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Nonequilibrium thermodynamics and rheology of viscoelastic polymer media

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Notations

a, ε, h, c	Eulerian tensors of finite strains
$a_i, \varepsilon_i, h_i, c_i$	their principal values
e	strain rate tensor
ω	vortex tensor
σ	stress tensor
a^{∇}	Jaumann tensor derivative of tensor a with respect to time
H, H_e	equilibrium thermodynamical flux
I_1, I_2, I_3	basis invariants of tensor C
ρ, ρ_0	density
T	temperature
S	specific entropy
f	specific free energy
W	elastic potential
q	heat flux vector
P_S	production of entropy
D	dissipation
p	pressure
v	speed vector
σ_p, e_p	nonequilibrium tensors of stress and strain respectively
σ_e, H_e	equilibrium tensors of stress and strain respectively
$M_{ij\alpha\beta}^{(k)}$	kinetic coefficients
x	heat conductivity tensor
r	thermal resistance tensor
$r_{ }, r_{\perp}$	its principal values
r_0	coefficient of thermal resistance in isotropic case
R_1, R_2	constitutive scalars of tensor r
c_{σ}	heat capacity
A	thermal equivalent of work
C_1, C_2	constitutive scalars of tensor e_p in Maxwellian case
λ	scalar coefficient of viscosity
W_S	symmetric elastic potential
μ	modulus of high-elasticity
M_c	molecular weight of polymer chain between crosslinks
M_*	molecular weight of segment
β	M_*/M_c
θ_0, θ_r	relaxation and retardation times respectively

s	θ_r/θ_0
η_0	maximum Newtonian viscosity
α	dimensionless parameter of elastic potential
T_f, T_g	flow temperature and glass transition temperature
$\Delta f^*, \Delta S^*, \Delta U^*$	free energy, entropy and internal energy of activation
R	gas constant
l, l_0	characteristic lengths of segments in the presence and absence of a field respectively
L_0, L_1, \dots, L_N	characteristic sizes of molecular network
$\theta_0, \theta_1, \dots, \theta_N$	characteristic relaxation times

Introduction

Viscoelastic polymer systems are capable of accumulating large recoverable strains under the effect of intensive external actions. Thus, the viscous and relaxational parameters become nonlinear functions of the deformation rate and normal stresses appear. Under very large external interactions the polymer liquids exhibit a number of "solid-like" properties: wall slip, cracking, brittle fracture during flow.

For theoretically investigating these phenomena we have to derive the rheological equations which describe the behaviour of fluid polymer materials in the range of large elastic strains. For sufficiently small elastic strains such equations have been derived in (1), (2) and they include almost all known rheological models as particular cases.

In this paper the methods of irreversible thermodynamics have been used for constructing the rheological equations containing a small number of parameters which describe the behaviour of fluid polymers in an unbounded range of variation of recoverable strains.

We have assumed that the high-elasticity state is the internal thermodynamical equilibrium state for viscoelastic polymer media. The high-elasticity state is characterized by very large recoverable strains.

Therefore in § 1 we have outlined all the theoretical facts pertaining to the behaviour of elastic media with arbitrary strains in the nontraditional Eulerian description which is convenient for application to viscoelastic materials.

In § 2 we have given a formal scheme of irreversible thermodynamics as applied to the construction of simple constitutive equations for viscoelastic media. This scheme differs from that described in (1), (2) in that any additional kinematic considerations are not needed for constructing its purely thermodynamical path.

The Maxwellian media – the most important case for the systems under consideration – have been examined in detail in § 3 and they have been classified with respect to different criteria.

In § 4 concrete equations for the nonlinear Maxwellian model have been constructed basing on a subsidiary hypothesis accounting for the orientation phenomena specific to viscoelastic polymer media. Similarly, a few parametric generalizations which account for a number of additional effects of these media are also considered.

Finally, the qualitative physical representations on the strains in polymer melts and concentrated polymer solutions are given in § 5.

§ 1. Eulerian description of the behaviour of nondissipative elastic medium (3)

The thermodynamical state of an elastic medium is completely determined by one of the thermodynamical functions, say, the specific free energy f dependent on temperature T and an arbitrary measure for the strain, symmetric tensor of the second rank $\mathbf{a} = \{a_{ij}\}$. For the sake of simplicity we shall assume that the medium is everywhere isotropic though most of the formulas are valid even for a non-isotropic medium. Moreover, without any loss of generality, we shall take a fixed Cartesian coordinate system as the Eulerian reference frame.

By definition, the tensor \mathbf{a} , the measure for the strain, is a sufficiently smooth reversible isotropic tensor function of the Eulerian tensor of finite strain $\boldsymbol{\varepsilon} = \{\varepsilon_{ij}\}$.

The tensor $\boldsymbol{\varepsilon}$ is introduced in the usual way as the difference of metric tensors in nondeformed ($t = 0$) and deformed (at the instant t) states (4). Simple measures which we shall use are of the following form

$$\mathbf{h} = -\frac{1}{2} \ln(\boldsymbol{\delta} - 2\boldsymbol{\varepsilon}), \quad [1.1]$$

$$\mathbf{c} = \exp(2\mathbf{h}) = (\boldsymbol{\delta} - 2\boldsymbol{\varepsilon})^{-1}, \quad [1.2]$$

$$\mathbf{c}^{-1} = \exp(-2\mathbf{h}) = \boldsymbol{\delta} - 2\boldsymbol{\varepsilon}, \quad [1.3]$$

where \mathbf{h} is the Hencky strain measure, \mathbf{c} is the Finger strain measure, and $\boldsymbol{\delta}$ is the unit tensor.

The tensors $\boldsymbol{\varepsilon}$, \mathbf{h} , \mathbf{c} , \mathbf{c}^{-1} are coaxial; the formulas [1.1]–[1.3] are satisfied after the substitution $\boldsymbol{\delta} \rightarrow 1$ for the respective principal components ε_i , h_i , c_i , and c_i^{-1} . These formulas show that the tensor \mathbf{c} is positively defined and for the principal components $\boldsymbol{\varepsilon}$, \mathbf{h} , \mathbf{c} we have the following domains of definition:

$$-\infty < \varepsilon_i < \frac{1}{2}, \quad -\infty < h_i < +\infty, \quad 0 < c_i < +\infty. \quad [1.4]$$

In the kinematic description of continuous finite strains, besides the finite strain tensor \mathbf{a} , we generally consider the kinematic tensor characteristics, namely, the symmetric tensor of strain rates $\mathbf{e} = \{e_{ij}\}$ and the antisymmetric vorticity tensor $\boldsymbol{\omega} = \{\omega_{ij}\}$ related with the velocity vector $\mathbf{v}(\mathbf{x}, t)$ as follows:

$$2e_{ij} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}, \quad -2\omega_{ij} = \frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i}. \quad [1.5]$$

If we introduce the Jaumann tensor derivative with respect to time

$$\mathbf{a}^\nabla = \dot{\mathbf{a}} + \boldsymbol{\omega} \cdot \mathbf{a} - \mathbf{a} \cdot \boldsymbol{\omega}$$

with

$$\dot{\mathbf{a}} \equiv \frac{d\mathbf{a}}{dt} = \frac{\partial \mathbf{a}}{\partial t} + v_x \frac{\partial \mathbf{a}}{\partial x_x}$$

then the relation between the deformation measures $\boldsymbol{\varepsilon}$, \mathbf{c} , \mathbf{c}^{-1} and the kinematic characteristics \mathbf{e} , $\boldsymbol{\omega}$ can be expressed as follows:

$$\boldsymbol{\varepsilon}^\nabla + \boldsymbol{\varepsilon} \cdot \mathbf{e} + \mathbf{e} \cdot \boldsymbol{\varepsilon} = \mathbf{e}, \quad [1.6]$$

$$\mathbf{c}^\nabla - \mathbf{c} \cdot \mathbf{e} - \mathbf{e} \cdot \mathbf{c} = 0, \quad [1.7]$$

$$\mathbf{c}^{-1\nabla} + \mathbf{c}^{-1} \cdot \mathbf{e} + \mathbf{e} \cdot \mathbf{c}^{-1} = 0. \quad [1.8]$$

Furthermore, if we apply the equations of conservation of mass, momentum and energy, as well as the Gibbs relation, then we can

obtain the balance equation for the specific entropy S

$$\rho \frac{dS}{dt} = - \frac{\partial}{\partial x_\alpha} \left(\frac{q_\alpha}{T} \right) + P_S,$$

$$T P_S = - \frac{1}{T} \mathbf{q} \cdot \nabla T + \boldsymbol{\sigma} : \mathbf{e} - \rho \dot{f} \Big|_T \geq 0 \quad [1.9]$$

where ρ is the density, $\boldsymbol{\sigma} = \{\sigma_{ij}\}$ is the symmetric stress tensor (for a medium with no internal rotations), $\mathbf{q} = \{q_\beta\}$ is the heat flux vector (contraction of two tensors is denoted by two dots $\boldsymbol{\sigma} : \mathbf{e} = \sigma_{\alpha\beta} e_{\beta\alpha}$ or occasionally as $\boldsymbol{\sigma} : \mathbf{e} = \text{tr}\{\boldsymbol{\sigma} \cdot \mathbf{e}\}$). The quantity P_S is the entropy production in the system, and according to the second law of thermodynamics it is positive for irreversible processes and vanishes for the equilibrium state.

A medium is said to be ideally elastic if the equality

$$T P_S \Big|_T = \boldsymbol{\sigma} : \mathbf{e} - \rho \dot{f} \Big|_T = 0 \quad [1.10]$$

holds true under isothermal strain conditions. It is known that the relation between the stresses and strains $\boldsymbol{\sigma} = \boldsymbol{\sigma}(\mathbf{a})$ follows from [1.10]. If this dependence is known beforehand, then all deformation measures prove to be identical, but in studying the relationship between these equations and the function $f = f(T, \mathbf{a})$ in the Eulerian description we find that the Hencky tensor \mathbf{h} has a special meaning. Thus, we have (3), (5)

$$\boldsymbol{\sigma} = \rho \frac{\partial f}{\partial \mathbf{h}} \Big|_T \left(\sigma_{ij} = \rho \frac{\partial f}{\partial h_{ij}} \Big|_T \right) \quad [1.11]$$

and, as a consequence from it, for an arbitrary deformation measure we obtain:

$$\sigma_{ij} = \rho \frac{\partial f}{\partial a_{\alpha\beta}} \Big|_T \frac{\partial a_{\alpha\beta}}{\partial h_{ij}}. \quad [1.12]$$

The proof of [1.11] follows directly from [1.6] and [1.10].

From now onwards, for the elastic deformation measure we shall use the tensor \mathbf{c} with the invariants

$$I_1 = \text{tr} \mathbf{c}, \quad I_2 = \frac{1}{2}(I_1^2 - \text{tr} \mathbf{c}^2), \quad I_3 = \det \mathbf{c} \quad [1.13]$$

obeying the Hamilton-Cayley identity:

$$\mathbf{c}^3 - I_1 \mathbf{c}^2 + I_2 \mathbf{c} - I_3 \boldsymbol{\delta} = 0. \quad [1.14]$$

For an isotropic medium $f = f(T, I_1, I_2, I_3)$, and from [1.12], we obtain

$$\boldsymbol{\sigma} = 2\rho \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{c}} \Big|_T \left(\sigma_{ij} = 2\rho c_{ik} \frac{\partial f}{\partial c_{kj}} \right). \quad [1.15]$$

By virtue of [1.2] and [1.5], from [1.10] for an isothermic process we find that

$$\begin{aligned} T P_S \Big|_T &= \boldsymbol{\sigma} : \mathbf{e} - \rho \dot{f} \Big|_T = \boldsymbol{\sigma} : \{\mathbf{e} - \dot{\mathbf{h}}\} \\ &= \boldsymbol{\sigma} : \{\mathbf{e} - \mathbf{h}^\nabla\} = 0. \end{aligned}$$

Nonetheless, evidently we have $\mathbf{e} \neq \dot{\mathbf{h}}$, $\mathbf{e} \neq \mathbf{h}^\nabla$, which follows from [1.6]–[1.8]. Now we shall determine the tensor $\mathbf{H}(\mathbf{c}, \mathbf{c}^\nabla)$ for which

$$\mathbf{H}(\mathbf{c}, \mathbf{c}^\nabla) = \mathbf{e}. \quad [1.16]$$

This problem reduces to solving the eq. [1.7] which can be expressed in a closed form¹⁾

$$\begin{aligned} \mathbf{H}(\mathbf{c}, \mathbf{c}^\nabla) &= \frac{1}{2}(I_1 I_2 - I_3)^{-1} \{(I_1^2 + I_2) \mathbf{c}^\nabla \\ &\quad + I_1 I_3 \mathbf{c}^{-1} \cdot \mathbf{c}^\nabla \cdot \mathbf{c}^{-1} + \mathbf{c} \cdot \mathbf{c}^\nabla \cdot \mathbf{c} \\ &\quad - I_3 (\mathbf{c}^{-1} \cdot \mathbf{c}^\nabla + \mathbf{c}^\nabla \cdot \mathbf{c}^{-1}) \\ &\quad - I_1 (\mathbf{c} \cdot \mathbf{c}^\nabla + \mathbf{c}^\nabla \cdot \mathbf{c})\}. \end{aligned} \quad [1.17]$$

The tensor \mathbf{H} has the following properties:

1. For any isotropic tensor function $\boldsymbol{\varphi}(\mathbf{h})$ we have

$$\begin{aligned} \text{tr}\{\boldsymbol{\varphi}(\mathbf{h}) \cdot \mathbf{H}(\mathbf{c}, \mathbf{c}^\nabla)\} &= \text{tr}\{\boldsymbol{\varphi}(\mathbf{h}) \cdot 2\mathbf{c}^{-1} \cdot \mathbf{c}^\nabla\} \\ &= \text{tr}\{\boldsymbol{\varphi}(\mathbf{h}) \cdot \mathbf{h}^\nabla\} = \text{tr}\{\boldsymbol{\varphi}(\mathbf{h}) \cdot \dot{\mathbf{h}}\} \end{aligned} \quad [1.18]$$

which follows directly from [1.17] and [1.14].

2. If $\mathbf{c} \rightarrow \boldsymbol{\delta}(\mathbf{h} \rightarrow 0)$, then from [1.17] it follows that

$$\mathbf{H}(\mathbf{c}, \mathbf{c}^\nabla) = \mathbf{h}^\nabla \{\boldsymbol{\delta} + \mathcal{O}(\mathbf{h}^3 \cdot \boldsymbol{\omega})\}, \quad [1.19]$$

3. $\mathbf{H}(\mathbf{c}^{-1}, \mathbf{c}^{-1\nabla}) = -\mathbf{H}(\mathbf{c}, \mathbf{c}^\nabla)$. [1.20]

The formula [1.20] is obtained directly from [1.17] if we take account of the following relations

$$\begin{aligned} (\mathbf{c}^{-1})^\nabla &= -\mathbf{c}^{-1} \cdot \mathbf{c}^\nabla \cdot \mathbf{c}, \quad I_1(\mathbf{c}^{-1}) = I_2(\mathbf{c})/I_3(\mathbf{c}), \\ I_2(\mathbf{c}^{-1}) &= I_1(\mathbf{c})/I_3(\mathbf{c}), \quad I_3(\mathbf{c}^{-1}) = 1/I_3(\mathbf{c}), \end{aligned} \quad [1.21]$$

which can be easily proved.

Now we shall separate the isotropic bulk and the shear components in the tensors $\mathbf{h}, \mathbf{c}, \mathbf{e}$ (ρ_0 is the density of the medium in nondeformed state):

$$\begin{aligned} \mathbf{h} &= \mathbf{h}' + \frac{1}{3} \boldsymbol{\delta} \text{tr} \mathbf{h}, \quad \mathbf{c} = \mathbf{c}' \exp\left(\frac{2}{3} \text{tr} \mathbf{h}\right), \\ \mathbf{e} &= \mathbf{e}' + \frac{1}{3} \boldsymbol{\delta} \text{tr} \mathbf{e}, \quad \text{tr} \mathbf{h}' = 0, \quad \det \mathbf{c}' = 1, \quad \text{tr} \mathbf{e}' = 0, \\ \text{tr} \mathbf{h} &= \ln(\rho/\rho_0), \quad \det \mathbf{c} = \exp(2 \text{tr} \mathbf{h}) = \rho_0^2/\rho^2, \end{aligned}$$

¹⁾ An implicit form of the solution of this equation is used in (3). The formula [1.17] derived by L. M. Zubov was communicated to us by A. I. Lur'e.

$$\text{tr } \mathbf{e} = \frac{d}{dt} \ln(\rho_0/\rho). \quad [1.22]$$

Now we if introduce the following invariants from [1.22] for the tensor \mathbf{c}' :

$$I_1 = \text{tr } \mathbf{c}' = I_1 I_3^{-1}, I_3 = \det \mathbf{c}' = 1$$

$$I_2 = \frac{1}{2}(I_1^2 - \text{tr } \mathbf{c}'^2) = \text{tr } \mathbf{c}'^{-1} = I_2 I_3^{-2/3} \quad [1.23]$$

then the Hamilton-Cayley identity for \mathbf{c}' takes the form:

$$\mathbf{c}'^3 - I_1 \mathbf{c}'^2 + I_2 \mathbf{c}' - \delta = 0. \quad [1.24]$$

Substituting [1.22] into [1.7] and [1.8], from [1.17] we can determine the function $\mathbf{H}(\mathbf{c}', \mathbf{c}'^v)$ having the properties 1.-3. The equalities [1.7], [1.8] and [1.16] remain valid even after the substitutions $\mathbf{c} \rightarrow \mathbf{c}'$, $\mathbf{e} \rightarrow \mathbf{e}'$.

For an isotropic elastic medium for which $f = f(T, \rho, I_1, I_2)$ the eq. [1.15] gives (6)

$$\boldsymbol{\sigma}/\rho = -\rho \left. \frac{\partial f}{\partial \rho} \right|_T \delta + 2 \left(\frac{\rho}{\rho_0} \right)^{2/3} \cdot \left[\left. \frac{\partial f}{\partial I_1} \right|_T \mathbf{c}' - \left. \frac{\partial f}{\partial I_2} \right|_T \mathbf{c}'^{-1} \right]. \quad [1.25]$$

For elastomers of cross-linked rubber type, we can neglect the volume strains as compared with the shear strains in the entire deformation range of practical interest (7). Therefore we can consider these materials as incompressible ($\rho = \text{const}$) and thus simplify the dependence so obtained. In this case we have $\mathbf{c} = \mathbf{c}'$, and the invariants in the principal axes are of the form (c_i is the principal value of \mathbf{c})

$$I_1 = c_1 + c_2 + c_1^{-1} c_2^{-1}, I_2 = c_1^{-1} + c_2^{-1} + c_1 c_2,$$

$$I_3 = c_1 c_2 c_3 = 1. \quad [1.26]$$

From [1.26] it follows that $I_1 \leftrightarrow I_2$ for $\mathbf{c} \leftrightarrow \mathbf{c}^{-1}$.

From [1.26] it follows that for independent changes in c_1, c_2 in the range $c_i > 0$ the functions $I_1(c_1, c_2), I_2(c_1, c_2)$ vary independently in the "wedge-shaped" region:

$$I_1^+(I_2) < I_1 < I_1^-(I_2), I_2^-(I_1) < I_2 < I_2^+(I_1). \quad [1.27]$$

The functions $I_1^+(I_2), I_1^-(I_2)$ and the corresponding inverse functions $I_2^+(I_1), I_2^-(I_1)$ are well defined for $I_1 > 3, I_2 > 3$, and they can be expressed in a parametric form as follows:

$$I_1^-(x) = I_2^+(x) = x + 2x^{-1/2},$$

$$I_1^+(x) = I_2^-(x) = x^{-1} + 2x^{1/2}. \quad [1.28]$$

The curves $I_2^\pm(I_1)$ represent monotonically increasing functions of the arguments; they are symmetrical with respect to the bisectors of the first quadrant [$I_1 = I_2$] of the planes I_1, I_2 and intersect at the points $I_1 = 3, I_2 = 3$ having identical slopes.

For an incompressible isotropic elastic medium, the function $\rho_0 f(T, \mathbf{c}) = W(T, I_1, I_2)$ is generally called the *elastic potential* and its domain of definition is given by the formulas [1.27], [1.28]. The formula [1.25] thus is converted into the *Finger* relation (8)

$$\boldsymbol{\sigma} = -p\delta + 2W_1 \mathbf{c} - 2W_2 \mathbf{c}^{-1}$$

$$\left(W_k = \frac{\partial W}{\partial I_k}, k = 1, 2 \right) \quad [1.29]$$

where p is the Lagrange multiplier determined from the boundary conditions with due regard for the incompressibility of the medium.

Now we shall study the thermodynamical stability of the stressed state in an incompressible elastic medium under a given elastic potential $W(T, I_1, I_2)$. First consider some "small" neighbourhood of a fixed stressed state with the tensor \mathbf{c} characterized by the small tensor $\delta \mathbf{c}$ for which

$$\text{tr} \{ \delta \mathbf{c} \} = \text{tr} \{ 2\mathbf{c} \cdot (\boldsymbol{\beta} + \boldsymbol{\beta}^2) + 0(\boldsymbol{\beta}^3) \},$$

$$\text{tr } \boldsymbol{\beta} = 0; \text{tr} \{ \delta \mathbf{c}^2 \} \ll 1 \quad [1.30]$$

where $\boldsymbol{\beta} = \delta \mathbf{h}$ is the increment in the Hencky deformation tensor.

Expanding I_1, I_2 in terms of the tensor $\boldsymbol{\beta}$ parameter and then substituting these expressions in the formula for the elastic potential $W = W(T, I_1, I_2)$ and retaining only the terms up to second order of we obtain

$$\delta W = W(\mathbf{c} + \delta \mathbf{c}) - W(\mathbf{c})$$

$$= \delta_1 W + \delta_2^{(1)} W + \delta_2^{(2)} W$$

$$\delta_1 W = 2W_1 \text{tr}(\mathbf{c} \cdot \boldsymbol{\beta}) - 2W_2 \text{tr}(\mathbf{c}^{-1} \cdot \boldsymbol{\beta})$$

$$\delta_2^{(1)} W = 2W_1 \text{tr}(\mathbf{c} \cdot \boldsymbol{\beta}^2) + 2W_2 \text{tr}(\mathbf{c}^{-1} \cdot \boldsymbol{\beta}^2)$$

$$\delta_2^{(2)} W = 4W_{11} \text{tr}^2(\mathbf{c} \cdot \boldsymbol{\beta}) - 8W_{21} \text{tr}(\mathbf{c} \cdot \boldsymbol{\beta}) \text{tr}(\mathbf{c}^{-1} \cdot \boldsymbol{\beta})$$

$$+ 4W_{22} \text{tr}^2(\mathbf{c}^{-1} \cdot \boldsymbol{\beta}),$$

with

$$W_{km} = \frac{\partial^2 W}{\partial I_k \partial I_m}; k, m = 1, 2. \quad [1.31]$$

The term $\delta_1 W$ in [1.31] is equal to the work of stresses in the main stressed state with the

deformation tensor \mathbf{c} , whereas the terms $\delta_2^{(1)}W$ and $\delta_2^{(2)}W$ characterize the dynamic stability of the elastic medium.

An ideally elastic medium is said to be *thermodynamically stable* in the neighbourhood of the stressed state \mathbf{c} if the difference between the variations in the elastic potential δW and the work of the stresses $\delta_1 W$ over small deformations is positive, i.e. for a stable system we have

$$\delta W - \delta_1 W = \delta_2^{(1)}W + \delta_2^{(2)}W > 0. \quad [1.32]$$

This definition is consistent with the definition of mechanical stability (8), and it is a trivial case for small deformations ($\mathbf{c} \rightarrow \delta$). The terms $\delta_2^{(1)}W$, $\delta_2^{(2)}W$ of second order in β , as can be easily seen, are independent of each other and therefore for stability it is necessary and sufficient that $\delta_2^{(1)}W > 0$, $\delta_2^{(2)}W > 0$ for any β . The second inequality holds valid if and only if

$$W_1 > 0, \frac{W_2}{W_1} > -\min c_i^2, W_{11} > 0, \\ W_{12}^2 < W_{11} W_{22}. \quad [1.33]$$

If $W_i = \text{const}$ and $W_{ij} = 0$, then the conditions [1.33] are satisfied for all \mathbf{c} if and only if

$$W_1 > 0, W_2 > 0. \quad [1.34]$$

In the general case the conditions [1.34], which are close to the necessary condition, will be called, for the sake of simplicity, as the *conditions of thermodynamical stability*.

In concrete situations we shall consider the *Mooney-Rivlin* potential (8)

$$W = \mu [I_1 - 3 + \alpha(I_2 - 3)]. \quad [1.35]$$

This potential has been derived based on the phenomenological considerations and satisfactorily describes the behaviour of rubber under small deformations if $\alpha \approx 0.1 \div 0.2$. When $\alpha = 0$, from [1.35] we obtain the classical potential of the network high-elasticity theory (7), which gives $\mu = \rho RT/M_c$ where R is the gas constant, M_c is the mean molecular weight of the chain between two links.

§ 2. Thermodynamical description of the behaviour of viscoelastic (dissipative) medium

In the nonequilibrium state we can make an attempt to retain the local description of the medium with the help of the specific free energy f dependent on temperature T and an internal

parameter, namely, the tensor of recoverable strains $\mathbf{a}_e = \{a_{e,ij}\}$ determined, say, by the element-wise loading of the medium (fictitious or factual in some cases). Thus, for small particles by virtue of the local equilibrium hypothesis, all relationships known in equilibrium thermodynamics remain to hold true by assumption.

Within the framework of this hypothesis we shall determine the thermodynamical flux \mathbf{H}_e and the force²⁾ σ_e due to the tensor parameter \mathbf{a}_e using the same considerations as in the equilibrium case, i.e. with the help of the formulas [1.11], [1.12] and [1.17]. Thus, the relationship between the reversible measures of deformation, by definition, is given by the formulas [1.1]–[1.3] in which all quantities have the suffix e , and all the properties of \mathbf{H}_e mentioned above are preserved.

For this case the eq. [1.9] gives

$$TP_S + T^{-1}q \cdot \nabla T = \sigma : \mathbf{e} - \rho \dot{f}_T \\ = \sigma : \mathbf{e} - \sigma_e : \mathbf{H}_e. \quad [2.1]$$

This equation shows that the discrepancy of both σ_e from σ and that of \mathbf{H}_e from \mathbf{e} accounts for the nonequilibrium in isothermic deformation of the medium under consideration. Therefore we can determine the tensors σ_p and \mathbf{e}_p which characterize the contribution of nonequilibrium properties of the system into the dissipations. These tensors vanish in the equilibrium thermodynamical state:

$$\mathbf{e}_p = \mathbf{e} - \mathbf{H}_e, \quad \sigma_p = \sigma - \sigma_e. \quad [2.2]$$

With the help of [2.2] we can rewrite the expression [2.1] in the form proposed in (9) for investigating the small viscoelastic strains:

$$TP_S = -T^{-1}q \cdot \nabla T + \sigma_p : \mathbf{e} + \sigma_e : \mathbf{e}_p > 0. \quad [2.3]$$

From the first tensor equality [2.2], which plays the role of "kinematic equation", we can obtain the equalities of the type [1.6]–[1.8] containing the difference $\mathbf{e} - \mathbf{e}_p$ for \mathbf{e} with the help of the formula [1.17]. In particular, analogous to [1.7] and [1.8] we obtain

$$\mathbf{c}_e^\nabla - \mathbf{c}_e \cdot (\mathbf{e} - \mathbf{e}_p) - (\mathbf{e} - \mathbf{e}_p) \cdot \mathbf{c}_e = 0, \\ (\mathbf{c}_e^{-1})^\nabla + \mathbf{c}_e^{-1} \cdot (\mathbf{e} - \mathbf{e}_p) + (\mathbf{e} - \mathbf{e}_p) \cdot \mathbf{c}_e^{-1} = 0. \quad [2.4]$$

In the subsequent pages we shall study the behaviour of isotropic viscoelastic media under

²⁾ The suffix e shows that the tensor quantities are reversible.

large recoverable strains so the volume effects can be neglected in most of the cases. The incompressibility condition takes the form:

$$\text{tr } e = 0, \text{tr } e_p = 0, \det c_e = 1. \quad [2.5]$$

Only two of the three conditions [2.5] are independent. The behaviour of a compressible viscoelastic medium has been investigated in (1, 2).

The right-hand side of the expression [2.3] is the sum of the products of thermodynamical fluxes (q, e_p, σ_p have been taken to be such fluxes) by their conjugate thermodynamical forces (in our case $\nabla T, \sigma_e, e$ respectively). The constitutive equations of the medium are the phenomenological relations between the thermodynamical fluxes and the forces which for the case considered (small deviation from the thermodynamical equilibrium) are assumed to be quasilinear with Onsager symmetry for the kinetic coefficients (10). Basing on simple properties of the tensor dimensionality, we can express these relations as

$$q_i = -x_{ij}(c_e) \frac{\partial T}{\partial x_j}, \quad [2.6]$$

$$\begin{aligned} \sigma'_{p,ij} &= M_{ija\beta}^{(1)}(c_e) e_{\beta x} + M_{ija\beta}^{(2)}(c_e) \sigma'_{e,\beta x}, \\ e_{p,ij} &= -M_{ija\beta}^{(2)}(c_e) e_{\beta x} + M_{ija\beta}^{(3)}(c_e) \sigma'_{e,\beta x}. \end{aligned} \quad [2.7]$$

The primes in [2.7] denote the deviators of the respective tensors. The eq. [2.6] corresponds to the law of heat conductivity, while the equation [2.7] to the rheological relation for a viscoelastic medium. As the scheme is quasilinear, i.e. the kinetic coefficients $x, M^{(k)}$ are dependent on the equilibrium parameter c_e , we can take account of the "induced anisotropy" that appears under large recoverable strains c_e . Similar relationships with due regard for the deformation anisotropy can be derived in considering diffusion, polarizability and other phenomena in viscoelastic media.

The tensor kinetic coefficients $M^{(k)}$ have a number of properties which follow from the symmetry of the tensors e, e_p, σ, σ_e and the incompressibility condition [2.5]

$$M_{ija\beta}^{(k)} = M_{jia\beta}^{(k)} = M_{ija\beta}^{(k)}, M_{iia\beta}^{(k)} = M_{ijia}^{(k)} = 0. \quad [2.8]$$

By virtue of [2.8] we can write the expression for $M_{ija\beta}^{(k)}(c_e)$ ($k = 1, 2, 3$) as follows:

$$\begin{aligned} M_{ija\beta}^{(k)}(c_e) &= \frac{1}{2} m_1^{(k)} (\delta_{ia} \delta_{j\beta} + \delta_{i\beta} \delta_{ja} - \frac{2}{3} \delta_{ij} \delta_{a\beta}) \\ &+ (m_2^{(k)} c'_{ij} + m_3^{(k)} c_{ij}^{-1'}) c'_{a\beta} \\ &+ (m_4^{(k)} c'_{ij} + m_5^{(k)} c_{ij}^{-1'}) c_{a\beta}^{-1'} \\ &+ m_6^{(k)} (c'_{ia} \delta_{j\beta} + c'_{ja} \delta_{i\beta} - \frac{2}{3} \delta_{ij} c'_{a\beta}) \\ &+ c'_{i\beta} \delta_{ja} + c'_{j\beta} \delta_{ia} - \frac{2}{3} \delta_{a\beta} c'_{ij} \\ &+ m_7^{(k)} (c_{ia}^{-1'} \delta_{j\beta} + c_{ja}^{-1'} \delta_{i\beta} - \frac{2}{3} \delta_{ij} c_{a\beta}^{-1'}) \\ &+ c_{i\beta}^{-1'} \delta_{ja} + c_{j\beta}^{-1'} \delta_{ia} - \frac{2}{3} \delta_{a\beta} c_{ij}^{-1'}. \end{aligned} \quad [2.9]$$

For the sake of convenience, in the expression [2.9] and further onwards we shall omit the suffix e , thus $m_2^{(k)} = m_2^{(k)}(T, I_1, I_2)$ are the governing scalars of the tensors, where

$$c' = c - \delta \frac{1}{3} I_1, \quad c^{-1'} = c^{-1} - \delta \frac{1}{3} I_2,$$

$$I_1 = \text{tr } c, \quad I_2 = \text{tr } c^{-1}.$$

The heat conductivity tensor $x(c)$ has the following structure:

$$\begin{aligned} x_{ij}(c) &= x_0(T, I_1, I_2) \delta_{ij} + x_1(T, I_1, I_2) c_{ij} \\ &+ x_3(T, I_1, I_2) c_{ij}^{-1}. \end{aligned} \quad [2.10]$$

Now if we substitute the phenomenological relations [2.6] and [2.7] into [2.3], we can express the entropy production as a quadratic form of the thermodynamical forces:

$$\begin{aligned} T P_S &= T^{-1} x_{ij} V_i T V_j T + M_{ija\beta}^{(1)} e_{ij} e_{a\beta} \\ &+ M_{ija\beta}^{(3)} \sigma'_{e,ij} \sigma'_{e,a\beta} \geq 0. \end{aligned} \quad [2.11]$$

Since the terms in [2.11] are independent, and this form is positively definite, we find that the tensors are also positive definite. The last tensor can be expressed as

$$\{x\} > 0, \{M^{(1)}\} > 0, \{M^{(3)}\} > 0. \quad [2.12]$$

Here the tensor kinetic coefficient $M^{(2)}$ is not positive definite.

Using the expression [2.9] we can explain the expression [2.7] considering the two terms:

$$\begin{aligned} M^{(1)}(c) \cdot e &= m_1^{(1)} e + \text{tr}(c \cdot e) (m_2^{(1)} c' + m_3^{(1)} c^{-1'}) \\ &+ \text{tr}(c^{-1} \cdot e) (m_4^{(1)} c' + m_5^{(1)} c^{-1'}) \\ &+ m_6(c \cdot e + e \cdot c - \frac{2}{3} \delta \text{tr}(c \cdot e)) \\ &+ m_7^{(1)} (c^{-1} \cdot e + e \cdot c^{-1} - \frac{2}{3} \delta \text{tr}(c^{-1} \cdot e)), \end{aligned} \quad [2.13]$$

$$\begin{aligned} M^{(3)}(c) \cdot \sigma'_e &\equiv \varphi(c) = C_1(T, I_1, I_2) c' \\ &- C_2(T, I_1, I_2) c^{-1'}. \end{aligned} \quad [2.14]$$

Thus, the rheological relations [2.7] for the nonlinear viscoelastic medium in general contain 16 governing scalar functions of the invariants of the recoverable deformation tensors \mathbf{c} , moreover very weak constraints [2.12] are imposed on $m_k^{(1)}$ (the constraints on the functions C_1, C_2 will be examined in the subsequent pages).

In some particular cases, the relation [2.7] is converted into the rheological equations for the Maxwellian nonlinear liquid ($\mathbf{M}^{(1)} = \mathbf{M}^{(2)} = \mathbf{O}$, $\boldsymbol{\sigma}_p = \mathbf{0}$, i.e. $\boldsymbol{\sigma}_e = \boldsymbol{\sigma}$) and the Kelvin-Voigt nonlinear medium ($\mathbf{M}^{(2)} = \mathbf{M}^{(3)} = \mathbf{O}$, $\mathbf{e}_p = \mathbf{0}$). For the last case, the general constitutive equations were derived in (11).

Now we shall briefly examine the nonisothermal behaviour of a viscoelastic medium. From [2.12] it follows that the positive definite tensor of thermic resistance $\mathbf{r}(\mathbf{c}) = \mathbf{x}^{-1}(\mathbf{c})$ exists.

The measurements of heat conductivity coefficients under uniaxial stretching of polymers in high-elasticity state for sufficiently high drawing rates have shown that the heat conductivity has a distinct anisotropy (12), and the tensor \mathbf{r} is coaxial with the tensor \mathbf{c} for which

$$r_{\parallel} + 2r_{\perp} = 3r_0 = \text{const} \quad [2.15]$$

is true under simple stretching. Here r_{\parallel} and r_{\perp} are the thermal resistances parallel and perpendicular to the stretching direction respectively, r_0 is the coefficient of thermal resistance in isotropic (nonstressed) state.

Within the framework of the local equilibrium hypothesis we can retain the equality [2.15] for the nonequilibrium case too, however, in a general case it leads to the following expression for the thermal resistance tensor:

$$\mathbf{r}(\mathbf{c}) = r_0 \boldsymbol{\delta} + R_1(I_1, I_2) \mathbf{c}' + R_2(I_1, I_2) \mathbf{c}^{-1} \quad [2.16]$$

where R_i is a function of the invariants of the tensor \mathbf{c} . Certain constraints following from the positive definiteness of the tensor \mathbf{r} are imposed on these functions R_i . At present adequate number of facts are not available so that we cannot further examine the behaviour of the tensor $\mathbf{r}(\mathbf{c})$.

Different expressions for the temperature variations are given in (1), for instance, one of them is

$$\rho_0 c_\sigma \frac{dT}{dt} = \frac{\partial}{\partial x_i} x_{ij} \frac{\partial T}{\partial x_j} + A T P_S|_T \quad [2.17]$$

where c_σ is the heat capacity for a constant

stress tensor and A is the thermal equivalent of work.

§ 3. Thermodynamics and rheology of Maxwellian nonlinear medium

In this section we shall consider a particular case of viscoelastic incompressible medium of Maxwellian type which gives a satisfactory qualitative description to the behaviour of concentrated polymer solutions and melts.

The equations which characterize this type of medium have the form:

$$\boldsymbol{\sigma} \equiv \boldsymbol{\sigma}_e = -p \boldsymbol{\delta} + 2W_1 \mathbf{c} - 2W_2 \mathbf{c}^{-1}, \quad [3.1]$$

$$\mathbf{c}^{\nabla} - \mathbf{c} \cdot \mathbf{e} - \mathbf{e} \cdot \mathbf{c} + 2\mathbf{c} \cdot \mathbf{e}_p(\mathbf{c}) = \mathbf{0}, \quad [3.2]$$

$$\det \mathbf{c} = 1, \quad \text{tr} \mathbf{e} = 0, \quad [3.3]$$

$$\mathbf{e}_p = C_1(\mathbf{c} - \frac{1}{3} \boldsymbol{\delta} I_1) - C_2(\mathbf{c}^{-1} - \frac{1}{3} \boldsymbol{\delta} I_2), \quad [3.4]$$

$$D \equiv T P_S|_T = \boldsymbol{\sigma}_e : \mathbf{e}_p = (\frac{1}{3} I_1 I_2 - 3) \cdot (C_1 W_2 + C_2 W_1) + C_1 W_1 (\text{tr} \mathbf{c}^2 - \frac{1}{3} I_1^2) + C_2 W_2 (\text{tr} \mathbf{c}^{-2} - \frac{1}{3} I_2^2), \quad [3.5]$$

where $W(T, I_1, I_2)$ is the elastic potential,

$W_k = \frac{\partial W}{\partial I_k}$, D is dissipation. The rheological

behaviour of the Maxwellian medium is completely determined by two scalar functions C_1, C_2 dependent on two basis invariants of the tensor \mathbf{c} , i.e. on $I_1 = \text{tr} \mathbf{c}$, $I_2 = \text{tr} \mathbf{c}^{-1}$. We shall assume that the elastic potential W characterizing the local equilibrium properties of the medium is given.

For $\mathbf{c} \neq \boldsymbol{\delta}$, then for the quantities contained in [3.5] we have the following inequalities:

$$W_1 > 0, \quad W_2 \geq 0, \quad I_1 I_2 > 9, \\ \text{tr} \mathbf{c}^2 - \frac{1}{3} I_1^2 = \frac{2}{3} (I_1^2 - 3 I_2) > 0, \\ \text{tr} \mathbf{c}^{-2} - \frac{1}{3} I_2^2 = \frac{2}{3} (I_2^2 - 3 I_1) > 0. \quad [3.6]$$

Therefore [3.5] together with [3.6] form the constraints imposed on C_1, C_2 .

Now we shall consider some simple particular cases which characterize the Maxwellian media.

1. Maxwellian isotropic viscous medium

By virtue of [3.1] the deviator of the stress tensor $\boldsymbol{\sigma}'_e$ has the form:

$$\boldsymbol{\sigma}'_e = 2W_1(\mathbf{c} - \frac{1}{3} \boldsymbol{\delta} I_1) - 2W_2(\mathbf{c}^{-1} - \frac{1}{3} \boldsymbol{\delta} I_2). \quad [3.7]$$

We shall assume that the relationship between $\boldsymbol{\sigma}'_e$ and \mathbf{e}_p is analogous to the Newtonian law:

$$e_p = (2\lambda)^{-1} \sigma'_e \quad [3.8]$$

where $\lambda = \lambda(T, I_1, I_2)$ is some scalar function having the meaning of viscosity. From [3.4], [3.7] and [3.8] we have

$$C_1 = W_1/\lambda, \quad C_2 = W_2/\lambda. \quad [3.9]$$

Substituting [3.9] into [3.5] we obtain

$$D = \frac{2}{3\lambda} \{(I_1 I_2 - 9)W_1 W_2 + W_1^2(I_1^2 - 3I_2) + W_2^2(I_2^2 - 3I_1)\} > 0. \quad [3.10]$$

Thus the quadratic forms in the curled brackets in [3.10] are positive definite, therefore $\lambda > 0$.

The relationships [3.9] satisfy the Ziegler principle of minimum irreversible forces (13), i.e.

$$\min \text{tr} \{e_p^2\}$$

for a given D defined by [3.5] and fixed c .

2. A simple case of the Maxwellian medium with anisotropic viscosity

Assume that

$$C_1(I_1, I_2, T) = C_2(I_2, I_1, T). \quad [3.11]$$

In this case, as is evident from [3.5], we have

$$C_1 > 0 (C_2 > 0).$$

And since $I_1 \leftrightarrow I_2$ for $c \leftrightarrow c^{-1}$ then for $c \rightarrow c^{-1}$ we have $e_p \rightarrow -e_p$. In this case, as it follows from [2.4] the kinematic eq. [3.2] is invariant with respect to the transformations $c \rightarrow c^{-1}$, and $e \rightarrow -e$.

Since for real rubber $W(I_1, I_2) \neq W(I_2, I_1)$, then there exists an anisotropic relationship between σ'_e and e_p given by some tensor of the fourth rank $M^{(3)}$ in [2.7].

It is really interesting that unlike [3.9], in the anisotropic case described by the formulas [3.11], a flat deformation state is possible in which

$$e = \begin{pmatrix} e_{11} & e_{12} & 0 \\ e_{12} & e_{22} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \omega = \begin{pmatrix} 0 & \omega_{12} & 0 \\ -\omega_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$c = \begin{pmatrix} c_{11} & c_{12} & 0 \\ c_{12} & c_{22} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad I_1 = I_2 = I. \quad [3.12]$$

Indeed, in this case, the eqs. [3.12] and [3.2] give

$$C_1(I_1, I_2)|_{I_1=I_2} = C_2(I_1, I_2)|_{I_1=I_2}$$

which is always satisfied by virtue of [3.11] but contradicts [3.9] – the potential W characteristic of real materials.

3. Maxwellian media with “nonequilibrium” potential

In this case in [3.4] we have

$$C_1 = 2 \frac{\partial \Psi}{\partial I_1}, \quad C_2 = 2 \frac{\partial \Psi}{\partial I_2} \quad (C_k = 2 \Psi_k; \quad k = 1, 2) \quad [3.13]$$

where $\Psi = \Psi(T, I_1, I_2)$ is the “nonequilibrium” potential. Then

$$e_p = 2c \cdot \frac{\partial \Psi}{\partial c} - q \delta = 2 \Psi_1 (c - \frac{1}{3} \delta I_1) - 2 \Psi_2 (c^{-1} - \frac{1}{3} \delta I_2) \quad [3.14]$$

where q is the Lagrange multiplier defined by the incompressibility condition $\text{tr} e_p = 0$.

In the case of [3.9] the potential Ψ has the form:

$$\Psi = \Psi(W) = \int \frac{dW}{\lambda(W)}. \quad [3.15]$$

In the case of [3.11], as can be easily seen, the potential Ψ given by the formulas [3.13] is a symmetrical function of I_1, I_2 , i.e.

$$\Psi(I_1, I_2) = \Psi(I_2, I_1). \quad [3.16]$$

§ 4. Some examples of Maxwellian models. Generalization

The rheological relations derived in § 2 and 3 are common for the viscoelastic media of different nature. They can be further improved and generalized only with an account of the specific properties of the viscoelastic media.

Therefore now we shall examine some simplifying hypotheses which account for the specific features of strains in polymer melts and concentrated solutions with the view of giving simple but adequate description to the basic nonlinear properties of media with the help of a few constants having simple physical meaning.

We shall first examine the constitutive relationships for the Maxwellian nonlinear model. We shall assume that the elastic potential is given (for example, by the expression [1.35]);

as it follows from the eqs. [3.1]–[3.5], it is necessary to specify the type of two functions:

$$C_1(I_1, I_2, T), C_2(I_1, I_2, T).$$

For this purpose we shall formulate several assumptions.

a) The nonequilibrium potential $\Psi(I_1, I_2, T)$ given by the formulas [3.13] and [3.14] may be used for describing the nonlinear rheological properties of the polymer media.

b) The viscosity of the system is anisotropic: the viscosity assumes maximum value in the direction where maximum stresses act. In a rough approximation this is described by the equality $e_p(c) \approx -e_p(c^{-1})$ i.e. the formulas [3.11] or [3.16].

c) The nonequilibrium potential Ψ satisfying the condition [3.16] depends only on the elastic potential and is related with it in a simple manner:

$$\Psi = \Psi(W_S), \quad 2W_S = W(I_1, I_2) + W(I_2, I_1). \quad [4.1]$$

Analogous to [3.15] we shall put that

$$\Psi(W_S) = \int \frac{dW_S}{\lambda(W_S)} \quad [4.2]$$

where $\lambda(W_S)$ has the meaning of a characteristic scalar coefficient of viscosity or (with the same dimensional factor) characteristic relaxation time.

d) The viscosity or the characteristic relaxation time steeply increases with the recoverable strain; this dependence is determined by a function of exponential type. From [4.2] we have

$$\lambda = \lambda_0(T) \exp \left\{ \frac{\beta}{\mu} W_S \right\}, \quad \beta = \text{const} > 0 \quad [4.3]$$

where $\mu(T)$ is the high-elasticity modulus contained in the definition of elastic potential W (see, for example [1.35]), β is a dimensionless constant depending only on the type of the polymer.

The assumption (a) corresponds to the “principle of maximum simplicity” of description; the assumption (c) accounts for the closeness of the system to the thermodynamical equilibrium state stipulated everywhere in this paper; the assumptions (b) and (d) take an account of the orientation of the polymer systems in strong mechanical fields. Thus, the assumption (b) corresponds to the effective

levelling of components of the nonrecoverable strain rates due to the growth of viscosity in the direction of maximum stress. This “induced orientation” is developed in nonlinear conditions only if $\sigma_e(c) \neq \sigma_e(c^{-1})$, and is especially obvious in considering the principal values of the tensors c, σ_e, e_p under simple stretching or simple shearing. From the assumption (d) (formula [4.3]) it follows that $\|e_p\| \rightarrow 0$ for $\|c\| \gg 1$, and that corresponds to the loss of fluidity under large recoverable strains observed in many experiments (14), (15). This is evident from the resultant formula for e_p obtained from [3.4], [3.13], [4.2] and [4.3]

$$e_p = \frac{2}{\lambda_0} \exp \left(- \frac{\beta}{\mu} W_S \right) \cdot \left[(c - \frac{1}{3} \delta I_1) W_{S,1} - (c^{-1} - \frac{1}{3} \delta I_2) W_{S,2} \right]. \quad [4.4]$$

The formulas [4.4], [3.1]–[3.3] form a closed system of constitutive equations for describing the isothermal behaviour of polymer systems within the framework of the Maxwellian nonlinear model.

Nevertheless, these equations do not predict the retardation phenomena inherent to the polymer systems. For describing this phenomenon we shall make use of the eqs. [2.7] assuming that $\sigma_p \equiv \sigma - \sigma_e \neq 0$. We shall stipulate the following simplifying assumptions:

e) Relaxation and retardation can be regarded as independent phenomena.

f) The kinetic coefficient $M^{(1)}$ in [2.7] is a scalar (anisotropic relaxation properties have already been taken into account in [4.4]). From the assumption (e) it follows that $M^{(2)} = 0$ in [2.7], whereas from the assumption (f) and the first equality of [2.7] we have

$$\sigma_p \equiv \sigma - \sigma_e = m(I_1, I_2, T) e \quad (m > 0). \quad [4.5]$$

f) The retardation viscosity m or the characteristic retardation time θ_r (differing from m by a dimensional constant) steeply increases with the growth in the recoverable strain. This dependence is similar to [4.3], i.e.

$$\theta_r \sim m = m_0(T) \exp \left\{ \frac{\beta}{\mu} W_S \right\}. \quad [4.6]$$

The physical meaning of the assumptions (e) and (f) leading to the formulas [4.3] and [4.6] is discussed in § 5.

If we take an account of the retardation, then the closed system of rheological equations takes the form:

$$\begin{aligned} \boldsymbol{\sigma} + p\boldsymbol{\delta} &= 2cW_1 - 2c^{-1}W_2 \\ &+ m_0(T) \exp\left\{\frac{\beta}{\mu}W_S\right\} \mathbf{e}, \quad \left(W_j = \frac{\partial W}{\partial I_j}\right) \\ c^{\nabla} - c \cdot \mathbf{e} - \mathbf{e} \cdot c + 2c \cdot \mathbf{e}_p(c) &= 0, \\ \text{tr } \mathbf{e} = 0, \quad \det c &= 1, \\ \mathbf{e}_p &= \frac{2}{\lambda_0(T)} \exp\left\{-\frac{\beta}{\mu}W_S\right\} \\ &\cdot \left[(c - \frac{1}{3}\boldsymbol{\delta}I_1)W_{S,1} - (c^{-1} - \frac{1}{3}\boldsymbol{\delta}I_2)W_{S,2}\right], \\ D = TP_S|_T &= \frac{4}{3\lambda_0(T)} \exp\left\{-\frac{\beta}{\mu}W_S\right\} \\ &\cdot \left\{(I_1I_2 - 9)(W_1W_{S,2} + W_2W_{S,1}) \right. \\ &+ 2(I_1^2 - 3I_2)W_1W_{S,1} + 2(I_2^2 - 3I_1)W_2W_{S,2} \\ &\left. + \frac{3\lambda_0(T)}{4m_0(T)} \text{tr}(\boldsymbol{\sigma}_p^2)\right\}, \end{aligned}$$

$$I_1 = \text{tr } c, \quad I_2 = \text{tr } c^{-1}, \quad W = \rho_0 f(T, I_1, I_2),$$

$$2W_S = W(I_1, I_2) + W(I_2, I_1), \quad W_{S,k} = \frac{\partial W_S}{\partial I_k}. \quad [4.7]$$

From these equations it follows that after the loss of fluidity ($e_p \rightarrow 0$), the behaviour of the medium is described by the equation of state of Kelvin-Voigt type.

The system of eqs. [4.7] contains four constants of the material $\beta, \lambda_0(T), m_0(T), \mu(T)$. We shall now give a method for determining the last three constants. In the linear region, from [4.7] we have

$$\begin{aligned} c &= \boldsymbol{\delta} + 2\mathbf{h} + 0(h^2), \quad \lim_{c \rightarrow \boldsymbol{\delta}} (W_1 + W_2) \\ &= \lim_{c \rightarrow \boldsymbol{\delta}} (W_{1,S} + W_{2,S}) = W_1^0 + W_2^0 \\ \boldsymbol{\sigma}' &\equiv \boldsymbol{\sigma} + p\boldsymbol{\delta} = m_0\mathbf{e} + 4(W_1^0 + W_2^0)\mathbf{h}; \\ \frac{\partial \mathbf{h}}{\partial t} + \mathbf{e}_p &= \mathbf{e}; \quad \mathbf{e}_p = \mathbf{h} \cdot \frac{4(W_1^0 + W_2^0)}{\lambda_0}. \quad [4.8] \end{aligned}$$

The formulas [4.6] lead to linear rheological equation:

$$\left(\theta_0 \frac{\partial}{\partial t} + 1\right) \boldsymbol{\sigma}' = 2\eta_0 \left(1 + \theta_r \frac{\partial}{\partial t}\right) \mathbf{e} \quad [4.9]$$

where the positive constants $\theta_0, \eta_0, \theta_r$ are the relaxation time, Newtonian viscosity, retardation time respectively, and $\theta_r = s\theta_0$ ($0 < s < 1$). These parameters are determined from the standard rheological measurements in the linear region, for example, from the dynamic experiments. On comparing the constants in [4.8] and [4.9], we find that

$$\begin{aligned} \lambda_0 &= 2\eta_0(1-s), \quad m_0 = 2\eta_0s, \\ 2(W_1^0 + W_2^0) &= \frac{\eta_0(1-s)}{\theta_0}. \quad [4.10] \end{aligned}$$

If we assume, for instance, that the type of the elastic potential is given by the expression [1.35], where $\alpha = 0.1 \div 0.2$ is known, then

$$W_1^0 + W_2^0 \equiv W_1 + W_2 = \mu(1 + \alpha)$$

and from [4.8] we obtain

$$\mu = \frac{1}{2}\eta_0(1-s)[\theta_0(1+\alpha)]^{-1}.$$

The parameter β which determines the physical nonlinearity in the behaviour of the material is found from additional considerations.

It is known that the rheological behaviour of polymer melts and concentrated polymer solutions in the linear region is described by sufficiently representative set of relaxation times. Therefore, the description of the behaviour of the systems by the eqs. [4.7] in the linear region reduces to a three-parameter model [4.9], and probably it cannot be an appropriate one.

Nonetheless, it is hoped that the nonlinear behaviour of these polymer liquids may be satisfactorily described by the system [4.7] in a wide range of strain rates as a consequence of the assumption that only the nonlinear mechanism gives the major contribution into the rheological behaviour.

However, we may assume, in addition to the eq. [4.7], that the nonlinear relaxation properties of the system can be described by a set of relaxation times. Such a description, naturally, is not consistent with the general description discussed in § 2. Therefore, for a simple concrete description of such a type, we shall formulate the following hypothesis.

g) The nonlinear viscoelastic behaviour of concentrated polymer liquids is described by a set of mutually non-intersecting linear relaxation "modes" with additional "viscous" friction. Loss of fluidity may take place only one of these modes (corresponding to the least characteristic

relaxation time in the linear region). The additional viscous friction depends only on the elastic strains at the first mode.

The corresponding equations are of the form:

$$\begin{aligned} \sigma + p\delta &= m_0(T) \exp\left\{\frac{\beta}{\mu_1} W_S^{(1)}\right\} e \\ &+ 2 \sum_k (c_k W_1^{(k)} - c_k^{-1} W_2^{(k)}) \\ c_k^v - c_k \cdot e - e \cdot c_k + 2c_k \cdot e_p^{(k)}(c_k) &= 0, \\ \text{tr } e &= 0, \quad \det c_k = 1, \\ e_p^{(k)} &= \frac{2}{\lambda_k^0(T)} \exp\left\{-\frac{\beta_k}{\mu_k} W_S^{(k)}\right\} \\ &\cdot \left\{(c_k - \frac{1}{3} \delta I_1^{(k)}) W_{S,1}^{(k)} - (c_k^{-1} - \frac{1}{3} \delta I_2^{(k)}) W_{S,2}^{(k)}\right\}, \\ I_1^{(k)} &= \text{tr } c_k, \quad I_2^{(k)} = \text{tr } c_k^{-1}, \quad \beta_k = \beta(k=1), \\ \beta_k &= 0 \quad (k > 1), \\ \rho_0 f = W &= \sum_k W^{(k)}, \\ 2W_S^{(k)} &= W^{(k)}(I_1^{(k)}, I_2^{(k)}) + W^{(k)}(I_1^{(k)}, I_1^{(k)}), \\ D = T P_S|_T &= m_0(T) \exp\left\{\frac{\beta}{\mu_1} W_S^{(1)}\right\} \text{tr } e^2 \\ &+ \frac{4}{3} \sum_k \frac{1}{\lambda_k^0} \exp\left\{-\frac{\beta_k}{\mu_k} W_S^{(k)}\right\} \\ &\cdot \left\{(I_1^{(k)} I_2^{(k)} - 9)(W_1^{(k)} W_{S,2}^{(k)} + W_2^{(k)} W_{S,1}^{(k)})\right. \\ &+ 2(I_1^{(k)2} - 3I_2^{(k)}) W_1^{(k)} W_{S,1}^{(k)} \\ &\left.+ 2(I_2^{(k)2} - 3I_1^{(k)}) W_2^{(k)} W_{S,2}^{(k)}\right\}. \end{aligned} \quad [4.11]$$

These formulas describe the relaxation phenomena both in a flowing polymer or after the loss of fluidity.

The independence of different nonlinear relaxation modes postulated in the assumption (g) can be explained by the fact that the relaxation phenomena are created by microprocesses taking place in different scales. The least scale corresponding to the least relaxation time and giving the major contribution into the proposed description is probably the supermolecular one (for details see § 5).

§ 5. Qualitative physical concepts on the deformation of polymer melts and concentrated polymer solutions

The assumptions made in §4 for specifying the type of equation of state for the polymer media

need to be substantiated from the viewpoint of polymer physics. However, the physical kinetics of this field is in such an unsatisfactory state that so far there is no theory that could adequately describe the relaxation behaviour of block polymers even in the linear region. Therefore, the viewpoint advanced in this section cannot claim to be anything else than a mere reformulation of the already existing hypotheses in a different language. The suitability of the hypothesis suggested and the proposed formulas has to be ultimately verified by the experiment.

We shall assume that the high-elastic behaviour of polymers both above and below the flow temperature T_f is a result of the existence of a labile network of "crosslinks" which unlike in the vulcanized rubber is of fluctuating nature. This gives rise to the irreversible flow in non-crosslinked polymers above the glass transition temperature T_g or the flow temperature T_f . If the polymer is amorphous, then no flow is developed in the range $T_g < T < T_f$ due to very strong effect of temperature on the viscosity. This temperature range is the region of high-elasticity behaviour of polymers (16); it is characterized by an ability for high recoverable strains caused by the entropy elasticity of macromolecular chain between two crosslinks of the fluctuating network. Though the behaviour of the material is of nonequilibrium type, yet the nonequilibrium may be exhibited weakly as in the case of chemically crosslinked systems. For this state of incomplete thermodynamical equilibrium the following relation holds valid (7) (as well as the eq. [1.35]):

$$\begin{aligned} W &= \rho_0 \Delta f \approx -T \Delta S = \mu \omega(I_1, I_2), \\ \mu &\sim \rho_0 R T \mu_c^{-1} \end{aligned} \quad [5.1]$$

where Δf and ΔS are the "deformation" variations in the specific free energy and entropy respectively, ω is some temperature independent function of two invariants of the tensor c .

In the nonequilibrium case (for example, in the presence of irreversible flow), within the framework of local thermodynamical equilibrium hypothesis, we can assume that the elastic potential W is given by the eq. [5.1].

Furthermore, we shall assume that in concentrated polymer liquids with a net structure, the characteristic processes of relaxation and viscous flow are mainly determined by the

activated formation and break of linkage between the neighbouring parts of macromolecules. Thus, the characteristic relaxation time can be expressed as (17):

$$\theta = \theta_1(T) \exp(\Delta f^*/RT), \quad \theta_1 \sim [T \rho_0(T)]^{-1}$$

$$\Delta f^* = \Delta U^* - T \Delta S^* \quad [5.2]$$

where ΔU^* , Δf^* , ΔS^* , are the specific internal energy, free energy and activation entropy respectively. When there no mechanical field, i. e. $\Delta S^* = \text{const}$, $\Delta U^* = \text{const}$, the last formula in [5.2] does not give any additional mechanical information. When there is a field, the term ΔS^* equal to the order of the entropy of the segment participating in the transfer act, diminishes as a result of orientation effect of the field. Therefore we can approximately assume that

$$\Delta S^* \approx -\beta \omega(I_1, I_2), \quad \beta \approx M_*/M_c \quad (0 < \beta \leq 1)$$
[5.3]

where M_* is the molecular weight of the segment.

The parameter β characterizing the flexibility of the macromolecular chains increases with increasing rigidity of molecules. Therefore we can take that the mean number of crosslinks per unit volume must decrease with increasing intensity³⁾. On the other hand, the orientation effect of the field must increase the chain rigidity and growth of M_* . Therefore, the parameter β in [5.3] can be taken to be approximately constant.

If the intensity of the mechanical field is so great that it distorts the potential barriers which govern the activation process, then, say, in the case of simple stretching with stress σ we have

$$\Delta U^* \approx \Delta U_0^* - \gamma \sigma. \quad [5.4]$$

This formula is usually used for describing the creep phenomenon under conditions close to the limiting oriented state when there are practically no entropy effects. For polymer solutions, for which the stresses are small, we can take in most cases

$$\Delta U^* \approx \Delta U_0^* = \text{const}. \quad [5.5]$$

On substituting [5.3] and [5.5] into [5.2] we obtain

$$\theta \approx \theta_0(T) \exp\{\beta \omega(I_1, I_2)\},$$

$$\theta_0(T) \approx \theta_1(T) \exp\left\{\frac{\Delta U^*}{RT}\right\} \quad [5.6]$$

which is in qualitative agreement with [4.3].

The dense packing in the polymer melts and their concentrated solutions calls for the need to account the additional "side" action of one segment with other neighbouring segments not belonging to that chain; and in the case of solutions with solvent molecules as well. This interaction is of viscous in nature and can be roughly estimated by the formulas [4.5] and [4.6]. The similarity of formulas [4.3] and [4.6] is in agreement with the assumption that the relaxation time θ and the retardation time θ_r increase with increasing segment length caused by the orientation effect of the mechanical field, i. e. $\theta/\theta_0 \approx \theta_r/\theta_r^0 \approx l/l_0 > 1$ where l and l_0 are the characteristic segment lengths in the presence and absence of a field respectively.

So far we developed a viewpoint based on simplified assumption on the statistically uniform fluctuating network with the characteristic scale L_0 and the corresponding relaxation time θ_0 . Under real conditions, however, the flowing block polymer can be represented as a set of "networks" enclosed in each other with the characteristic length L_k and times θ_k with minimum length L_0 and time θ_0 . If we are not interested in the processes in the scale of a few monomer units, then we can neglect the rapid relaxation processes and thus "average" the relaxation characteristics. If the inequality $L_0 \ll L_1 \ll \dots \ll L_N$ ($\theta_0 \ll \theta_1 \ll \dots \ll \theta_N$) hold true, then the relaxation processes in different scales will evidently be uncorrelated, i. e. mutually independent (see assumption *g*). Besides, if the relaxation transition into solid state takes place in the least size network, then it will not have any effect on the "network" of larger sizes, and thus we can neglect the transitions in higher order networks as the time scales in different "networks" are not interrelated.

Everywhere in this paper we employed the term "transition into high-elasticity state", which is realized according to the kinetic criteria, if $T > T_f$ under the effect of strong mechanical fields. The residence time of the material in this state, however, under given external conditions strongly depends on the nature of the

³⁾ Probably, this will be the case if the intensity of the field is not so high as to cause secondary effects associated with crystallization.

polymer (flexibility of the chains, their branching, specific polymer-solvent interaction, etc.).

For rigid chain polymers this residence time will be minimum, and as soon as the fluidity is lost, the polymer may pass from the high-elasticity state into glass-like or crystalline state depending on the chain structure. For flexible chain polymers we may expect that they reside in the high-elasticity state for a sufficiently long time. In this and other cases, this residence time is restricted by the strength considerations.

Incidentally, if the field is removed after the kinetic transition of the system into a solid-like state under isothermal conditions, the polymer may pass back into its viscous state. Therefore, for fixing the oriented state under a strong external mechanical field, the polymer has to be either cooled down or it must develop strong (say, chemical) crosslinks.

These physical concepts are applicable to highly concentrated systems with a distinct net structure. They cannot predict many of the effects characteristic to dilute polymer solutions for which the parameters characterizing the phase composition may have a significant bearing. Besides, the effects already mentioned, phase equilibrium and kinetic effects may play a decisive role in these systems. They may give rise to demixing in the polymer-solvent systems under strong mechanical fields.

Conclusions

The theory of rheological behaviour of concentrated polymer solutions, proposed in this paper, is based on the assumption that the irreversible thermodynamical states of these systems are close to the high-elasticity state—the state of an elastic medium with giant recoverable strains. This assumption is supplemented with the orientation effects for these systems in strong mechanical fields where direct relaxation transition may take place into high-elasticity state at temperatures far exceeding the melt point. Many of the “solid-like” effects observed in polymer solutions at higher rates of deformation can be explained from this viewpoint.

In terms of the irreversible thermodynamics, the polymer liquid is an interesting example of weakly nonequilibrium system whose non-linear behaviour is strongly dependent on the nonlinearity of the local-equilibrium state; the

dissipative phenomena may diminish in this system under strong external fields.

A comparison of the theory with the experimental results will be published in a subsequent communication.

Summary

Nonlinear constitutive equations for viscoelastic polymer media have been derived with the help of irreversible thermodynamical methods. These equations contain a small number of constants which have obvious physical meaning. The work is based on the hypothesis that the high-elasticity state characterized by large elastic strains is the local equilibrium thermodynamical state of these media. A theoretical description is given to explain the kinetic transition of fluid polymer media into high-elasticity state at temperatures above the flow temperature.

Zusammenfassung

Mit Hilfe der Methoden der Thermodynamik irreversibler Prozesse werden nichtlineare rheologische Stoffgleichungen für viskoelastische Polymere abgeleitet. Diese Gleichungen enthalten nur wenige Konstanten, die eine klare physikalische Bedeutung haben. Die Untersuchung ist auf die Hypothese gegründet, daß der hochelastische Zustand, der durch große elastische Dehnungen gekennzeichnet ist, der Zustand des lokalen thermodynamischen Gleichgewichts dieser Stoffe ist. Es wird eine theoretische Erklärung des kinetischen Übergangs von flüssigen Polymeren in den hochelastischen Zustand bei Temperaturen oberhalb der Fließtemperatur gegeben.

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