# NONISOTHERMAL DEFORMATION OF A VISCOELASTIC MEDIUM

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One of the current problems of the mechanics of viscoelastic media is the question of the effect of temperature. This problem was first raised in the work of A. A. Aleksandrov and Yu. S. Lazurkin who set forth the basic ideas of the principle of temperature-time superposition for isothermal loading at different temperatures. A similar approach was adopted by Leaderman, Ferry, and others. Subsequently, in the work of Morland and Lee [1] the principle was formally extended to the case of variable temperatures.

In this paper the problem of the nonisothermal deformation of a viscoelastic medium is examined on the basis of the thermodynamics of irreversible processes. Given sufficiently well justified assumptions about the construction of the basic thermodynamic potential, this approach inescapably leads to the conclusion that the state of the viscoelastic medium depends not only on the current value of the temperature field but also on its history of variation. The relations obtained are similar to those proposed in [1], thus providing a theoretico-physical basis for the above-mentioned principle and its extension to the case of nonisothermal processes.

§1. With the usual assumptions of continuum mechanics concerning the absence of changes in the electromagnetic fields, chemical potentials, etc., taking into account only thermomechanical effects, we can write the energy balance equation in the form

$$u^{\cdot} = \sigma^{ij}\varepsilon_{ij}^{\cdot} + q^{i}{}_{,i}, \qquad q^{i}{}_{,j} \equiv \frac{\partial q^{i}}{\partial x^{j}}, \quad q^{i}{}_{,i} \equiv \frac{\partial q^{i}}{\partial x^{j}} g^{ij}.$$

Here u is the internal energy density, $q^i$ is the heat flowrate vector, and $g^{ij}$ is the metric tensor (a dot above a function denotes the time derivative). Let s be the entropy density, and $f$ the free energy density,

$$f = u - \mathrm{T}s. \tag{1.2}$$

Then Eq. (1.1) can be rewritten as

$$f^{\cdot} = \sigma^{ij}\varepsilon_{ij}^{\cdot} + q^{i}{}_{,i} - \mathrm{T}s^{\cdot} - s\mathrm{T}^{\cdot}. \tag{1.3}$$

The rate of increase of entropy for the system as a whole can be represented as a sum

$$S^{\cdot} = S_e^{\cdot} + \int\limits_V \eta^{\cdot} dV. \tag{1.4}$$

Here $S_e$ is the external entropy flux, and $\eta$ is the internal entropy source density. Since

$$\int\limits_V \frac{q^{i}{}_{,i}}{\mathrm{T}} dV = \int\limits_F \frac{q^i}{\mathrm{T}} n_i dF + \int\limits_V \frac{q^i \mathrm{T}_{,i}}{\mathrm{T}^2} dV, \tag{1.5}$$

where F is the surface bounding the volume V in question, from (1.3) and (1.4) we get

$$\eta^{\cdot} = \frac{1}{\mathrm{T}}\left[-f^{\cdot} + \sigma^{ij}\varepsilon_{ij}^{\cdot} - s\mathrm{T}^{\cdot} - \frac{q^i \mathrm{T}_{,i}}{\mathrm{T}}\right]. \tag{1.6}$$

§2. An especially important role in the thermodynamic analysis is played by the choice of the basic system of parameters. All possible changes in the viscoelastic medium are macroscopically manifested in changes in at least one of the quantities $\sigma^{ij}$, $\varepsilon_{ij}$ or T. Therefore as a complete system of parameters of state of an element of the medium we can take

$$\{\sigma^{ij},\ \varepsilon_{ij},\ \mathrm{T}\}. \tag{2.1}$$

We shall isolate from the total deformation a part $\varepsilon_{ij}^{(1)}$ following instantaneously from changes in the external conditions. As experiments show, we may with sufficient accuracy assume that it is perfectly elastic:

$$\varepsilon_{ij}{}^{(1)}(t) = G_{ijkl}\,\sigma^{kl} + \alpha\delta_{ij}(\mathrm{T} - \mathrm{T}_0). \tag{2.2}$$

This, roughly speaking, is attributable to the fact that the instantaneous strain is conditioned by changes in the interatomic distances, i. e., has the same nature as the small strains of ordinary low-molecular materials. In this case the aftereffect is given by

$$\varepsilon_{ij}^{(2)} = \varepsilon_{ij} - \varepsilon_{ij}^{(1)}. \tag{2.3}$$

It is easy to observe that the system of parameters

$$\{\varepsilon_{ij}^{(1)},\ \varepsilon_{ij}^{(2)},\ \mathrm{T}\} \tag{2.4}$$

is equivalent to system (2.1) and may be taken as the basic system.

Since $f$ is a function of state, from (1.6) we obtain

$$\eta^{\cdot} = \frac{1}{\mathrm{T}}\left[\left(\sigma^{ij} - \frac{\partial f}{\partial \varepsilon_{ij}^{(1)}}\right)\varepsilon_{ij}^{(1)\cdot} + \left(\sigma^{ij} - \frac{\partial f}{\partial \varepsilon_{ij}^{(2)}}\right)\varepsilon_{ij}^{(2)\cdot} - \left(\frac{\partial f}{\partial \mathrm{T}} + s\right)\mathrm{T}^{\cdot} - \frac{q^i \mathrm{T}_{,i}}{\mathrm{T}}\right]. \tag{2.5}$$

In accordance with the second law of thermodynamics

$$\dot{\eta} \geqslant 0, \tag{2.6}$$

the equality applying only in the case of reversible processes.

In analyzing the deformation processes we shall make use of the ideas expounded in [2]. As distinct from the material investigated in that study, a viscoelastic medium is characterized by several types of reversible deformation processes. This is because for such a medium reversible processes are possible at different rates of change of the external conditions.

a) We shall assume that the external forces vary "instantaneously," i. e., in the course of an interval of time so short that the aftereffect is unable to develop. The temperature field is uniform and also varies instantaneously, remaining uniform,

$$\varepsilon_{ij}{}^{(2)} = 0, \ \mathrm{T}_{,i} = 0.$$

Then from (2.5) we obtain

$$o = \left(\sigma^{ij} - \frac{\partial f}{\partial \varepsilon_{ij}^{(1)}}\right)\varepsilon_{ij}^{(1)\cdot} - \left(\frac{\partial f}{\partial T} + s\right)\mathrm{T}^{\cdot}. \tag{2.7}$$

Hence, thanks to the independence of $\varepsilon_{ij}^{(1)\cdot}$ and $T^{\cdot}$, it follows that

$$\sigma^{ij} - \frac{\partial f}{\partial \varepsilon_{ij}^{1}} = 0, \qquad (2.8)$$

$$\frac{\partial f}{\partial T} + s = 0. \qquad (2.9)$$

In the case in question the viscoelastic medium behaves as if it were perfectly elastic.

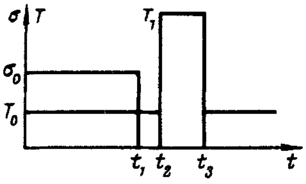

Fig. 1

b) Let all the external conditions vary quasi-statically (at "infinitesimal" rates) for a uniform temperature field. Then from (2.5)

$$0 = \left(\sigma^{ij} - \frac{\partial f}{\partial \varepsilon_{ij}^{(1)}}\right) d\varepsilon_{ij}^{(1)} + \\ + \left(\sigma^{ij} - \frac{\partial f}{\partial \varepsilon_{ij}^{(2)}}\right) d\varepsilon_{ij}^{(2)} - \left(\frac{\partial f}{\partial T} + s\right) dT. \qquad (2.10)$$

Hence

$$\sigma^{ij} - \frac{\partial f}{\partial \varepsilon_{ij}^{(1)}} = 0, \quad \sigma^{ij} - \frac{\partial f}{\partial \varepsilon_{ij}^{(2)}} = 0, \quad \frac{\partial f}{\partial T} + s = 0. \qquad (2.11)$$

Solving the first equation of (2.11) for $\varepsilon_{ij}^{(1)}$, and the second for $\varepsilon_{ij}^{(2)}$ with account for the fact that $\varepsilon_{ij}^{(1)} + \varepsilon_{ij}^{(2)} = \varepsilon_{ij}$, we get the final expressions relating the stress tensor with the total strain tensor. This case of reversible and equilibrium viscoelastic deformation may be formally incorporated in the physically nonlinear theory of elasticity.

c) We shall assume, finally, that the external forces vary instantaneously and the temperature field quasi-statically, remaining uniform,

$$\varepsilon_{ij}^{(2)\cdot} = 0, \quad T_{,i} = 0, \quad T^{\cdot} = 0.$$

In this case from (2.5) we get

$$0 = \left(\sigma^{ij} - \frac{\partial f}{\partial \varepsilon_{ij}^{(1)}}\right) \varepsilon_{ij}^{(1)\cdot}. \qquad (2.12)$$

From this there again follows Eq. (2.8), whereas Eq. (2.9) and the third of Eqs. (2.11) are no longer satisfied. Thus, (2.8) is valid for any reversible change in the state of the viscoelastic medium. A reversible process of at least one of the above-mentioned types is realizable from any state; consequently, (2.8) must also be valid for any state. As distinct from (2.8), Eq. (2.9) and the third of Eqs. (2.11) are not valid for any state.

With this in mind, we may assert that in the general case of viscoelastic deformation the expression for the entropy source density has the form

$$\eta^{\cdot} = \frac{1}{T}\left[\left(\sigma^{ij} - \frac{\partial f}{\partial \varepsilon_{ij}^{(2)}}\right) \varepsilon_{ij}^{(2)\cdot} - \left(\frac{\partial f}{\partial T} + s\right) T^{\cdot} - \frac{q^{i} T_{,i}}{T}\right]. \qquad (2.13)$$

We also note that from (2.8), by virtue of (2.2), it directly follows that

$$f(\varepsilon_{ij}^{(1)}, \varepsilon_{ij}^{(2)}, T) = f_1(\varepsilon_{ij}^{(1)}, T) + f_2(\varepsilon_{ij}^{(2)}, T). \qquad (2.14)$$

The last equation is obviously valid at any point of phase space.

§3. In accordance with the concepts of the thermodynamics of irreversible processes [3], the thermodynamic forces may be represented in the form of a linear combination of fluxes. As may be seen from (2.13), in the given case the role of thermodynamic forces is played by

$$(\sigma^{ij} - \partial f_2 / \partial \varepsilon_{ij}^{(2)}), \ (\partial f / \partial T + s), \ T_{,i},$$

while the corresponding fluxes are the quantities $\varepsilon_{ij}^{(2)\cdot}$, $T^{\cdot}$ and $q^{i}$.

Consequently, we can write

$$\sigma^{ij} - \frac{\partial f_2}{\partial \varepsilon_{ij}^{(2)}} = B^{ijkl} \varepsilon_{kl}^{(2)\cdot} + B^{ij} T^{\cdot} + B^{i} q^{j} + B_{k}^{\ ij} q^{k}. \qquad (3.1)$$

We assume

$$f_2(\varepsilon_{ij}^{(2)}, T) = \overset{mnkl}{A}(T)\, \varepsilon_{mn}^{(2)} \varepsilon_{kl}^{(2)} + \varphi_2(T). \qquad (3.2)$$

(Essentially, this is the usual assumption about the linearity of the rheological relations.)

If we assume that the material is isotropic, then the last two terms in (3.1) are eliminated by virtue of the Curie principle. Hence, using (2.14), we obtain the following system of ordinary differential equations:

$$\sigma^{ij} - A^{ijkl} \varepsilon_{kl}^{(2)} = B^{ijmn} \varepsilon_{mn}^{(2)\cdot} + B^{ij} T^{\cdot}. \qquad (3.3)$$

We shall write it in the usual form, solving for the components of the aftereffect strain rate tensor $\varepsilon_{mn}^{(2)\cdot}$

$$\varepsilon_{mn}^{(2)\cdot} + L_{mn}^{kl}(T)\, \varepsilon_{kl}^{(2)} = P_{mnij} \sigma^{ij} - Q_{mn} T^{\cdot}. \qquad (3.4)$$

The structure of L, P, and Q is easily determined from the condition of isotropy. Henceforth we shall be interested in the case

$$L_{kl}^{mn}(t) = L_{mn}^{kl}(t) \quad \text{at any } t. \qquad (3.5)$$

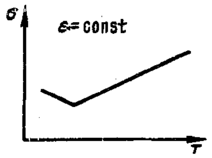

Fig. 2

We shall introduce the object $\Omega(t)$ satisfying the equation

$$[\Omega_{ij}^{rs}(t)]^{\cdot} = -L_{ij}^{mn}(t)\, \Omega_{mn}^{rs}(t), \qquad (3.6)$$

with initial conditions

$$\Omega_{ij}^{rs} = \delta_{i}^{\ r} \delta_{j}^{\ s} \quad \text{at } t = 0$$

($\Omega$ is often called the matrizant).

Then the general solution of (3.4) may be written in the form

$$\varepsilon_{ij}^{(2)}(t) = \Omega_{ij}^{mn}\varepsilon_{mn}^{(2)}(t=0) + \\ + \int_0^t K_{ij}^{mn}(t,\tau)\left[P_{mnkl}\sigma^{kl}(\tau) - Q_{mn}\mathrm{T}^{\cdot}(\tau)\right]d\tau, \qquad (3.7)$$

where $K_{ij}^{mn}(t, \tau)$ is the so-called Cauchy matrix (in the given case a fourth-order tensor),

$$K_{ij}^{mn}(t,\tau) = \Omega_{ij}^{rs}(t)\left[\Omega_{rs}^{mn}(\tau)\right]^{-1}. \qquad (3.8)$$

From the assumed existence of a starting unstressed and undeformed state at $t = 0$ it follows that

$$\varepsilon_{mn}^{(2)}(t=0) = 0. \qquad (3.9)$$

As a result, the relation between the stress tensor, the total strain tensor and temperature has the form

$$\varepsilon_{ij}(t) = G_{ijkl}\sigma^{kl}(t) + \alpha\delta_{ij}(\mathrm{T} - \mathrm{T}_0) + \\ + \int_0^t K_{ij}^{mn}(t,\tau)\left[P_{mnkl}\sigma^{hl}(\tau) - Q_{mn}\mathrm{T}^{\cdot}(\tau)\right]d\tau. \qquad (3.10)$$

To determine the matrizant, we represent it in the form of a multiplicative integral:

$$\Omega_{ij}^{rs}(t) = \int_0^t (\delta_i^r\delta_j^s - L_{ij}^{rs}dt). \qquad (3.11)$$

When condition (3.5) is satisfied, (3.11) reduces to a tensor of the form

$$\exp\left(-\int_0^t L_{ij}^{rs}(\theta)\,d\theta\right). \qquad (3.12)$$

Then, by virtue of (3.8),

$$K_{ij}^{mn}(t,\tau) = \exp\left(-\int_0^t L_{ij}^{rs}(\theta)\,d\theta\right)\exp\int_0^\tau L_{rs}^{mn}(\theta)\,d\theta = \\ = \exp\left(-\int_\tau^t L_{ij}^{pq}(\theta)\,d\theta\right)\exp\left(-\int_0^\tau L_{pq}^{rs}(\theta)\,d\theta\right)\exp\int_0^\tau L_{rs}^{mn}(\theta)\,d\theta. \qquad (3.13)$$

Since

$$\exp\left(-\int_0^\tau L_{pq}^{rs}(\theta)\,d\theta\right)\exp\int_0^\tau L_{rs}^{mn}(\theta)\,d\theta = \delta_p{}^m\delta_q{}^n, \qquad (3.14)$$

we finally get

$$K_{ij}^{mn}(t,\tau) = \exp\left(-\int_\tau^t L_{ij}^{mn}(\theta)\,d\theta\right). \qquad (3.15)$$

§4. Let us consider the uniform strain in some simple stress state, e.g., that of a cylindrical test piece in uniaxial tension. Then (3.17) becomes

$$\varepsilon(t) = \frac{\sigma(t)}{E} + \alpha(\mathrm{T}(t) - \mathrm{T}_0) + \\ + \int_\tau^t \exp\left(-\int_0^t k(\theta)\,d\theta\right)\left[\frac{p(\mathrm{T})}{E_r}\sigma(\tau) - \beta\mathrm{T}^{\cdot}(\tau)\right]d\tau. \qquad (4.1)$$

Hence for isothermal loading we have

$$\varepsilon(t) = \frac{\sigma(t)}{E} + \int_0^t \frac{p(\mathrm{T}_0)}{E_r}\exp\left[-k(\mathrm{T}_0)(t-\tau)\right]\sigma(\tau)\,d\tau. \qquad (4.2)$$

In (4.2) the temperature enters as a parameter. It is easy to see, however, that in the general case the deformation of a viscoelastic medium can not depend on the value of the temperature only at the current instant t (or only at the instant $\tau$). In fact, let us consider the process illustrated in Fig. 1,

$$\sigma(t) = \begin{cases}\sigma_0 & \text{at} \quad t < t_1, \\ 0 & \text{at} \quad t \geqslant t_1,\end{cases} \qquad \mathrm{T}(t) = \begin{cases}\mathrm{T}_0 & \text{at} \quad t < t_2 \text{ и } t > t_3, \\ \mathrm{T}_1 & \text{at} \quad t_2 \leqslant t \leqslant t_3.\end{cases}$$

For real viscoelastic materials (e.g., high polymers) the aftereffect is very sensitive to changes in temperature, since its internal mechanism is intimately connected with the thermal motion of the molecules. Therefore an increase in temperature on the interval $(t_2, t_3)$ has an effect on the strain at any moment $t > t_3$. However, if we assume that (4.2) is also valid for nonisothermal deformation (when $k = k(\mathrm{T})$, where $\mathrm{T} = \mathrm{T}(t)$ or $\mathrm{T} = \mathrm{T}(\tau)$), then these changes in temperature will have no effect on the state of the material at time $t > t_3$.

Apparently, these considerations served as a basis for the extension of an expression of the type (4.2) to the nonisothermal case proposed in [1]. From this extension there follows an equation similar to (4.1), if we set $\beta \equiv 0$ in the latter.

We shall stress the following two points: 1) the rheological equation (4.1) was obtained above on the basis of a thermodynamic analysis; 2) the term with the coefficient $\beta$ in the integrand is of considerable significance. This follows from the results of the classic experiments of Meyer and Ferry, Huth and coworkers, etc. (see, for example, [4]).

We recall that in these experiments the variation in stress was investigated for a specimen with fixed strain upon variation of temperature. A typical curve obtained in such experiments on elastomers has the form shown in Fig. 2. At a value of T smaller than a certain characteristic value for the given elastomer and a specified $\varepsilon = \mathrm{const}$, $\sigma$ decreases with increase in T (for ordinary materials this occurs at any T). At a temperature greater than that indicated, $\sigma$ increases with increase in T (almost linearly).

From (4.1) it follows that

$$\sigma(t) = E\left\{\varepsilon(t) - \alpha(\mathrm{T}(t) - \mathrm{T}_0) + \right. \\ \left. + \int_0^t \exp\left[-\int_\tau^t k(\theta)\,d\theta\right]\beta\mathrm{T}^{\cdot}(\tau)\,d\tau\right\} - \\ - \lambda\int_0^t \Gamma(t,\tau,\lambda)\left\{\varepsilon(\tau) - \alpha(\mathrm{T}(\tau) - \right. \qquad (4.3) \\ \left. - \mathrm{T}_0) + \int_0^\tau \exp\left[-\int_s^\tau k(\theta)\,d\theta\right]\beta\mathrm{T}^{\cdot}(s)\,ds\right\}d\tau,$$

where $\lambda = E/E_r$. The last term in (4.3) takes into account the relaxation effects, whose influence on the above-mentioned experiments was reduced to a minimum. This means that in these experiments the nature of the stress-temperature relation is given by

$$\sigma(t) \approx E\left\{\varepsilon(t) - \alpha(\mathrm{T} - \mathrm{T}_0) + \right. \\ \left. + \int_0^t \exp\left[-\int_\tau^t k(\theta)\,d\theta\right]\beta\mathrm{T}^{\cdot}(\tau)\,d\tau\right\}. \qquad (4.4)$$

Hence it is clear that for a suitable choice of $\beta = \beta(\varepsilon, \mathrm{T})$, Eq. (4.1) describes the experimentally established increase in stresses with increase in temperature. However, if we set $\beta = 0$ (in this case, it should be stressed, (4.1) reduces to the expression proposed in [1]), then instead of (4.4) we get

$$\sigma(t) \approx E\,[\varepsilon(t) - \alpha(T - T_0)],$$

which for $\varepsilon$ = const gives the usual effect of decrease in stress with increase in T.

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