operatorname{grad} T}{T} + \left(\frac{\mathbf{d}^{-1} \cdot \mathbf{t} + \mathbf{t} \cdot \mathbf{d}^{-1}}{2} - \varrho \frac{\partial u}{\partial \mathbf{d}} \right) : \overset{\circ}{\mathbf{d}} - - \sum_i \alpha_i : \overset{\circ}{\alpha}_i - \sum_j \beta_j : \overset{\circ}{\beta}_j \tag{3.7}$$

Now, the energy dissipation may be regarded as a bilinear form of the currents: $\mathbf{J}_q$, $\overset{\circ}{\mathbf{d}}$, $\overset{\circ}{\alpha}_i$, $\overset{\circ}{\beta}_j$, — and of the conjugated forces: $-\dfrac{1}{T} \operatorname{grad} T$,

$$\frac{\mathbf{d}^{-1} \cdot \mathbf{t} + \mathbf{t} \cdot \mathbf{d}^{-1}}{2} - \varrho \frac{\partial u}{\partial \mathbf{d}}, \qquad -\alpha_i, \qquad -\beta_j.$$

In equilibrium the energy dissipation vanishes in such a way that both the currents and forces become zero. This condition as well as the general connection between the forces and currents is expressed in linear order by Onsager's linear constitutive relations [1, 2, 3].

Before dealing with them, we show how to get the physical meaning of the tensor $\dfrac{\partial u}{\partial \mathbf{d}}$ in (3.7) from the condition of forces vanishing in equilibrium. Since the coefficient of the tensor $\overset{\circ}{\mathbf{d}}$ in (3.7) becomes zero in equilibrium, we have

$$\frac{\partial u}{\partial \mathbf{d}} = \frac{1}{\varrho} \frac{\mathbf{d}^{-1}\mathbf{t} + \mathbf{t}\mathbf{d}^{-1}}{2}. \tag{3.8}$$

Now, it is found that the equilibrium stress tensor $\mathbf{t}^e$ is an isotropic function of the tensor $\mathbf{d}$. Therefore their sequence can be inverted and from (3.8) we can conclude that

$$\frac{\partial u}{\partial \mathbf{d}} = \frac{1}{\varrho} \mathbf{d}^{-1} \cdot \mathbf{t}^e , \tag{3.9}$$

from which

$$\mathbf{t}^e = \varrho \frac{\partial u}{\partial \mathbf{d}} \cdot \mathbf{d} . \tag{3.10}$$

By using (3.10), the form of the energy dissipation (3.7) is rewritten as

$$\begin{aligned} T\sigma_s = -\mathbf{J}_q \cdot \frac{\operatorname{grad} T}{T} + (\mathbf{t} - \mathbf{t}^e) : \frac{1}{2} (\mathring{\mathbf{d}} \cdot \mathbf{d}^{-1} + \mathbf{d}^{-1} \mathring{\mathbf{d}}) - \sum_i \alpha_i : \mathring{\alpha}_i - \\ - \sum_j \beta_j : \mathring{\beta}_j . \end{aligned} \tag{3.11}$$

Now let us turn to the Onsager linear laws.

Because the medium is isotropic, the heat flux only depends on the force conjugated to it. The Onsager linear laws are separated into two parts. The first is the equation of heat conduction

$$\mathbf{J}_q = -L\, qq \frac{\operatorname{grad} T}{T} = -\lambda \operatorname{grad} T , \tag{3.12}$$

and the second part is the set of constitutive equations describing the structural changes of the body:

$$\begin{aligned} \frac{1}{2} (\mathring{\mathbf{d}} \cdot \mathbf{d}^{-1} + \mathbf{d}^{-1} \mathring{\mathbf{d}}) &= L^{dd} (\mathbf{t} - \mathbf{t}^e) - \sum_i L_i^{d\alpha}\, \alpha_i - \sum_j L_j^{d\beta}\, \beta_j \\ \mathring{\alpha}_k &= L_k^{\alpha d} (\mathbf{t} - \mathbf{t}^e) - \sum_i L_{ki}^{\alpha\alpha}\, \alpha_i - \sum_j L_{kj}^{\alpha\beta} \beta_j \\ \mathring{\beta}_r &= L_r^{\beta d} (\mathbf{t} - \mathbf{t}^e) - \sum_i L_{ri}^{\beta\alpha}\, \alpha_i - \sum_j L_{rj}^{\beta\beta} \beta_j \end{aligned} \tag{3.13}$$

The phenomenological coefficients obey the Onsager—Casimir reciprocal relations [1—3]:

$$L_i^{\alpha d} = L_i^{d\alpha} ; \quad L_j^{d\beta} = -L_j^{\beta d} ; \quad L_{ik}^{\alpha\alpha} = L_{ki}^{\alpha\alpha} ; \quad L_{kj}^{\alpha\beta} = -L_{jk}^{\beta\alpha} ; \quad L_{rj}^{\beta\beta} = L_{jr}^{\beta\beta} . \tag{3.14}$$

Remark that the restrictions on the variables α and β expanded above do not unify the set of the independent variables but they leave the possibility to diagonalize the matrices of the phenomenological coefficients $L^{\alpha\alpha}$ and $L^{\beta\beta}$.

Another remark is that the phenomenological coefficients in (3.13) are not constant in every case but they may depend on the thermodynamical state variables of the medium, that is, they can be functions of the temperature T and the tensors $\mathbf{d}$, α_i and β_j. In this case — which is called quasi-linear [1, 29] — the equations describe not only the linear viscoelasticity but the phenomena of thixotropy and reopexy as well.

4. The general theory of linear viscoelasticity

The set of equations (3.13) may be regarded as the general constitutive equations of viscoelasticity. To get the well-known models of the strictly linear viscoelasticity, we have to impose restrictions on the medium. First, we have to omit the case of phenomenological coefficients depending on the state variables, i.e. to take them constant. Another restriction is that the angular velocity and the deformation of the body be so small that the relations

$$\frac{1}{2}(\mathring{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}^{-1}\mathring{\mathbf{d}}) = \mathring{\mathbf{d}} \tag{4.1}$$

$$\mathring{\alpha}_i = \dot{\alpha}_i$$

$$\mathring{\beta}_j = \dot{\beta}_j$$

could be taken true.

For the sake of brevity we introduce the viscous stress tensor

$$\mathbf{t}^v = \mathbf{t} - \mathbf{t}^e \tag{4.2}$$

which is defined in the customary way [1, 3, 4]. If the moving body has a uniform temperature and the equalities (4.1) hold, the energy dissipation (3.11) reduces to

$$T\sigma_s = \mathbf{t}^v : \mathbf{d} - \sum_i \alpha_i : \dot{\alpha}_i - \sum_j \beta_j : \dot{\beta}_j , \tag{4.3}$$

and the constitutive relations (3.13) get the form:

$$\begin{aligned}
\dot{\mathbf{d}} &= L^{dd}\mathbf{t}^v - \sum_i L_i^{d\alpha}\,\alpha_i - \sum_j L_j^{d\beta}\,\beta_j , \\
\dot{\mathbf{d}}_k &= L_k^{\alpha d}\mathbf{t}^v - \sum_i L_{ki}^{\alpha\alpha}\,\alpha_i - \sum_j L_{kj}^{\alpha\beta}\,\beta_j , \\
\beta_r &= L_r^{\beta d}\,\mathbf{t}^v - \sum_i L_{ri}^{\beta\alpha}\,\alpha_i - \sum_j L_{rj}^{\beta\beta}\,\beta_j .
\end{aligned} \tag{4.4}$$

This set of linear differential equations is solvable in the usual way if one of the tensors $\mathbf{d}$ and $\mathbf{t}^{\nu}$ is known.

For getting a general picture of the content of the equations, let us confine ourselves to functions of form e^{pt} as it is usual in the theory of networks. Here p is a complex number, the so-called complex frequency. For this case the equations (4.4) reduce to a set of algebraic equations, which are homogeneous except the first one. Having solved this system of equations by Cramer's rule, we get

$$\mathbf{t}^{\nu} = Y(\mathrm{p})\,\dot{\mathbf{d}}, \tag{4.5}$$

where $Y\,(p)$ is a rational function of the complex frequency with real coefficients. Because of the second law of thermodynamics, the function $Y\,(p)$ has no zero and no singular point on the closed right half-plane, thus the positivity of the energy dissipation on the imaginary axis involves that the function $Y\,(p)$ is a positive real one, i.e. it can be regarded as the immittance of an electric network. By virtue of this circumstance the problems of linear viscoelasticity can be depicted onto those of linear electric networks, which consist of capacitances, inductances and resistances, as it has been proved by Bott and Duffin [20]. For the well-developed theory of networks, all the problems of linear viscoelasticity can be regarded as those solved from a theoretical point of view when the formula (4.5) has been established. Let us mention that in the simple case where the medium needs parameters of type α only for being described and the system of equations (4.4) can be diagonalized, disregarding the first one, the electric model of the body consists of resistances and capacitances alone. In this case, the electric models can be established with the help of Forster's method and the models are equivalent to the mechanical ones containing springs and dashpots, which are well known in the rheology [21—23].

For the sake of perfect agreement with the classical theory, let us write the stress tensor with the help of (4.2) and (4.5):

$$\mathbf{t} = \mathbf{t}^{e}(\mathbf{d}) + Y(p)\,\dot{\mathbf{d}}. \tag{4.5}$$

If the motion of the body has started from a stress-free reference configuration and the function $\mathbf{t}^{e}\,(\mathbf{d})$ is linear, we get

$$\mathbf{t} = 2\,\mu \int_{t_0}^{t} \dot{\mathbf{d}}\,dt + Y\,(p)\,\dot{\mathbf{d}} = \left[\frac{2\mu}{p} + Y\,(p)\right]\dot{\mathbf{d}} = Y^{*}\,(p)\,\dot{\mathbf{d}} \tag{4.7}$$

which is in perfect agreement with the classical theory, where μ is one of Lamé's coefficients. It is stressed once more that the tensor $\mathbf{t}$ in the present argumentation stands for the stress deviator, since we have disregarded volume changes.

If volume changes have to be calculated, the whole sequence of ideas can be repeated with scalar variables and equations analogous to (4.6) and (4.7) but the immittances occurring in them are different of the former.

5. The Flow of Viscoelastic Fluids

In describing the motion of a fluid, the equations can be reduced by choosing a suitable reference configuration. [4,5,6]. For this reason, it is convenient to use the present configuration. In this case, the hypothesis of the smallness of the deformations means no restriction at all, since the actual values of the tensors **d** (or **D**) and **R** are equal to the unit tensor. From this it follows also that the tensor $\mathbf{t}^e$ in (3.10) must equal zero. This way the constitutive equations reduce to

$$\begin{aligned} \mathring{\mathbf{d}} &= L^{dd}\,\mathbf{t} - \sum_i L_i^{d\alpha}\,\alpha_i - \sum_j L_j^{d\beta}\,\beta_j, \\ \mathring{\alpha}_k &= L_k^{\alpha d}\,\mathbf{t} - \sum_i L_{ki}^{\alpha\alpha}\,\alpha_i - \sum_j L_{kj}^{\alpha\beta}\,\beta_j, \\ \beta_r &= L_r^{\beta d}\,\mathbf{t} - \sum_i L_{ri}^{\beta\alpha}\,\alpha_i - \sum_j L_{rj}^{\beta\beta}\,\beta_j. \end{aligned} \tag{5.1}$$

Here, $\mathring{\mathbf{d}}$ is identical with the symmetric part of the velocity gradient and ω is identical with the antisymmetric part of it. Because of its practical importance we analyze the shearing flow in detail. The results can be generalized for any kind of viscometric flows [24].

For the calculation, let us choose a Cartesian frame moving together with a point of the fluid, but not rotating, the axis of which is chosen so that the velocity is given by the formula

$$\mathbf{v} = \varkappa\, y\, \mathbf{i} \tag{5.2}$$

The present form of the tensors **d** and ω can be given easily:

$$\begin{aligned} \mathring{\mathbf{d}} &= \frac{\varkappa}{2}(\mathbf{i} \circ \mathbf{j} + \mathbf{j} \circ \mathbf{i}), \\ \omega &= \frac{\varkappa}{2}(\mathbf{i} \circ \mathbf{j} - \mathbf{j} \circ \mathbf{i}). \end{aligned} \tag{5.3}$$

Here $\varkappa$ is the rate of shear and the sign "o" stands for the dyadic product of vectors.

Making use of the stationarity following from (5.2) the components of all the tensors needed concerning to the z axis are seen to equal zero, and the calculations can be confined to the x, y plane. The second-order tensors of the plane form a linear associative algebra, in which

$$\begin{aligned} \mathbf{E}_1 &= \mathbf{i} \circ \mathbf{i} + \mathbf{j} \circ \mathbf{j}, \\ \mathbf{E}_\sigma &= \mathbf{i} \circ \mathbf{i} - \mathbf{j} \circ \mathbf{j}, \\ \mathbf{E}_\tau &= \mathbf{i} \circ \mathbf{j} + \mathbf{j} \circ \mathbf{i}, \\ \mathbf{E}_\omega &= \mathbf{i} \circ \mathbf{j} - \mathbf{j} \circ \mathbf{i}, \end{aligned} \tag{5.4}$$

can be taken as base elements. Some of the multiplication rules they satisfy will be used, namely

$$\begin{aligned} \mathbf{E}_\sigma \cdot \mathbf{E}_\omega &= - \mathbf{E}_\omega \cdot \mathbf{E}_\sigma = \mathbf{E}_\tau \\ \mathbf{E}_\tau \cdot \mathbf{E}_\omega &= - \mathbf{E}_\omega \cdot \mathbf{E}_\tau = - \mathbf{E}_\sigma \end{aligned} \tag{5.5}$$

By means of these relations, the symmetric tensors with zero trace and their generalized time derivatives are given easily as:

$$\begin{aligned} \mathbf{T} &= T_\sigma \mathbf{E}_\sigma + T_\tau \mathbf{E}_\tau \\ \mathring{\mathbf{T}} &= \mathring{T}_\sigma \mathbf{E}_\sigma + \mathring{T}_\tau \mathbf{E}_\tau = \\ &= (T_\sigma \mathbf{E}_\sigma + T_\tau \mathbf{E}_\tau) \frac{\varkappa}{2} \mathbf{E}_\omega - \frac{\varkappa}{2} \mathbf{E}_\omega (T_\sigma \mathbf{E}_\sigma + T_\tau \mathbf{E}_\tau). \end{aligned} \tag{5.6}$$

The components of the time derivatives are:

$$\begin{aligned} \mathring{T}_\sigma &= - \varkappa T_\tau \\ \mathring{T}_\tau &= \varkappa T_\sigma. \end{aligned} \tag{5.7}$$

The symmetric tensors of zero trace form a two-dimensional vector space spanned by $\mathbf{E}_\sigma$ and $\mathbf{E}_\tau$ as base vectors. Mapping this vector space onto the complex numbers with the formula

$$z_{\mathbf{T}} = T_\sigma + \mathrm{i}\, T_\tau, \tag{5.8}$$

we find that (5.7) is equivalent to the relationship

$$z^{\circ}_{\mathbf{T}} = i\, \varkappa z_{\mathbf{T}}. \tag{5.9}$$

Since the mapping is homogeneous and linear, the linear equations (5.1) are valid both for the tensors and for their images, the complex numbers. Because of the isomorphism, the distinction between the tensors and their images is superfluous, so the notation z will be omitted. If p stands for $i\,\varkappa$, the set of equations (5.1) gets the same form as (4.4). Hence, the stresstensor is given by (4.5)

$$\mathbf{t} = Y(p)\dot{\mathbf{d}} = Y(i\,\varkappa) i\,\varkappa. \tag{5.10}$$

From the complex number form of the stress tensor

$$\mathbf{t} = \sigma + i\,\tau \tag{5.11}$$

and from (5.10) the viscometric functions can be deciphered. The expression (5.10) shows that the complex viscosity is the same for relaxation phenomena as for viscometric flows.

The expression (5.10) for the complex stress makes it clear that some non-Newtonian flows, regarded as typical non-linear phenomena, belong to the sphere of the linear thermodynamics. The theory of plasticity and viscoplasticity may possibly be based upon the non-equilibrium thermodynamics on a similar way.

At last we mention that the tensors α and β used here get a physical meaning whenever a molecular model is the starting point, and that they may be invariants of higher order tensors or functionals as well.

6. The birefringence of viscoelastic media

In this section we shall investigate the form of the dielectric tensor of transparent isotopic media moving without changing its volume, as the dielectric tensor gives the key to calculate the optical properties of the media.

First of all, the equilibrium form of the dielectric tensor will be studied. If an isotropic reference configuration has been chosen, the dielectric tensor is an isotropic function of the deformation tensor $\mathbf{d}$. This is easy to seen since it is known from the electromagnetic theory of the light that the dielectric tensor is a real, symmetric, second-order tensor and it depends only on the frequency of the light and the state variables of the medium. In equilibrium, the thermodynamic state of the body is determined by its temperature and the deformation, so we get

$$\epsilon = \epsilon^{e}(T,\ \mathbf{d},\ \mathbf{R}). \tag{6.1}$$

The changes of the temperature will be disregarded. To prove that the function $\epsilon^e(\mathbf{d}, \mathbf{R})$ is isotropic, the frames will be changed both for the reference configuration and for the scenery of motions. The new radius vectors marked by asterisks are got by the transformations

$$\begin{aligned} \mathbf{R}'^* - \mathbf{R}_0'^* &= \mathbf{Q}'(\mathbf{R}' - \mathbf{R}_0') \\ \mathbf{r}^* - \mathbf{r}_0^* &= \mathbf{Q} \cdot (\mathbf{r} - \mathbf{r}_0) \end{aligned} \tag{6.2}$$

where $\mathbf{Q}$ and $\mathbf{Q}'$ are orthogonal tensors. Since the dielectric tensor is an objective one, it does not vary with the changes of the frames.

$$\mathbf{Q} \cdot \epsilon^e(\mathbf{d}, \mathbf{R})\, \mathbf{Q}^T = \epsilon^e(\mathbf{Q} \cdot \mathbf{d} \cdot \mathbf{Q}^T, \mathbf{Q} \cdot \mathbf{R} \cdot \mathbf{Q}'^T) \tag{6.3}$$

Choosing $\mathbf{Q}'$ suitably we get the relationship

$$\epsilon^e(\mathbf{d}, \mathbf{R}) = \mathbf{Q}^T \cdot \epsilon^e(\mathbf{Q} \cdot \mathbf{d} \cdot \mathbf{Q}^T, \delta) \cdot \mathbf{Q} \tag{6.4}$$

Q. E. D.

In the case of small deformations, the dielectric tensor is well approximated by a linear function

$$\varepsilon = \varepsilon\delta + \varepsilon_d(\mathbf{d} - \delta) + \sum_i \varepsilon_\alpha^i \alpha_i = \varepsilon^e(\mathbf{d}) + \sum_i \varepsilon_\alpha^i \alpha_i . \tag{6.2}$$

Here δ stands for the unit tensor, ε for the dielectric constant of the medium and the epsilons with sub- and superscripts are material coefficients. Only the α-parameters occur as independent variables in (6.5) (ϵ is of type α).

First, functions of the form e^{pt} are considered. The tensors α_i are calculated from (4.4) by Cramer's rule

$$\alpha_i = Y_i(p)\, \dot{\mathbf{d}} \tag{6.6}$$

where the functions $Y_i(p)$ are fractional ones, having the same denominator as the function $Y(p)$ in (4.5). Making use of (6.6) we get the actual form of the dielectric tensor from (6.5):

$$\epsilon = \epsilon^e(\mathbf{d}) + \sum_i \varepsilon_\alpha^i Y_i(p)\, \dot{\mathbf{d}} = \epsilon^e(\mathbf{d}) + Y_\varepsilon(p)\, \dot{\mathbf{d}}. \tag{6.7}$$

In the case of viscometric flow we obtain similar results. The function ϵ^e for motion preserving volume of fluids is independent of $\mathbf{d}$ and the tensor $\epsilon - \epsilon^e$ has no component with respect to the z axis if the motion is described by the function (5.2). Thus, with (5.6), (5.7), (5.8) and (5.9), the simple shearing flow leads to equations analogous to (6.6) and (6.7):

$$z_s - \epsilon\,\delta = Y_e(i\,\varkappa)i\,\varkappa. \tag{6.8}$$

Here an attempt has been made to develop a unified thermodynamical theory of deformation and flow. We endeavoured to express the conditions and the results as general as we could avoiding great mathematical difficulties. We have shown that a general theory of deformation and flow embracing the conventional theories of linear viscoelasticity, that of the generalized Newtonian fluids and of rheooptics can be based on the Onsagerian linear thermodynamics. It is stressed that the method developed here is based on the linear thermodynamics still it is able to give a picture of phenomena known as typical non-linear ones.

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Summary

This paper is concerned with the theoretical investigation of dissipative viscoelastic processes. The methods of classical thermodynamics of irreversible processes are used and it is shown by using internal parameters of second order tensors, that this theory suits to describe the viscoelastic properties of materials and to organize the hierarchy of the viscoelastic bodies. A general method for calculating the viscometric functions of viscoelastic bodies is worked out and the streaming birefringence is dealt with.

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