ENTROPY PRINCIPLE IN THE THEORY OF CREEP
AND LONG-TIME STRENGTH OF POLYMERIC MATERIALS

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The possibilities of applying thermodynamic methods in the theory of creep and long-time strength are considered. General principles are employed to construct creep equations for certain types of media and to formulate a criterion of long-time strength.

1. Concerning the Role of Thermodynamics in Continuum Mechanics

When applied to the deformation process, the first and second laws of thermodynamics and, moreover, the basic principles of kinetics (thermodynamics of irreversible processes) lead to a series of fundamental relations, which must be satisfied by various real materials with specific physical properties.

In particular, these relations make it possible to reduce the total amount of experimentation needed to develop a specific theory of deformation applicable to a given group of materials.

When the experimentation is carried out on a scale sufficient to construct a purely empirical theory of deformation, the fundamental relations of thermodynamics still retain their importance as a means of testing the experimental results. For nonlinear elastic media in the case of small deformations the thermodynamic relations include, for example,

\[
\frac{\partial \sigma_{ik}}{\partial \varepsilon_{pq}} = \frac{\partial \sigma_{pq}}{\partial \varepsilon_{in}}, \quad (1.1)
\]

\[
\frac{\partial}{\partial \varepsilon_{l2}} \left( \Pi_1 - \Pi_1 \sqrt{\frac{3\Pi_2 - \Pi_1^2}{3\Pi_2 - \Pi_1^2}} \right) = \frac{3}{2} \frac{\partial}{\partial \varepsilon_{l1}} \sqrt{\frac{3\Pi_2 - \Pi_1^2}{3\Pi_2 - \Pi_1^2}} \quad \text{etc.,} \quad (1.2)
\]

where \( \Pi_1, \Pi_2 \) and \( \varepsilon_1, \varepsilon_2, \varepsilon_3 \) are the first and second invariants of the stress and strain tensors, i.e., \( \Pi_1 = \sigma_{ik}\delta_{ik}; \Pi_2 = \sigma_{ik}\sigma_{ik}; \varepsilon_1 = \varepsilon_{lk}\delta_{lk}; \varepsilon_2 = \varepsilon_{lk}\varepsilon_{lk} \). Similarly, in the case of arbitrary finite deformations we have

\[
\frac{\partial}{\partial \varepsilon_{l1}} \left( \frac{\sigma_2}{\rho(1-2\varepsilon_3)} \right) = \frac{\partial}{\partial \varepsilon_{l2}} \left( \frac{\sigma_3}{\rho(1-2\varepsilon_1)} \right) = \frac{\partial}{\partial \varepsilon_{l3}} \left( \frac{\sigma_1}{\rho(1-2\varepsilon_2)} \right), \quad (1.3)
\]

where \( \rho \) is the density of the medium; \( \sigma_k, \varepsilon_k (k = 1, 2, 3) \) are the principal stresses and principal strains.

These differential relations not only make it possible sharply to reduce the volume of experimentation in establishing relations between the stresses, strains, and temperature but also enable the scope and character of the experiments needed to solve the problem to be accurately established.

For the sake of clarity, it should be noted that the above relations \( (1.1), (1.2), (1.3), \) etc. can also be obtained even in the nonlinear theory of elasticity starting only from the assumption of the existence of a

"potential" energy of deformation. This has led to the erroneous belief that in this respect deformation thermodynamics contributes nothing new. However, only by using the first and second laws of thermodynamics is it possible to demonstrate the validity of the above-mentioned relations in cases when the constitutive equations contain not only stresses and strains but also temperature. It should be especially emphasized that it is not necessarily a question of high temperatures.

Consider, for example, the reversible deformation of rubber at ordinary (room) temperatures. As Treloar and others [1] have shown, isothermal extension has practically no effect on the energy of rubber, but its entropy changes. In other words, the reversible stretching of rubber is such that all the work done is transferred to the ambient medium in the form of heat. In no way does it follow that under these deformation conditions the relations (1.1), (1.2), (1.3), etc. will be satisfied. In particular, it does not follow that the isothermal work increment is a total differential. All these relations and assertions can be proved only by thermodynamic methods. The example with rubber has been presented only because the process of rubber deformation is extremely interesting from the thermodynamic standpoint. Considerable heat exchange with the ambient medium also occurs in connection with the deformation of other materials, for example, metals and alloys at room temperature.

It follows that the deformation process (equilibrium or nonequilibrium) is a typical thermodynamic process and that at ordinary temperatures the purely "mechanical" approach is rather arbitrary.

The role of thermodynamics is particularly important at high temperatures. As a typical example one might mention the omnidirectional adiabatic compression of metals or alloys, when in the deformation process the temperature rises by hundreds of degrees. This adiabatic temperature rise can only be calculated by thermodynamic methods.

The basic laws of thermodynamics make it possible to formulate variational principles of thermoelasticity, which is exceptionally important, since it permits the use of the direct methods of the calculus of variations for solving problems of thermoelasticity. We also note the importance of Onsager's principle in linear viscoelasticity.

Thermodynamics has numerous applications in continuum mechanics. As typical examples it is possible to mention shock wave theory, the theory of damping of elastic waves of acoustic frequency, etc.

Below, we propose to discuss certain possibilities of using thermodynamic methods to construct creep equations and develop a theory of long-time strength.

2. Thermodynamic Creep Theory

We will consider media of two types. The first type includes media for which the total strain tensor can be represented in the form of a sum of the tensor of the reversible elastic part and the creep strain tensor. The second type includes media for which the total stress tensor can be represented in the form of a sum of the elastic (reversible) stress tensor and the irreversible or viscous stress tensor. Moreover, we assume that in the constitutive equations the time derivatives of the stress or strain tensors are sufficiently small.

It should be emphasized that these constraints are not essential; however, they make it easier to demonstrate the thermodynamic method of constructing the creep equations.

Media of the First Type. We assume that the total strain increment $\delta e_{ik}$ is composed additively of two parts—a reversible (elastic) part $\delta e^e_{ik}$ and an irreversible part $\delta e^c_{ik}$, which can be identified with the creep strain. Thus, $\delta e_{ik} = \delta e^e_{ik} + \delta e^c_{ik}$. The work done by the external forces, corresponding to the total strain increment $\delta e_{ik}$, can be calculated from the expression $\delta W = \sigma_{ik} \delta e_{ik} = \sigma_{ik} (\delta e^e_{ik} + \delta e^c_{ik})$. We introduce the following notation for the work done by the stresses on the irreversible strains $\delta e^c_{ik}$: $\delta W^c = \sigma_{ik} \delta e^c_{ik}$. We call this quantity the dissipation energy.

If the deformation process is reversible, then

$$\frac{1}{T} \delta Q = dS.$$  \hspace{1cm} (2.1)

Here $\delta Q$ is the heat increment; $T$ is absolute temperature; $S$ is the entropy.

In the case of an irreversible process: