

## Thermodynamic Description of Relaxation Phenomena in Polymers

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### Synopsis

The analysis of various deformations of an ordinary elastic body and a highly elastic body accompanied by temperature changes shows that, in distinction to isothermic conditions, under adiabatic conditions the dynamic characteristics of a polymer in a highly elastic state depend on the amplitude of the applied stress (in particular, their position on a frequency or temperature scale), which is associated with the entropic nature of the highly elastic deformation.

When describing the relaxation phenomena caused by the response of the system of interacting kinetic units to the external perturbation, the nonequilibrium thermodynamics relationship between the "flow" and the "generalized force" is nonlinear even at small deviations from the equilibrium state. In this case the dependency of the kinetic factor on the response can be presented by eq. (40).

Considered herein were such particular relaxation phenomena as creep and stress relaxation. The calculated dependencies agree well with the experimental data.

The thermodynamics of irreversible processes has extensive application in the description of relaxation phenomena in a great variety of systems.<sup>1</sup> Its method, as applied to chemical reactions, has been developed earlier in De Donder's work.<sup>2,3</sup> Then Mandelshtam and Leontovich<sup>4,5</sup> independently worked out a thermodynamic method applicable to the relaxation processes in gases and liquids.

Onsager's<sup>6</sup> determination of "mutuality" relationships between factors of linear equations, which essentially are the phenomenological laws governing nonequilibrium processes, and another formulation of these relationships proposed by Casimir<sup>7,8</sup> which made them applicable to a greater variety of irreversible phenomena than those initially presupposed by Onsager, resulted in the development by Meixner<sup>9,10</sup> and then by Prigogine<sup>11</sup> of a coordinated phenomenological theory. Further different trends appeared to have rapidly developed within this theory. The applicability of the nonequilibrium thermodynamics as developed is limited by the description of irreversible processes possessing linear characteristics. It is assumed that, in general, at least in the case of small deviations from the thermodynamic equilibrium, the relationships between "flows" and "generalized forces" should be linear. However, when describing relaxa-

tion phenomena depending on the response of the system of interacting kinetic units to an external perturbation, these relationships appear to be nonlinear even at small deviations from the equilibrium.

As has been previously stated,<sup>12</sup> dynamic measurements made during the study of relaxation properties of polymers are adiabatic rather than isothermic. The evaluation of the difference between the adiabatic and isothermic module of both ordinary elastic bodies and those whose shear modulus is directly proportional to  $T$  is based on thermodynamic calculations, with time dependencies not taken into account, and shows that in many cases time dependency can be neglected.<sup>12</sup>

In deformations accompanied by temperature changes, with time dependencies being taken into account, attempts are made to evaluate what the energy dissipation caused by heat flow contributes to the mechanical losses and, hence, to evaluate the magnitude of change in the pseudopositions of the modulus at the transition from isothermic to adiabatic conditions.<sup>12</sup> Analysis of viscoelasticity with the help of the thermodynamics of irreversible processes<sup>13</sup> has shown that in the case of adiabatic conditions the relaxation spectrum occurs at somewhat smaller time values than in the case of isothermic conditions.

The deformations accompanied by changes in the temperature of a body have been considered.<sup>14,15</sup> The final dependencies of stress upon deformation and temperature changes obtained in these works in the considered approximation (when external effects, temperature changes, and deviations from the thermodynamic equilibrium are not very high) are supposed to be applicable to ordinary elastic bodies. It may be actually shown that such relationships are inherent in highly elastic bodies (inverse sign of thermal effect at the deformation should be taken into account in this case), while more simple dependencies are characteristic of the ordinary elastic bodies.

For this reason, it is necessary to analyze the different effects of the adiabatic conditions of deformation upon the dynamic characteristics of an ordinary elastic body and a highly elastic one. Such an analysis shows that when the deformations are adiabatic, the dynamic characteristics of highly elastic bodies depend upon the amplitude of the applied stress even at small external effects.

### Nonisothermic Deformations

Firstly, let us briefly consider the deformation process of an ordinary elastic body which accompanies temperature changes. For simplification, we shall consider only a linear stress state and one relaxation mechanism (described by one relaxation time), which in the case of polymers in the highly elastic state can be represented by the orientation of macromolecule segments in the field of action of mechanical forces, this orientation being characterized by an internal parameter.

Assuming that the free energy of a unit volume of the deformed body is  $F = F(\epsilon, \xi, T)$ , in a first approximation we can write

$$F = F_0 + \gamma(T - T_0)\epsilon + 1/2a_1\epsilon^2 + a_2\epsilon\xi + 1/2a_3\xi^2 \quad (1)$$

where  $F_0$  is the free energy;  $T_0$  is the temperature of a body in the nondeformed state,  $\gamma$ ; and  $a_1$ ,  $a_2$ , and  $a_3$  are material constants.

It is considered in this case that in the state of the thermodynamic equilibrium at  $\epsilon = 0$  and  $T = T_0$ ,  $\sigma = (\partial F / \partial \epsilon)_{T, \xi} = 0$ , the free energy reaches its minimum value and  $\partial^2 F / \partial \xi \partial T = -\partial S / \partial \xi \epsilon$ . Therefore, in distinction to Fustov<sup>14</sup> and Shermergor,<sup>15</sup>  $(\partial^2 F / \partial T \partial \xi)(T - T_0)$  member is absent in the decomposition eq. (1). This in turn makes the equilibrium value  $\bar{\xi}$  independent of temperature changes. Actually, the minimum of free energy in the equilibrium state gives  $\bar{\xi} = -a_2/a_3\epsilon$ . Then eq. (1) for free energy may be written as follows:

$$F = F_0 + \gamma(T - T_0)\epsilon + 1/2 \left( a_1 - \frac{a_2^2}{a_3} \right) \epsilon^2 + 1/2 a_3 (\xi - \bar{\xi})^2 \quad (2)$$

As follows from the ordinary elasticity theory,<sup>16</sup> in the case of linear stressed state the expression for free energy takes the following form:

$$F = F_0 - [E_\infty \alpha (T - T_0) \epsilon] + 1/2 E_\infty \epsilon^2. \quad (3)$$

Comparing expressions (2) and (3) at  $\xi = \bar{\xi}$ , we finally obtain

$$F = F_0 - [E_\infty \alpha (T - T_0) \epsilon] + 1/2 E_\infty \epsilon^2 + 1/2 a_3 (\xi - \bar{\xi})^2 \quad (4)$$

where  $E_\infty$  is the equilibrium (relaxed) elasticity modulus and  $\alpha$  is the linear thermal expansion factor.

Using the linear phenomenological relationship from the nonequilibrium thermodynamics between the "flow" and "generalized force,"  $X =$

$-\left(\frac{\partial F}{\partial \xi}\right)_{T, \epsilon}$ , and taking into account that  $\sigma = \left(\frac{dF}{d\epsilon}\right)_{T, \epsilon}$ , from expression (4) we shall find that

$$\sigma = E_\infty \epsilon - [E_\infty \alpha (T - T_0)] + \int_{-\infty}^t E' e^{-\frac{t-t'}{\tau'}} \dot{\epsilon}(t') dt' \quad (5)$$

where  $E' = a_2^2/a_3$ ,  $\tau' = 1/a_3 L$ ,  $L$  is the kinetic factor, and  $E_0 = (E_\infty + E')$  is the nonrelaxed isothermic modulus. Should the equilibrium value of the inner variable depend upon temperature changes, according to eqs. (12) and (13), we obtain

$$\sigma = E_\infty \epsilon - E_\infty \alpha (T - T_0) + \int_{-\infty}^t E' e^{-\frac{t-t'}{\tau'}} \dot{\epsilon}(t') dt' - \int_{-\infty}^t E' \alpha' e^{-\frac{t-t'}{\tau'}} \dot{T}(t') dt' \quad (6)$$

instead of eq. (5).

The nondependence of the equilibrium value  $\xi$  on temperature changes is natural in the considered approximation for an ordinary elastic body whose deformation is associated mainly with the changes of intrinsic energy. At the same time, in the case of a highly elastic body whose deformation is governed by the relationship between the orienting effect of the mechanical force field and the disorienting effect of the heat flow of macromolecule segments, the equilibrium value of the inner parameter will obviously depend on temperature changes, which leads to eq. (6).

Now we shall take into account the heat exchange between the body and the ambient medium. From eq. (4) we shall obtain the following relation for the entropy per unit volume of the deformed body:

$$S = S_0 + E_\infty \alpha \epsilon. \quad (7)$$

The amount of heat released by unit volume of body per time unit  $Q$  (if, for example, the body temperature is higher than that of the ambient medium) is equal to  $-T_0 \dot{S} + X \dot{\xi}$ .

On the other hand, in the approximation of the nonequilibrium thermodynamics,<sup>17,18</sup>

$$\dot{Q} = \beta(T - T_0) \quad (8)$$

where  $\beta > 0$  is the heat coefficient.

Then we shall find from eqs. (7) and (8) a linearized relative to  $\xi$ :

$$\dot{T} + \frac{1}{\tau_T} (T - T_0) = -E_\infty \alpha \frac{T_0}{C_\epsilon} \dot{\epsilon} \quad (9)$$

where  $C_\epsilon$  is the thermal capacity at the constant deformation. It can be seen from eq. (9) that at  $\epsilon = \text{const.}$ ,  $\tau_T = \frac{C_\epsilon}{\beta}$  is the relaxation time determining the rate at which the thermal equilibrium is obtained between the body and the ambient medium.

Integrating eq. (9) with respect to eq. (5), we obtain

$$\sigma = E_\infty \epsilon + \int_{-\infty}^t E_\infty \alpha^2 \frac{T_0}{C_\epsilon} e^{-\frac{t-t'}{\tau_T}} \epsilon(t') dt' + \int_{-\infty}^t E' e^{-\frac{t-t'}{\tau'}} \dot{\epsilon}(t) dt. \quad (10)$$

As we consider small deformations accompanied by small temperature changes, changes in  $\tau'$  as well as  $\tau_T$  with temperature in the deformation process are neglected.

The first summand of expression (10) incorporates the equilibrium deformation of the body, the second summand incorporates the relaxation caused by the process of heat exchange between the body and the ambient medium, and the third incorporates the relaxation associated with the deviation of  $\xi$  from the equilibrium value.

If the deformation process passes at such a rate that at every given moment the thermal equilibrium ( $\tau_T \ll t$ ) is obtained between body and ambient medium, instead of eq. (10) we shall have

$$\sigma = E_{\infty}\epsilon + \int_{-\infty}^t E' e^{-\frac{t-t'}{\tau'}} \dot{\epsilon}(t') dt' \quad (11)$$

If the deformation occurs so rapidly that the process of heat exchange between the body and the medium fails to occur ( $\tau_T \ll t$ ), we obtain

$$\sigma = E_{\infty ad}\epsilon + \int_{-\infty}^t E' e^{-\frac{t-t'}{\tau'}} \dot{\epsilon}(t') dt' \quad (12)$$

where  $E_{\infty ad} = E_{\infty} + E_{\infty}^2 \frac{\alpha^2 T_0}{C_{\epsilon}}$  is the adiabatic relaxed modulus of elasticity (ordinary relation determined by equilibrium thermodynamics).

At  $\epsilon = \epsilon_0 e^{i\omega t}$  we shall have for the complex modulus of elasticity

$$E^*(\omega) = E_{\infty} + E' \frac{i\omega\tau'}{1 + i\omega\tau'} + E_{\infty}^2 \frac{\alpha^2 T_0}{C_{\epsilon}} \cdot \frac{i\omega\tau_T}{1 + i\omega\tau_T} \quad (13)$$

Now let us proceed to the consideration of the deformation processes of highly elastic bodies. As is known, polymers can be in three physical states, namely, glassy, highly elastic, and viscofluidic states. As far as deformation behavior is concerned, polymers are close to solid bodies in the glassy state and to fluids in the viscofluidic state. Highly elastic deformation is inherent only in polymers and is caused by changes in entropy during the course of deformation. In the case of isothermic deformation, instead of eq. (4) we have

$$F = F_0 + \frac{1}{2} E_{\infty} \epsilon^2 + \frac{1}{2} a_3 (\xi - \bar{\xi})^2 \quad (14)$$

Since  $S = -\partial F / \partial T$ , we find that the entropy change in the deformation process is equal to zero and hence eq. (14) does not incorporate the peculiarities of the highly elastic state. If the constants in eq. (14) depend on temperature, the entropy changes in the deformation process will differ from zero. Actually it can be shown that the expression for the free energy of an isothermally deformed polymer in the highly elastic state has the form of eq. (14), but with the constants linearly depending on temperature. Write  $F(\epsilon, \xi, T)$  into a sequence with accuracy up to members of the third order. Since considered herein are small deformations and small deviations from the thermodynamic equilibrium state, we omit members of the third order relative to  $\epsilon$  and  $\xi$  in the given decomposition and obtain

$$F = F_0 + \gamma T \epsilon + \frac{1}{2} a_1 \epsilon^2 + a_2 \epsilon \xi + \frac{1}{2} a_3 \xi^2 + T \left( \frac{1}{2} \gamma' T \epsilon + \frac{1}{2} \gamma'' T \xi + \frac{1}{2} B_1 \epsilon^2 + B_2 \epsilon \xi + \frac{1}{2} B_3 \xi^2 \right) \quad (15)$$

As can be seen from the comparison of eq. (15) with eq. (1), member appears in the decomposition due to the temperature changes in the course of deformation. Naturally, it may be supposed that the  $\gamma' T \epsilon$  and  $\gamma'' T \xi$  members are contained in eq. (15) for the same reason. Then, in the case

of the isothermal process of deformation, eq. (15) may be written in the following form:

$$F = F_0 + 1/2 a_1 \epsilon^2 + a_2 \epsilon \xi + 1/2 a_3 \xi^2 + T(1/2 B_1 \epsilon^2 + B_2 \epsilon \xi + 1/2 B_3 \xi^2) \quad (16)$$

where three summands are associated with the changes of intrinsic energy at the deformation and the summands at  $T$  are associated with the changes of entropy in the deformation process which is caused by the heat motion of macromolecule segments. The positive sign in front of  $T$  is due to the fact that  $B_1 = (\partial^3 F)/(\partial \epsilon^2 \partial T)$ ,  $B_2 = (\partial^3 F)/(\partial \epsilon \partial \xi \partial T)$ ,  $B_3 = (\partial^3 F)/(\partial \xi^2 \partial T)$ , and  $S = -\partial F/\partial T$  (in the state of thermodynamic equilibrium entropy is maximum and  $\epsilon = 0$ ,  $\sigma = 0$ ). It is obvious that using eq. (16) we shall obtain dependence  $\sigma = f(\epsilon)$  of the eq. (11) form, but with  $E$  and  $E'$  depending on  $T$ .

Consider then the deformation of a polymer in the highly elastic physical state, with temperature changes taken into account and the elastic component of the full deformation being neglected. Then we may write the following for the entropy of the deformed polymer:

$$S = S_0 - \gamma'(T - T_0) - \gamma''(T - T_0)\xi - 1/2 B_1 \epsilon^2 - B_2 \epsilon \xi - 1/2 B_3 \xi^2, \quad (17)$$

where the  $\gamma T \epsilon$  member of decomposition eq. (15) is omitted, since  $\gamma = \partial^2 F/\partial \epsilon \partial T = -\partial S/\partial \epsilon$ . When only the highly elastic component of the full deformation is taken into account,  $\sigma = -T \left( \frac{dS}{d\epsilon} \right)_{T, \xi}$  and hence  $\gamma = 0$ ,

since at  $\epsilon = 0$ ,  $\sigma = 0$ . As at  $T = T_0$  the body is in the nondeformed state,  $T_0$  is introduced into the decomposition. Based on the condition that the entropy in the thermodynamic equilibrium state is at its maximum, we find  $\bar{\xi} = -(B_2/B_3)\epsilon - [\gamma''/B_3(T - T_0)]$ . Then in the same way as that used for the ordinary elastic body we obtain

$$\sigma = E_\infty \epsilon + E_\infty \alpha (T - T_0) + E' \int_{-\infty}^{\epsilon} e^{-\frac{t-t'}{\tau'}} \dot{\epsilon}(t') dt' + E' \alpha' \int_{-\infty}^{\epsilon} e^{-\frac{t-t'}{\tau'}} \dot{T}(t') dt' \quad (18)$$

where  $E' = (B_2^2/B_3)T$ ,  $E' \alpha' = (B_2 \gamma''/B_3)T$ ,  $E_\infty = [B_1 - (B_2^2/B_3)]T$ ,  $E_\infty \alpha = [\gamma' - (\gamma'' B_2/B_3)]T$ . Unlike in eq. (5), the presence of the summand with  $\dot{T}(t')$  in this expression is caused by the dependence of the inner parameter of the equilibrium value upon the temperature change. Now take into account the heat exchange between the body and the ambient medium. Proceeding in the same way which was used for the ordinary elastic body, we shall use eq. (17) with the reverse sign of thermal effects at the deformation of a highly elastic body being taken into account. As a result we obtain

$$\dot{T} + \frac{\beta}{C_\epsilon^\alpha} (T - T_0) - \frac{B_2 T_0}{C_\epsilon^\alpha} (\xi - \bar{\xi}) \dot{\xi} = \frac{\sigma}{C_\epsilon^\alpha} \dot{\epsilon} \quad (19)$$

where  $C_\epsilon^\alpha = C_0 - E_\infty \alpha \epsilon - \gamma' T_0 (\xi - \bar{\xi}) + \frac{\gamma''}{B^3} T_0 (T - T_0)$  and is the dynamic thermal capacity at the constant deformation and inner parameter, and  $C_p$  is the equilibrium thermal capacity. Since considered herein are small deviations from the state of thermodynamic equilibrium, taking account of  $\dot{\xi} = -\frac{1}{\tau} (\xi - \bar{\xi})$  we shall have instead of expression (19)

$$\dot{T} + \frac{\beta}{C_\epsilon^\alpha} (T - T_0) = \frac{\sigma}{C_\epsilon^\alpha} \dot{\epsilon}. \quad (20)$$

For the ordinary elastic body  $C_\epsilon^\alpha$  will convert into  $C_p$ , and then considering the expression for the free energy of a low molecular weight solid body, eq. (4), we can write

$$\frac{\sigma}{C_\epsilon^\alpha} = -\frac{T_0}{C_p} \frac{\partial S}{\partial \epsilon} = \frac{T_0}{C_p} \frac{\partial^2 F}{\partial \epsilon \partial T} = -T_0 \frac{E_\infty \alpha}{C_p}.$$

In the case of adiabatic deformation we obtain from eq. (20)

$$dT = \frac{\sigma}{C_\epsilon^\alpha} d\epsilon \quad (21)$$

which is the so-called thermomechanical effect which simply results from the equilibrium thermodynamic theory of the highly elastic deformation. The only difference is that in eq. (21) the thermal capacity changes at the deformation, while in the equilibrium theory it is assumed to remain constant.

The experimental data relating to small elongations are in satisfactory agreement with the relation obtained from equilibrium thermodynamics. Hence, in the first approximation the changes of thermal capacity in the course of deformation may be neglected in eq. (21). Then introducing eq. (21) into eq. (18) we obtain the following expression at  $\epsilon = \epsilon_0 e^{i\omega t}$ :

$$\begin{aligned} \frac{\sigma}{\epsilon} = E_\infty + E' \frac{i\omega\tau'}{1 + i\omega\tau'} + \frac{i\omega E_\infty \alpha}{C_\epsilon} \int_0^\infty \sigma(t - U_1 W) e^{-i\omega U} dU \\ + \frac{i\omega E' \alpha'}{C_\epsilon} \int_0^\infty \sigma(t - U_1 w) e^{-i\omega U} dU - \frac{U}{\tau}. \quad (22) \end{aligned}$$

Thus, while in the case of an ordinary elastic body the transition from the isothermic to the adiabatic deformation is accompanied only by the replacement of  $E$  (relaxed isothermic modulus) with  $E_{\infty ad}$  (adiabatic modulus), which can be neglected, in the case of the highly elastic body an addition appears in the expression for  $E^*$ , which depends on  $\omega\tau'$  and on the amplitude of the applied stress. Thus, as can be seen from eq. (22), under adiabatic conditions the position of dynamic characteristics on a frequency or temperature scale depends on the amplitude of the applied stress.

### RESPONSE TO THE EXTERNAL PERTURBATION OF INTERACTING KINETIC UNITS

If  $\sigma$  and  $T$  are taken as independent variables, the thermodynamic potential  $\phi$  should be used instead of free energy  $F$ , eq. (14). Any solid body, including a polymeric one, possesses a set of relaxation mechanisms. In the given case we shall consider the mobility of only certain kinetic units. In this case, response  $R$  of the system of kinetic units (for example, the segments of macromolecules) to the external perturbation will be used as the inner parameter. Under certain present external conditions (nature and rate of external perturbation, temperature), the considered system responds to the effect of the applied force thus causing a respective relaxation phenomenon in a certain range of the time (or frequency) scale. In this case (as before, we consider linear stressed state) we can write the following for the isothermic deformation:

$$\epsilon = J_0\sigma + \lambda R \quad (23)$$

where  $\lambda$  is the factor of proportionality. If the velocity is infinitely high, the system fails to respond to the effect of the external force. In this case,  $R = 0$  and  $J_0$  represents nonrelaxed pliability. At the infinitely slow effect of the external force the process of the system's response will be thermodynamically reversible and in the linear approximation we shall have the following expression for the equilibrium response:

$$\bar{R} = X(0)\sigma \quad (24)$$

where  $X(0)$  is the static mechanical susceptibility. Instead of eq. (23) we may write  $\epsilon = J_\infty\sigma$ , where  $J_\infty = (J_0 + \lambda X(0)\sigma)$  is the relaxed pliability. If the response to the external perturbation is not thermodynamically reversible, by decomposing the thermodynamic potential of the responded system  $\phi = \phi(\sigma RT)$  with respect to  $R$  degrees with an accuracy up to the members of the second order, we obtain

$$\phi = A(T) + B(\sigma_1 T)R + C(\sigma_1 T)R^2. \quad (25)$$

Assuming that in the equilibrium state the thermodynamic potential reaches its minimum and using eq. (24) and taking into account that in the case of equilibrium response process  $R$  of the considered system of kinetic units  $\phi = \phi_0 - \sigma X(0)\sigma^2/2$  is  $-(\partial\phi/\partial\sigma)_T$ , we find factors  $B = -\sigma$  and  $C = 1/2\chi$  in decomposition eq. (25). We then obtain

$$\phi = \phi_0 - \sigma R + \frac{R^2}{2X}. \quad (26)$$

Using the linear phenomenological relation of nonequilibrium thermodynamics between "flow"  $R$  and "generalized force"  $X = -(\partial\phi/\partial R)_{T,\sigma}$ , we obtain

$$\dot{R} = LX. \quad (27)$$



Taking into account eq. (26), we find

$$\dot{R} = -\frac{1}{\tau} (R - X\sigma) \quad (28)$$

where  $\tau = \frac{X(0)}{L}$  and  $L$  is the kinetic factor. Instead of eq. (28) we may write

$$\dot{\xi} + \frac{1}{\tau} \xi = -X\dot{\sigma} \quad (29)$$

where  $\xi = R - \bar{R}$ . Integrating eq. (29) and taking into account eq. (23), we obtain

$$\epsilon = J_{\infty}\sigma - \int_{-\infty}^t \lambda X e^{-\frac{t-t'}{\tau}} \dot{\sigma}(t') dt', \quad (30)$$

or excluding  $\xi$  and  $\dot{\xi}$  from eq. (29) and using eq. (23), we have

$$\dot{\epsilon} + \frac{1}{\tau} \epsilon = J_0 \dot{\sigma} + \frac{J_{\infty}}{\tau} \sigma \quad (31)$$

where  $\tau' = (E_{\infty}/E_0)\tau$  and  $\dot{\sigma} + (1/\tau')\sigma = E_0\dot{\epsilon} + (E_{\infty}/\tau')\epsilon$ .

When particular relaxation phenomena are described, the relations of eqs. (11) and (30) or (31) type give dependencies qualitatively agreeing with experimental data. In essence, the quantitative disagreement between theory and experiment can be eliminated if it will be taken into account that the body possesses a number of relaxation mechanisms and that every particular relaxation mechanism causing a relaxation phenomenon is characterized by definite relaxation and retardation times. It may be shown,<sup>19</sup> however, that quantitative disagreement between theory and experiment can be eliminated by considering the interactions (cooperation) in the system of kinetic units, and in this case the phenomenological relationship between "flow" and generalized force" becomes non-linear. We shall consider a certain relaxation mechanism associated with the motion of certain interacting kinetic units and, as was shown above, manifesting itself under respective preset external conditions in a respective range of the time (frequency) scale. The motion of particles in such a system obviously is of cooperative nature.

The dependence of time, which is supposed to be a constant value due to the linearity of relation (27), upon the activation energy and the temperature is usually expressed by an Arrhenius-type relation

$$\tau = A e^{U/kT} \quad (32)$$

where  $A = \text{const.}$  and  $k$  is the Boltzmann constant. Taking into account that  $\tau = X(0)/L$ , we may write  $L = L_0' e^{-U/kT}$ .

In the system of kinetic units responding to the external perturbation, a certain internal rearrangement will occur whose degree can be characterized

by value  $R$  (or  $\Delta R$  if at the initial time  $R \neq 0$ ). Naturally, in the presence of interaction in the considered system the rearrangement will also have an effect on the profile of the potential surface, i.e., a portion of the potential barrier caused by the interaction of particles responding to the external perturbation will change in the process of the system's response.

At the same time the contribution made to the value of the potential barrier by the interaction with kinetic fragments forming another subsystem in the given body will remain unchanged in the process of response, since these fragments do not respond to the preset external perturbation. It may be considered in the first approximation that the value of the potential barrier change is proportional to  $R$  (or  $\Delta R$ ), i.e.,  $\Delta U = \gamma R$ .

Assume then that when the external field is applied, the mobility of kinetic units characterized by value  $L$  will decrease owing to the increase of the potential barrier in the process of the internal rearrangement.

Thus, when considering the response of the system of interacting particles to the effect of external force, we arrive at the conclusion that the phenomenological relationship between the "flow" and the "generalized force" is nonlinear:

$$R = L(R)X \quad (33)$$

where  $L = L_0 e^{-\frac{U+\gamma R}{kT}}$ ,  $L = L_0 e^{-\alpha R}$ , and  $\alpha = \gamma/kT$  can characterize the degree of the cooperative relaxation process. At  $\alpha \ll 1$ , when the interaction in the considered system is negligibly small, the ordinary relation (27) takes place instead of eq. (33). Note that in this case the nonlinearity does not result from considering the great deviations from the equilibrium state, but from the interaction in the responded system of kinetic units of the given kind.

Thus, using eq. (33) instead of eq. (27), we can in the usual way (as was done above) obtain equations similar to eq. (31) but having factors depending on  $R$ .

Note at once the difference between the relation for  $\tau$  resulting from the above-mentioned (this relation is  $\tau = A e^{\frac{U+\gamma R}{kT}}$ ) and the formula  $\tau = A e^{\frac{U-\alpha\sigma}{kT}}$  proposed by Alexandrov and Gurevich. Value  $U$  is the energy of interaction of kinetic units with the external field, while value  $\gamma R$  is the change of the potential barrier caused by the motion of kinetic units in the process of response to the external perturbation. As follows from the formula presented by Alexandrov and Gurevich, the processes of relaxation of deformation or creep will be described by the constant  $\tau$ , while the dependency  $\tau = \tau(R)$  shows that  $\tau$  will change with time. Besides, if the external perturbations considered herein are not so great, the value of  $\alpha\sigma$  can be neglected.

As is known,<sup>20-22</sup> the experimental data associated with the relaxation of stress may be well approximated with the help of Kolraush's empirical

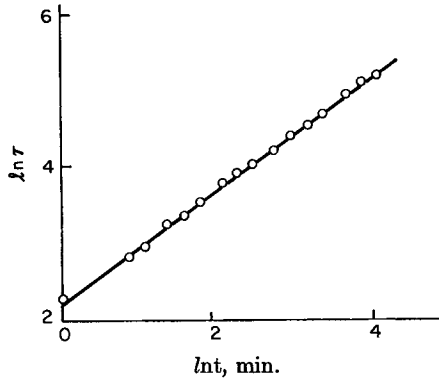


Fig. 1. Dependency of  $\tau'$  on time for polyethylene of high density at temperature of 20°C (extension deformation 2.5%).

relation  $\sigma = \sigma_{\infty} + \sigma' e^{at^k}$ , where  $a$  and  $K$  are constants ( $0 < K < 1$ ). From eq. (31) we obtain for the stress relaxation

$$\dot{\sigma} + \frac{1}{\tau'} \sigma = \frac{E_{\infty}}{\tau'} \epsilon. \quad (34)$$

Solving this equation to obtain  $\sigma$ , we have

$$\sigma = \sigma_{\infty} + \sigma' e^{-f(t)} \quad (35)$$

where  $f(t) = \int_0^t dt'/\tau'_0 \exp\{\alpha''[\sigma_0 - \sigma(t')]\}$ ,  $\alpha'' = \alpha/\lambda E_0$ ,  $\sigma' = \sigma_0 - \sigma_{\infty} = E' \epsilon$ ,  $\tau' = E_{\infty}/E_0 \tau_0 \exp(\alpha R)$ , and  $R$  is determined by eq. (23).

To determine the form of function  $f(t)$ , it is necessary to plot the dependency of  $\tau'$  on time, using for the purpose the experimental data and relation  $\tau' = \tau'_0 \exp\{\alpha''[\sigma_0 - \sigma(t)]\}$ . Dependencies of  $\tau'$  on time are presented in Figures 1 and 2 in double logarithmic coordinates. These dependencies are calculated on the basis of data taken from works<sup>20, 23</sup> for polyethylene of high density at a temperature of 20°C and lump isotactic polypropylene at a temperature of 18°C, with the following constant values:  $\alpha'' = 0.083 \text{ cm}^2/\text{kg}$ ,  $\tau'_0 = 0.45 \text{ min}$ ,  $\sigma_{\infty} = 80 \text{ kg/m}^2$ ,  $\sigma_0 = 180 \text{ kg/mm}^2$ , and  $\alpha'' = 0.057 \text{ cm}^2/\text{kg}$ ,  $\tau'_0 = 0.0227 \text{ min}$ ,  $\sigma_{\infty} = 102 \text{ kg/cm}^2$ ,  $\sigma_0 = 299.3 \text{ kg/mm}^2$ , respectively. It is seen from the figures that the dependency of  $\tau'$  on time may be approximated by the relation  $\tau' = 1/Kat^{1-k}$  and, as at  $t = 0$ ,  $\sigma = \sigma_0$  and  $\tau' = \tau'_0$ , but not zero, it can be approximated more precisely by relation

$$\tau' = \frac{1}{Ka} (t + t_0)^{1-K} \quad (36)$$

where  $t_0 = \text{const}$ . Then for  $f(t)$  we have  $f(t) = a(t + t_0)^K at_0^K$  and instead of eq. (35) we can write  $-a(t + t_0)^K + at_0^K$

$$\sigma = \sigma_{\infty} + \sigma' e. \quad (37)$$

At  $t = 0$ , as it should be,  $\sigma = \sigma_0$ ; and at  $t \rightarrow \infty$ ,  $\sigma \rightarrow \sigma_{\infty}$ .

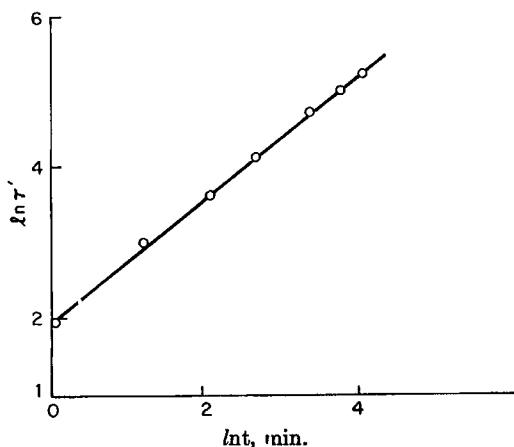


Fig. 2. Dependency of  $\tau'$  on time for lump isotactic polypropylene at temperature of 18°C (compression deformation 5.8%).

The tangent of the inclination angle of the straight lines shown in Figures 1 and 2 is equal to 0.75 and 0.80, respectively, which corresponds to the values of the constants  $a$  and  $K$  at which the used experimental data are approximated by the Kolraush relation. The constant  $t$  is sufficiently small (for polyethylene,  $t_0 = 0.0196$  min), i.e., it can be taken into consideration only for sufficiently small time intervals, while for other intervals this constant can be practically neglected. Note also that at  $t \rightarrow \infty$  it follows from eq. (36) that  $\tau' = \infty$ , while according to  $\tau' = \tau_0' - e^{\alpha''[\sigma_0 - \sigma(t)]}$ ,  $\tau' \rightarrow \tau_p'$ . It can be supposed that at sufficiently high times the dependency of  $\tau'$  on time of eq. (43) type is disturbed and, hence, the Kolraush relation will deviate from the experimental dependencies or the following should be supposed: at sufficiently high  $t$  (considerably higher than  $\tau\sigma = (1/\alpha)^{1/K}$ ), which practically tends toward infinity,  $\sigma$  in eq. (37) reaches its equilibrium value. This time interval is final, however, and for any other process it can be sufficiently small (considerably smaller than  $\tau\sigma$  characterizing this process). Therefore it cannot occur during the considered interval  $t$  (the system of kinetic units fail to respond to the external perturbation). Hence, in eq. (36),  $t$  is high but final and therefore the value of  $\tau'$  determined by this relation is also final.

From the physical viewpoint, the tendency of  $\tau'$  toward  $\tau_p$  at the transition of the systems from one equilibrium state to another is quite reasonable. At  $t \rightarrow \infty$ ,  $\sigma = \sigma_\infty$  and  $\tau' \rightarrow \tau_p'$ , where  $\tau_0'$  characterizes the mobility of kinetic units in the absence of the external field and  $\tau_p'$  characterizes the mobility of these units in the presence of this field when the relaxation process has stopped and the system is in the equilibrium state.

In the case of creep, we obtain from eq. (31)

$$\dot{\epsilon} + \frac{1}{\tau} \epsilon = \frac{J_\infty}{\tau} \epsilon \quad (38)$$

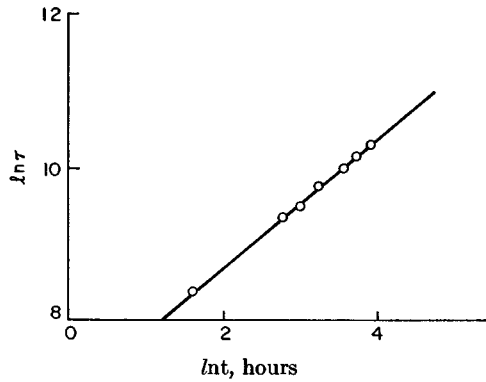


Fig. 3. Dependency of  $\tau$  on time for poly(methyl methacrylate) at temperature of 20°C (initial stress  $\sigma = 252 \text{ kg/cm}^2$ ).

or

$$\epsilon = \epsilon_{\infty} - \epsilon' e^{-(t)}$$

where  $(t) = \int_0^t dt'/\tau_0 \exp\{\epsilon(t') - \epsilon_0\}$ ,  $\alpha' = \frac{\alpha}{\lambda}$ , and  $\epsilon' = \epsilon_{\infty} - \epsilon_0 = \lambda X$ .

As it follows from eq. (31), times  $\tau$  and  $\tau'$  are proportional and therefore the dependency of  $\tau$  on time should be identical. Accordingly, we may write

$$\epsilon = \epsilon_{\infty} - \epsilon' e^{-B(t-t_0^K) + Bt_0^K} \quad (39)$$

or, as  $t_0$  is small,

$$\epsilon = \epsilon_{\infty} - \epsilon' e^{-Bt^K}$$

At small values of constant  $B$  in respective time intervals we can restrict ourselves by two members of decomposition eq. (39) and for  $\epsilon$  we shall have the known relation  $\epsilon = \epsilon_0 + B\epsilon't^K$ .

Figure 3 presents the dependency of  $\tau$  on time plotted according to relation  $\tau = \tau_0 e^{\alpha'[\epsilon(t) - \epsilon_0]}$  on the base of the experimental data obtained by A. P. Patrikeev for poly(methyl methacrylate) at a temperature of 20°C. It turns out that value  $B$  is equal to 0.006 and therefore within a sufficiently large time interval this data can be described by the power relation used instead of eq. (39). The plot of the dependency presented in Figure 4 is based on the following values of constants:  $\epsilon_0 = 0.437\%$ ,  $\epsilon' = 136.33\%$ ,  $B = 0.006$ , and  $K = 0.152$ . Writing the solution of eqs. (34) and (38) relative to time, the solution of eq. (34) is as follows:

$$t = -\tau_0' e^{\alpha''\sigma'} \{ [-E_i(-\alpha''\sigma')] - [-E_i(-\alpha''(\sigma - E_{\infty}\epsilon))] \} \quad (40)$$

where  $[-E_i(-X)]$  is the integral exponential function tabulated in ref. 24. Obviously, at  $\sigma = \sigma_0$ ,  $t = 0$ ; at  $\sigma \rightarrow \sigma_{\infty}$ ,  $t \rightarrow \infty$ ; and at  $\alpha \ll 1$ ,  $\sigma = \sigma_{\infty} + \sigma' e^{-t/\tau_0'}$ .

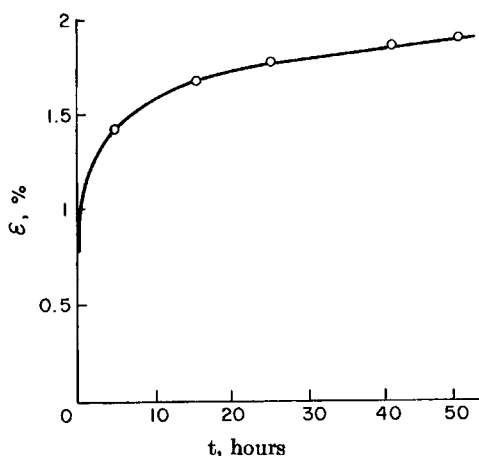


Fig. 4. Comparison of experimental and calculated curves of creep for poly(methyl methacrylate) at temperature of 20°C (initial stress  $\sigma = 252 \text{ kg/cm}^2$ ).

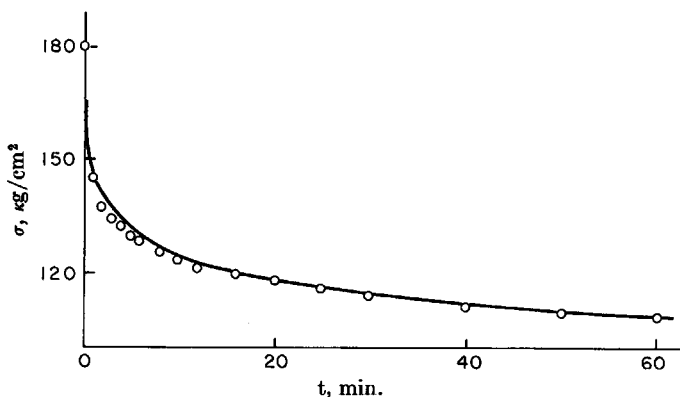


Fig. 5. Comparison of experimental and calculated curves of stress relaxation for polyethylene of high density at temperature of 20°C (extension deformation 2.5%).

The solution of eq. (38) will be as follows:

$$t = -\tau_0 e^{\alpha' \epsilon'} \{ [-E_i(-\alpha' \epsilon')] - [-E_i(-\alpha'(J_\infty \sigma - \epsilon))] \}. \quad (41)$$

At  $\epsilon = \epsilon_0$ ,  $t_0 = 0$ ; at  $\epsilon \rightarrow \epsilon_\infty$ ,  $t \rightarrow \infty$ ; and at  $\alpha \ll 1$ ,  $\epsilon = \epsilon_\infty - \epsilon' e^{-t/\tau}$ .

Relation (41) is similar to that obtained by Rabinovich<sup>25</sup> from the so-called generalized Maxwell equation. Figures 5 and 6 present the experimental data used in Figures 1 and 2 and the curves calculated from eq. (40) at the constant values are shown in Figures 1 and 2.

Thus, in the region where a relaxation phenomenon is observed clearly,  $\tau$  changes from  $\tau_0$  to  $\tau_p$ . Formally, it is possible to take a set of times  $\tau_i$  each of which corresponds to  $\tau = \tau(R)$  at a certain moment. And further, assuming each  $\tau_i$  has its inner parameter, we obtain in the usual way

$$\epsilon = J_{\infty}\sigma - \int_{-\infty}^t \sum_i \lambda_i X_i \dot{\sigma}(t') e^{-\frac{t-t'}{\tau_i}} dt'. \quad (42)$$

Or, passing to the continuous set of  $\tau$  and taking this set of  $\tau$  into account' we shall obtain the ordinary relation of the linear theory of viscoelasticity

$$\epsilon = J_{\infty}\sigma - \int_{-\infty}^t dt' \dot{\sigma}(t') \int_{\tau_0}^{\infty} d\tau J(\tau) e^{-\frac{t-t'}{\tau}} \quad (43)$$

where  $J(\tau)$  is the function of the distribution of  $\tau$  times.

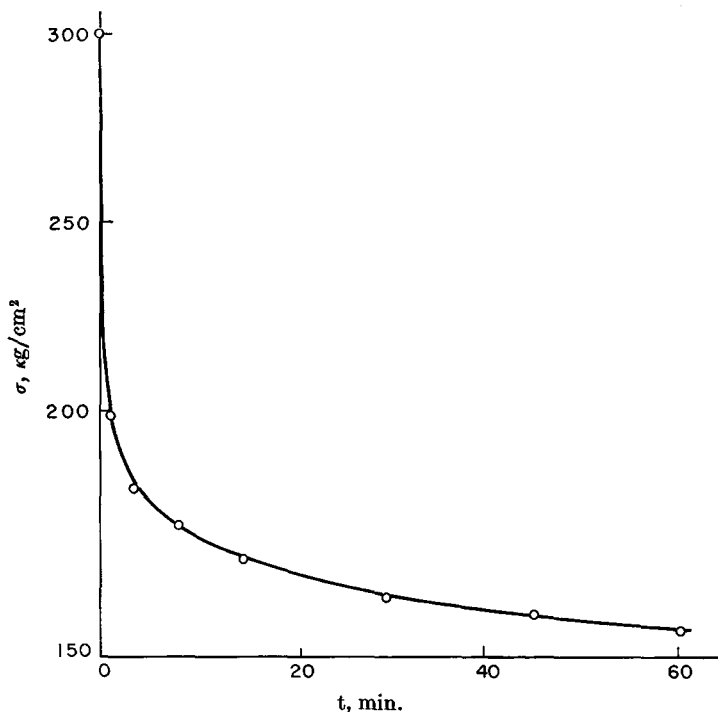


Fig. 6. Comparison of experimental and calculated curves of stress relaxation for isotactic polypropylene (compression deformation 5.8%).

In this case the description with the help of a set of  $\tau$  also leads to the nonlinearity of the relationship between the "flow" and the "generalized force."<sup>26</sup>

Really, at  $\sigma = \text{const.}$  we obtain from eq. (43) the following expression for  $R$ :

$$R - \bar{R} = -\bar{R} \int_{\tau_0}^{\infty} J(\tau) e^{-t/\tau} d\tau \quad (44)$$

Differentiating eq. (44) in time and dividing the obtained expression by eq. (44) we find

$$\dot{R} = -\psi(t)(R - \bar{R}) \quad (45)$$

where  $\psi(t) = \int_{\tau_0}^{\tau_p} J(\tau)\tau e^{-t/\tau} d\tau / \int_{\tau_0}^{\tau_p} J(\tau)e^{-t/\tau} d\tau$ . It is quite obvious that if eq. (27) is not linear, we obtain eq. (45).

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