Orientation ordering and the mechanical properties of solid polymers

M. I. Shliomis and Yu. L. Raĭkher

Polymer Physics Division of the Urals Scientific Center, USSR Academy of Sciences

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The character of the deformation curves of a broad class of solid polymers points to an important role of orientation effects in the mechanics of these media. The stretching of a polymer gives rise to partial orientation of the chain molecules in the direction of extension. The extent of the resulting orientation increases on account of the intermolecular attractive forces, and this leads to additional elongation of the sample (orientational striction). The developed statistical-thermodynamic theory of the deformation properties of polymers is based on the self-consistent field method. The resulting equation for the orientation state interprets orientation crystallization as a first-order phase transition. In this case the connection between the orientation, strain, and stress tensors is such that a discontinuous change in the order parameter at the transition point is accompanied by a deformation jump (a "bottleneck"). The orientation kinetics is studied by the methods of the theory of rotational Brownian motion. The Fokker-Planck equation for the orientation distribution function of the molecular segments is constructed, and on its basis a macroscopic equation of motion is derived for the orientation tensor by means of the method of moments, the relaxation times of the components of this tensor are computed, and the stability of the uniaxial (nematic) ordering against weak perturbations of arbitrary symmetry is investigated. The equation for the orientation tensor is used together with the equations of the theory of elasticity to study the acoustic and relaxation properties of oriented polymers.

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§1. INTRODUCTION

The striking deformation properties of polymers are predetermined by the anisotropy of the molecular forces, which is implicit in the very nature of these compounds: the strength of the bonds along the polymer chain molecule is significantly stronger than the intermolecular interactions. The principal chemical bond between the atoms within a macromolecule is a covalent bond; its dissociation energy is ~2–3 eV. Between the molecules and their individual units not joined by covalent bonds act van der Waals attractive forces. They are at least two orders of magnitude weaker than the covalent forces: a typical value of the energy of the intermolecular attraction is 10^{-2} eV/Å: from 8×10^{-3} for polyethylene to 5×10^{-2} eV/Å for the polyamides.[1] Therefore, a chain molecule can easily be stretched, but difficult to rupture. Linear (nonbranching) polyethylene, for example, can be stretched 1000% without rupturing it at room temperature.

In the case of uniaxial stretching of a solid polymer the molecules of the polymer tend to orient themselves in the direction of the extension. In a fully extended sample the molecular axes are laid out almost parallel to each other, while the centers of gravity of the macromolecules are distributed chaotically—in the theory of liquid crystals this type of ordering is called nematic. The straightening of the molecules of a polymer during its stretching has been confirmed by double-refraction experiments and electron and x-ray diffraction analyses.[1]

In the absence of mechanical stresses the molecules of an amorphous polymer are either rolled up into coils (globules), or they are unrolled and arranged in bundles,[2] the regions of preferred mutual orientation being similar to those of mesomorphic clusters.[3] In a solid polymer a bundle is, apparently, an elementary structural unit of the hypomolecular organization, whereas the globular structure is more peculiar to polymer solutions. The initial phase of the extension process is accompanied by quite complex changes in the hypomolecular organization, the nature of these changes being determined by the type of elementary structural unit. It is, however, significant that in every case the extension, by partially straightening the molecular chains, helps the van der Waals forces stretch them out fully and thereby facilitate the orientation crystallization of the polymer. In its turn, a consequence of the crystallization should be additional elongation of the sample in the extension direction, i.e., a decrease in the stress necessary for the production of a given deformation. The foregoing considerations are attested by the character of the deformation curves of a broad class of solid polymers. Figure 1 illustrates the dependence of stress on strain at different temperatures. The initial slope of the curves is proportional to the temperature: at small strains a polymer exhibits entropic elasticity, similar to the resilience of an ideal gas. Underlying the mechanism of entropic elasticity, which leads to Mackian polymer elasticity, is a decrease in the number of possible conformations of the

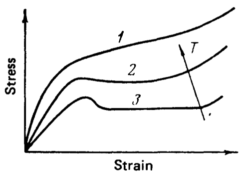

FIG. 1.

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macromolecules during extension. Orientation crystallization occurs at the central (mildly sloping) part of the curves; this process leads to large extensions for a small increase (the curve 1), or even a decrease (the curves 2 and 3), in the stress. The final stage of the orientation crystallization—the parallel arrangement of the macromolecules—is accompanied by a hardening of the sample in the direction of the extension; therefore, further deformation requires large tensile stresses.

Figure 1 reminds us of van der Waals isotherms: the dependence of the tensile stress on the extension of a polymer is similar to the dependence of pressure on the density of a real gas. This similarity was noted back at the end of the forties by Alfrey,[4] ten years later by Thompson and Tackett (see the discussion on Barenblatt's paper[5]), and, finally, quite recently this similarity was again pointed out by Ginzburg *et al.*[6] Thus, it is natural to assume that a mechanical deformation of a polymer can be accompanied by a first-order phase transition.

The possibility of such a transition occurring during orientation crystallization is connected with the character of the symmetry of the order parameter, which in the case under consideration is a second-rank tensor. In an orientable polymer, as in a liquid crystal,[7] the symmetric traceless tensor $\eta_{ik}=\langle s_{ik}\rangle$, defined as the mean of the "microscopic" quantity

$$s_{ik}=3/2\,(\nu_i\nu_k-{}^1/_3\delta_{ik}), \tag{1.1}$$

characterizing the orientation of the uniaxial elementary structural unit, can serve as the order parameter; here ν is the unit vector along the axis of the bundle or in the direction of an individual segment of the chain molecule (for example, in the "folding yardstick" model[3]). The macroscopic order parameter η_{ik} is obtained, as usual, by averaging the tensor ϵ_{ik} over a small volume element that nevertheless contains a large number of bundles or segments.

In the case of uniaxial ordering, induced, for example, by an extension along the axis **n**, the tensor η_{ik} can be written in the form

$$\eta_{ik}=3/2\,\eta(n_in_k-{}^1/_3\delta_{ik}),\quad \eta={}^3/_2\langle(\boldsymbol{\nu}\mathbf{n})^2\rangle-{}^1/_2, \tag{1.2}$$

where η is a scalar anisotropy parameter. The value $\eta=1$ is attained when the molecules are fully oriented in the direction **n** (in the theory of liquid crystals this unit vector is called the director); in the isotropic case $\eta=0$. The normalization in the definition (1.2) has been chosen such that in the system of coordinates where $\mathbf{n}=(0,0,1)$ we have $\eta_{zz}=\eta$.

In the present paper we construct a statistical theory of the elasticity of orientable polymers. The order of the exposition is as follows. In §2 we derive the equation of the orientation state, which equation determines the dependence of the equilibrium order parameter η on the mechanical stress and the temperature. Here we use the molecular-field model proposed by Mayer and Saupe[8] for the description of the phase transition in nematic liquid crystals. Section 3 is devoted to the thermodynamics of the orientation. In §4 we establish a relation between the orientation state of a polymer and its elastic properties; the obtained relations enable us to describe the deformation curves in Fig. 1. The kinetics of the orientation processes is connected with the Brownian rotational motion of the microscopic structure elements. In §5 we construct the Fokker-Planck equation for the orientation distribution function of the molecular segments, from which the equation of motion of the tensor η_{ik} is then derived by the method of moments and the dependence of the orientation relaxation times on temperature and stress is found. With the aid of these formulas we investigate in §6 the stability of the uniaxial configuration (1.2) against weak perturbations of arbitrary symmetry. In the last two sections we consider on the basis of the simultaneous solution of the system of equations of motion of the solid and the orientation tensor the elastic longitudinal vibrations of a rod (§7) and the propagation of sound in the unbounded medium (§8).

Notice that in this work we study the equilibrium states (§§2–4) and the weakly nonequilibrium processes (§§5–8) during which the system does not stratify into phases with different orientations. The problem of the formation of a heterophase structure (the formation and growth of nucleating centers in the course of the orientation crystallization, the appearance and propagation of a bottleneck[5] during the extension of the polymer), as well as the problem of the fluctuation of the order parameter near the critical points will be considered elsewhere.

§2. ORIENTATION CRYSTALLIZATION. THE SELF-CONSISTENT FIELD METHOD

For the construction of the statistical thermodynamics of an orientable polymer let us use the well-known concepts of molecular-field theory. We shall assume that the orienting influence experienced by the individual ordering "microscopic" element (e.g., a segment of a chain molecule) is determined by the mechanical stress σ_{ik} and the degree, η_{ik}, of orientation already attained. Then, as in the Weiss theory of ferromagnetism, we can introduce the "effective field,"

$$H_{ik}=\gamma\sigma_{ik}+\lambda\eta_{ik}, \tag{2.1}$$

acting on the microscopic element; here γ and λ are the parameters of the material,1) λ is a constant of the molecular field (for the linear intermolecular interaction energy density indicated in §1 and a segment length ~10 Å, we have $\lambda\sim10^{-1}$ eV). The orientation part of the energy of the individual element in the field (2.1) is equal to $E=-s_{ik}H_{ik}$, where s_{ik} is defined by the formula (1.1). Omitting an unimportant constant, we have

$$E=-{}^3/_2(\lambda\eta_{ik}+\gamma\sigma_{ik})\nu_i\nu_k. \tag{2.2}$$

At equilibrium the probability for the various orientations of the segment is proportional to $e^{-E/T}$; with allowance for (1.1) and (2.2) the normalized distribution function has the form

$$W_0=Z_0^{-1}\exp\left[\frac{3}{2T}(\lambda\eta_{ik}+\gamma\sigma_{ik})\nu_i\nu_k\right],$$
$$Z_0=\int\exp\left[\frac{3}{2T}(\lambda\eta_{ik}+\gamma\sigma_{ik})\nu_i\nu_k\right]d^2\boldsymbol{\nu}. \tag{2.3}$$

These expressions contain the macroscopic orientation tensor η_{ik}, which by its definition is the average of the "microscopic" tensor s_{ik} with the function W_0. Thus, for η_{ik} we obtain the self-consistent equation:

$$\eta_{ik}=\int s_{ik}W_0\,d^2\boldsymbol{\nu}. \tag{2.4}$$

We shall consider a uniaxial orientation of a polymer [see (1.2)]. Such ordering is possible both in the presence of a uniform extension or contraction along the axis n and in the absence of stresses. In the latter case the direction of the director is degenerate; for real samples this degeneracy can be removed (completely or partially) by imposing boundary conditions. Substituting into (2.4) the expressions (1.2), (2.3) and $\sigma_{ik}=\sigma n_i n_k$, we obtain an integral equation for the scalar order parameter:

$$\eta=\frac{3}{2}\int_0^1\left(x^2-\frac{1}{3}\right)\exp\left[\left(\frac{9\lambda\eta}{4T}+\frac{3\gamma\sigma}{2T}\right)x^2\right]dx \Big/ \int_0^1\exp\left[\left(\frac{9\lambda\eta}{4T}+\frac{3\gamma\sigma}{2T}\right)x^2\right]dx; \tag{2.5}$$

the polar axis of the system of coordinates is directed along n, $x\equiv\boldsymbol{\nu}\cdot\mathbf{n}$. It is convenient to introduce the notation

$$\xi=\frac{9\lambda}{4T}\eta+\frac{3\gamma}{2T}\sigma,\quad R(\xi)=\int_0^1\exp(\xi x^2)\,dx, \tag{2.6}$$

and reduce Eq. (2.5) to the set of transcendental equations:

$$\eta=\frac{3}{2}\left[\frac{R'(\xi)}{R(\xi)}-\frac{1}{3}\right] \tag{2.7}$$

$$\eta=\frac{4T}{9\lambda}\xi-\frac{2\gamma\sigma}{3\lambda}, \tag{2.8}$$

which determines the dependence $\eta(T,\sigma)$ in parametric form (the role of the parameter is played by ξ). The scheme of the graphical solution of this system is shown in Fig. 2. For $\sigma=0$ (see Fig. 2a) the values of the function $\eta(T)$ are equal to the ordinates of the points of intersection of the curve described by Eq. (2.7) with the straight lines (2.8), whose slope is proportional to the temperature: $\mathrm{tg}\psi=4T/9\lambda$. As can be seen from the figure, there exists a maximum value of the angle $\psi=\psi_c$ such that for $T>T_c$ and $\sigma=0$ the system (2.7), (2.8) has only one solution with $\eta=0$, i.e., at high temperatures the unstressed polymer is isotropic. Spontaneous orientation first appears at $T=T_c$, $\eta(T_c)=\eta_c$ being nonzero (first-order transition). There exists two nontrivial solutions in the interval $T_c>T>T_*$; one of them, for which $\partial\eta/\partial T>0$, is evidently unstable. This solution vanishes at the temperature T_*, when the straight line (2.8) touches the curve (2.7) at the coordinate origin. The value of T_* is itself determined from the condition for the equality of the slopes at the point $\xi=0$. The linearization of Eq. (2.7) in the vicinity of this point yields[2)] $\eta=2\xi/15$; from a comparison with (2.8) we find $T_*=3\lambda/10$. In the region $T<T_*$ there exist, as before, two nontrivial solutions, to one of which now corresponds a negative value of the order parameter. In the low-temperature limit the positive solution tends asymptotically to $\eta=1$, while the negative solution tends to $\eta=-\frac{1}{2}$. The first case, as indicated above, corresponds to perfect nematic ordering of the molecules in the direction of the director (an "easy-axis" type of anisotropy). In the second case the long axes of all the molecules lie in planes perpendicular to n (an "easy-plane" type of anisotropy); as can be seen from (1.2), the value $\eta=-\frac{1}{2}$ is obtained in the case when $\boldsymbol{\nu}\mathbf{n}=0$.

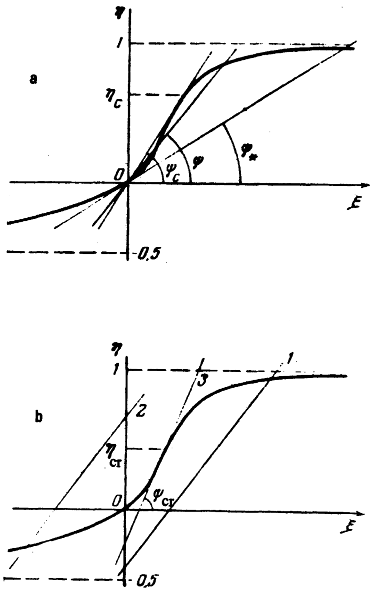

FIG. 2. Scheme for the graphical solution of the equation of the orientation state: a) $\sigma=0$, b) $\sigma\neq 0$.

In the presence of stresses (see Fig. 2b) the trivial solution ($\eta=0$) of the system (2.7), (2.8) disappears: the straight lines described by Eq. (2.8) make on the ordinate axis intercepts proportional to σ. To the parallel straight lines 1 and 2 in Fig. 2b correspond at the same temperature different—in magnitude and sign—stresses: $\sigma_1>0$ (extension) and $\sigma_2<0$ (contraction). The points of intersection of the straight lines 1 and 2 with the curve (2.7) determine in the first case a positive, and in the second a negative, value of the order parameter. This result is quite understandable: an extension either itself produces an "easy-axis" type of anisotropy ($\eta>0$), or increases an already existing one, whereas a contraction leads to an "easy-plane" type of anisotropy($\eta<0$). In Fig. 2b we show a characteristic straight line, 3, touching the curve (2.7) at the point of inflection; the angle ψ_{cr}, of inclination of the tangent determines the critical temperature T_{cr}. In the region $T>T_{cr}$ the system (2.7), (2.8) has a unique solution for all σ.

The result of the numerical solution of the system of equations (2.7), (2.8) is shown in Figs. 3 and 4. The curves 1 in Fig. 3, a) and b), which are characteristic of a first-order transition, describe the orientation state, $\eta(T)$, of an unstressed polymer; the thermodynamically stable sections of the branches (see §3) are depicted by the heavy curves. As the tensile stresses

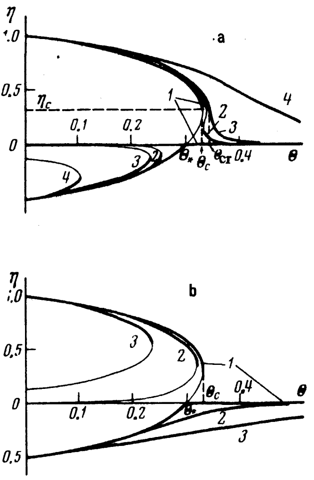

FIG. 3. Dependence of the order parameter η on the dimensionless temperature $\Theta = T/\lambda$ for different $\Pi = \gamma\sigma/\lambda$ in the case of a) extension, b) contraction: (a) 1) $\Pi = 0$, 2) $\Pi = 0.01$, 3) $\Pi = 0.02$, 4) $\Pi = 0.20$; (b) 1) $\Pi = 0$, 2) $\Pi = -0.02$, 3) $\Pi = -0.20$.

increase (Fig. 3a), the phase transition becomes smeared out: the orientation jump decreases and shifts toward the region of higher temperatures—from T_c to T_{cr}. When $\sigma = \sigma_{cr}$ (the curve 3 in Fig. 3a) the jump disappears, and at stresses higher than the critical stress the orientation becomes a monotonic function of the temperature.

Figure 4 shows the variation of the equilibrium orientation under the influence of mechanical stresses. At low temperatures (the curves 1 and 2) there occurs spontaneous crystallization of the polymer into a structure of the "easy-axis" type ($\eta > 0$). This type of ordering is preserved not only in the subsequent extension ($\sigma > 0$) in the direction of the director, but also during contraction ($\sigma < 0$) if the contractive forces are not too strong. A sufficiently large contraction sends the polymer into a state with an "easy-plane" type of anisotropy ($\eta < 0$). The proturberances on the isotherms in Fig. 4 disappear at $T > T_{cr}$ (the curve 3 is the critical isotherm).

§3. THE FREE ENERGY

The assumption, (2.1), made above the structure of the effective field leads to the following procedure for computing the free energy of an orientable polymer. Regarding H_{ik} as the derivative of the macroscopic internal energy, U, with respect to the orientation tensor,

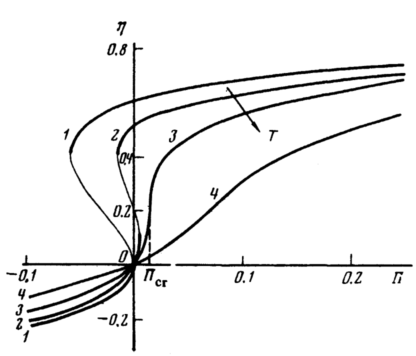

FIG. 4. Dependence of the order parameter on Π for different Θ: 1) $\Theta = 0.300$, 2) $\Theta = 0.320$, 3) $\Theta = \Theta_{cr} = 0.346$, 4) $\Theta = 0.400$.

$$H_{ik} = -\frac{1}{n}\frac{\partial U}{\partial \eta_{ik}}, \tag{3.1}$$

we obtain after substituting (2.1) into (3.1) and integrating

$$U = -n\left(\frac{\lambda}{2}\eta_{ik}^2 + \gamma\sigma_{ik}\eta_{ik}\right). \tag{3.2}$$

Here U is the volume density of the orientation part of the internal energy and n is the concentration of the elementary structure units.

For the computation of the free energy we use the definition of the entropy in terms of the distribution function: $S = -n\langle \ln W\rangle$. With the aid of (2.3) we find for the equilibrium entropy

$$S = -\frac{n}{T}\left[\eta_{ik}(\lambda\eta_{ik} + \gamma\sigma_{ik}) + \frac{\gamma}{2}\sigma_{ll} - T\ln Z_0\right]. \tag{3.3}$$

Now from (3.2) and (3.3) we can construct an expression for the orientational part of the free energy $F = U - TS$

$$F = n\left(\frac{\lambda}{2}\eta_{ik}^2 + \frac{\gamma}{2}\sigma_{ll} - T\ln Z_0\right). \tag{3.4}$$

In the case being considered by us of uniaxial ordering,$^{3)}$ when η_{ik} is defined by the formula (1.2) and $\sigma_{ik} = \sigma n_i n_k$, the free energy assumes the form

$$F = n[{}^3/_4\lambda\eta(\eta+1) + {}^1/_2\gamma\sigma - T\ln R(\xi)], \tag{3.5}$$

with $R(\xi)$ given by (2.6). The condition for equilibrium, $\partial F/\partial\eta = 0$, coincides, of course, with the self-consistency equations (2.7), (2.8).

The equilibrium values of the order parameter can also be determined directly from (3.5) as the minimum points of the function $F(\eta)$ for fixed T and σ. The plots of this function for the temperature $T = 2T_*/3$ are shown in Fig. 5. At so low a temperature the polymer is spontaneously oriented, a fact which is attested by the minima on the curve 1 of Fig. 5; the principal minimum corresponds to an "easy-axis" type of state ($\eta > 0$); the "easy-plane" state ($\eta < 0$) is metastable. An extension enhances the stability of the structure with positive orientation: the main potential well becomes deeper and the minimum point shifts to the right. At the same time the metastable state becomes less

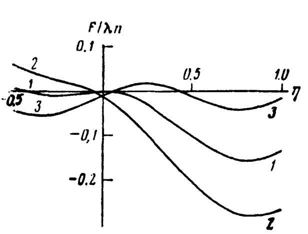

FIG. 5. Dependence of the orientational part of the free energy on the order parameter at a temperature of $\Theta = 0.2$. The curve 1) $\Pi = 0$, 2) $\Pi = 0.15$, 3) $\Pi = -0.15$.

stable, and at a sufficiently large extension (the curve 2) the minimum in the region $\eta < 0$ disappears. A contractive stress (the curve 3), on the other hand, facilitates the metastable orientation, so that the state with $\eta > 0$ now becomes metastable, while the state with $\eta < 0$ becomes stable.

The computation of the function $F(T, \sigma)$ allows the selection of the thermodynamically stable states from the solutions of the equation of the orientation state $\eta(T, \sigma)$ (see Figs. 3 and 4). The procedure for making such a selection is illustrated in Fig. 6. Figure 6a shows a plot of the dependence $F(\sigma)$ for two different temperatures. At low temperatures the free energy depends on the dimensionless stress $\Pi = \gamma\sigma/\lambda$ in quite a complicated fashion: the isotherm 1 in Fig. 6a above the point of self-intersection C forms a quasi-triangular loop ABC whose width determines the region along the Π axis where $\eta(\sigma)$ is a three-valued function (see the curve 1 in Fig. 6b). The segments ACE and BCD of the curve 1 in Fig. 6a are lines of minima of the function $F(\sigma)$, while the segment AOB is a line of maxima. As can be seen from Fig. 6, a) and b), on the right of the point of self-intersection to the absolute minimum of the free energy corresponds the state with $\eta > 0$ (the segments CE), while to the left of the point C the absolute minimum of F corresponds to the orientation with $\eta < 0$ (the segments CD). A metastable state with with $\eta > 0$ is possible along the segment AC, while one with $\eta < 0$ is possible along BC; the boundaries of the existence domain of the metastable phases are marked by single arrows in Fig. 6b. To the point of self-intersection in Fig. 6a, where the free energies of the easy-axis and easy-plane types of phases coincide, corresponds the line, C-C, of equilibrium transitions in Fig. 6b. As the temperature is raised, the nonuniqueness loop shrinks, and disappears at $T \geqslant T_{\rm cr}$ (the curves 2 in Fig. 6).

We do not give here the free energy-versus-temperature plots; they are in many respects similar to the $F(\sigma)$ curves shown in Fig. 6a. In particular, at not too high stresses the function $F(T)$ has a self-intersection point that determines the equilibrium transition point $T_t(\sigma)$. T_t values, calculated for $\sigma = 0$, are given in Table I together with other characteristic parameters of the transition.

For small values of the order parameter the free energy (3.5) can be represented in the form of the Landau expansion. Retaining the terms not higher than the fourth-order terms in η, and limiting ourselves to the linear approximation in σ, we obtain

$$\frac{F}{\lambda n} = \frac{3}{4\Theta}\left(\Theta - \frac{3}{10}\right)\eta^2 - \frac{9}{280} \times \frac{\eta^3}{\Theta^2} + \frac{81}{11200}\frac{\eta^4}{\Theta^3} - \frac{3}{10}\frac{\Pi\eta}{\Theta}. \tag{3.6}$$

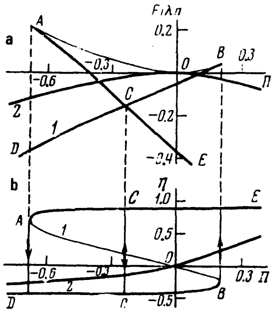

FIG. 6. Dependences of F and η on stress at temperatures $\Theta = 0.1$ (the curves 1) and $\Theta = 0.5$ (the curves 2).

In this expansion there is a term with η^3 (first-order transition), while the coefficient in front of η^2 changes it sign, as it should, at the temperature $\Theta = 0.3$, which coincides with Θ_* (see Table I). All the coefficients, except the first, depend weakly on temperature. Taking into account the fact that the Landau expansion is applicable only in the vicinity of the point Θ_*, we can replace Θ by Θ_* everywhere, retaining the difference $\Theta - \Theta_*$ only in the first term of the formula (3.6):

$$F/\lambda n = {}^5/_2(\Theta - \Theta_*)\eta^2 - {}^5/_{14}\eta^3 + {}^{15}/_{14}\eta^4 - \Pi\eta.$$

Computing from here the derivative $\partial F/\partial\eta$, and equating it to zero, we obtain for η the cubic equation

$$\eta[\eta(\eta - 1) + {}^{14}/_3(\Theta - \Theta_*)] = {}^{14}/_{15}\Pi,$$

which for small Π correctly imparts the character of the curves of Fig. 3 near Θ_*.

§4. THE ORIENTATION-ELASTIC PROPERTIES

For the study of the deformation properties of a polymer we need the density of the total free energy $\mathfrak{F}$. This quantity is made up of the orientational part of the free energy F, (3.4), and the normal elastic energy[10]:

$$\mathcal{F} = F + \mu(u_{ik} - {}^1/_3 u_{ll}\delta_{ik})^2 + K u_{ll}^2/2, \tag{4.1}$$

where u_{ik} is the strain tensor and μ and K are the shear and bulk moduli. Since F contains the stress, σ_{ik}, in its explicit form, but not the strain, it is convenient to go over to the thermodynamic potential $\Phi = \mathfrak{F} - \sigma_{ik}u_{ik}$, for which the role of independent variables is played by the components of the σ_{ik} tensor. Expressing in (4.1) u_{ik} in terms of σ_{ik},[10] and using (3.4), we find

TABLE I. Characteristic values of the dimensionless parameters of the first-order orientation phase transition.

Parameters	Index of point			
	*	t	c	K
Θ	0.300	0.330	0.334	0.346
η	0.614	0.429	0.324	0.214
Π	–	0	–	0.016

Note. The definitions of the dimensionless temperature Θ and the dimensionless stress Π are indicated in the caption to Fig. 3; the values of η_* and η_t are given for the upper (stable) branch of the function $\eta(T)$ (see the curve 1 in Fig. 3).

$$\Phi=\frac{n\lambda}{2}\eta_{ik}^2-nT\ln Z_0-\frac{1}{4\mu}\left(\sigma_{ik}-\frac{1}{3}\sigma_{ll}\delta_{ik}\right)^2+\frac{1}{2}\left(n\gamma-\frac{1}{9K}\right)\sigma_{ll}^2. \quad (4.2)$$

The strain tensor is obtainable from here by differentiating the potential Φ with respect to the corresponding components of the σ_{ik} tensor:

$$u_{ik}=-\frac{\partial\Phi}{\partial\sigma_{ik}}=\frac{1}{2\mu}\left(\sigma_{ik}-\frac{1}{3}\sigma_{ll}\delta_{ik}\right)+\frac{1}{9K}\sigma_{ll}\delta_{ik}+n\gamma\eta_{ik}. \quad (4.3)$$

(Here we have used the relation $\partial Z_0/\partial\sigma_{ik}=\gamma(2\eta_{ik}+\delta_{ik})/2T$, which follows from the definition (2.3) for Z_0.)

The formula (4.3) contains all the orientation-elastic effects. It follows, in particular, from it that a change in the degree of orientation of the polymer leads to its deformation (orientational striction). In the absence of internal stresses only the strictional deformation $u_{ik}=n\gamma\eta_{ik}$, which is linear in the order parameter, remains. On the other hand, if for some reason a deformation is not possible (e.g., the polymer sample may be confined by a rigid sheath), then the formula (4.3) allows the determination of the stresses that arise as a result of orientation crystallization.

In the case of uniform extension in the direction of the director (the z axis), the following expression follows from (4.3) for $u_{zz}=u$:

$$u=\sigma/G+n\gamma\eta, \quad G=9\mu K/(\mu+3K) \quad (4.4)$$

(G is the Young modulus). The orientation phase transition considered above is possible in the temperature interval between T_* and T_{cr} when $\sigma<\sigma_{cr}$. The isothermal extension of a polymer in this temperature range[4)] induces, upon the attainment of a certain value of $\sigma_0(T)$, a discontinuous increase in the order parameter η, which, in its turn, according to (4.4), leads to a discontinuous elongation of the sample—"orientational flow." Equation (4.4) together with the system (2.7), (2.8) explains the shape of the deformation curves shown in Fig. 1. To the "orientational flow" correspond the horizontal plateaus in the bottom curves of this figure; the height of a plateau determines the "triggering" stress $\sigma_0(T)$. The appearance of a hump at the left edge of the plateau is apparently connected with the nonequilibrium nature of the deformation process: extension always proceeds at a finite rate. If this assumption is valid, then the height of the hump should increase with increasing rate of extension, approaching its limiting value determined by the width of the metastability region on the $\eta(\sigma)$ isotherm (see Fig. 6).

At temperatures $T>T_{cr}$ the phase transition disappears: the order parameter becomes a single-valued function of the stress. For low stresses the relation between η and σ can be assumed to be linear, so that Eq. (4.4) goes over into the conventional Hooke law for hyperelastic materials[3]:

$$u=(1/G+1/G_{el})\sigma, \quad (4.5)$$

where G_{el} is the modulus of Mackian elasticity. At high temperatures ($\xi\ll 1$) the solution to Eqs. (2.7) and (2.8) is $\eta=\gamma\sigma/5(T-T_*)$. Substituting this expression into (4.4), we find from a comparison with (4.5) that

$$G_{el}=5(T-T_*)/n\gamma^2. \quad (4.6)$$

The coefficient γ, which characterizes the "orientational susceptibility" of the molecular segments with respect to stress, has the dimension of volume. It is natural to assume that the quantity γ is determined by the volume of the elementary structure unit, i.e., $\gamma\sim n^{-1}$. Indeed, for $n\gamma\sim 1$ and $T\gg T_*$, the formula (4.6) gives the well-known result of the theory of Mackian elasticity $G_{el}=CnT$, where C is a numerical coefficient of the order of unity. Setting $n\sim 10^{21}$ cm^{-3}, we have that at room temperature $G_{el}\sim 10^2$ kgf/cm^2. Notice also that, for $\gamma=10^{-21}$ cm^3 and $\lambda\sim 10^{-1}$ eV, to the value of the dimensionless stress $\Pi=1$ corresponds $\sigma\sim 10^2$ kgf/cm^2.

As has already been noted, a change in the spontaneous orientation of the sample under conditions when its deformation is impossible is accompanied by the appearance of internal strictional stresses. These stresses, according to general principles, tend through their effect on the orientation to weaken the cause that gives rise to them. Indeed, setting $u=0$ in (4.4), we find $\sigma=-Gn\gamma n$. Allowance for the strictional stress in the formulas (2.5)–(2.8) amounts to a simple renormalization of the molecular-field constant: $\tilde{\lambda}=\lambda-2Gn\gamma^2/3$. The replacement of λ by $\tilde{\lambda}$ implies the lowering of all the characteristic temperatures (e.g., the transition temperature turns out to be equal to $T_t=0.330\tilde{\lambda}$). Thus, at a fixed temperature the degree of orientation is always higher in the case when $\sigma=0$ than in the $u=0$ case. In the latter case the necessary condition for orientation crystallization to occur is, evidently, $\tilde{\lambda}>0$, i.e.,

$$\lambda>{}^2/_3Gn\gamma^2. \quad (4.7)$$

For real polymers with $G\sim 10^4$ kgf/cm^2 and the above-indicated n, γ, and λ values the inverse of the inequality (4.7) is fulfilled, so that spontaneous orientation is, apparently, impossible in the absence of strains.

§5. EQUATION OF MOTION FOR THE ORIENTATION TENSOR

The plan of this section is as follows: first, we construct a kinetic equation for the orientation distribution function of the microscopic structure elements and then derive from this equation by the method of moments the equation of motion of the macroscopic order parameter.

According to the developed approach, the orientation of a polymer is accomplished by means of a rotation of the elementary structure units. The relative smallness of the linear dimensions of these objects implies that their dynamics is influenced considerably by the rotational Brownian motion. Thus, the orientation distribution density, $W(\nu)$, for the microscopic elements should be described by a Fokker-Planck type of equation, to the derivation of which we now proceed.

Having in mind to consider further small deviations from the spatially-homogeneous equilibrium orientation, we include in the expression, (3.2), for the internal-energy density a term describing the possible inhomogeneity of the order parameter:

$$U=-n\left[\frac{\lambda}{2}\eta_{ik}^2+\gamma\sigma_{ik}\eta_{ik}-\frac{\alpha}{2}\left(\frac{\partial\eta_{ik}}{\partial\mathbf{r}}\right)^2\right]. \tag{5.1}$$

For a slight inhomogeneity in the macroscopic orientation (the long-wave approximation), allowance for the derivative term in (5.1) does not require a reconsideration of the self-consistency equations. The "effective field" acting on a structure element is determined by the variational derivative

$$H_{ik}=-\frac{1}{n}\frac{\delta U}{\delta\eta_{ik}}=-\frac{1}{n}\left(\frac{\partial}{\partial\eta_{ik}}-\frac{\partial}{\partial x_l}\frac{\partial}{\partial(\partial\eta_{ik}/\partial x_l)}\right)U, \tag{5.2}$$

so that for the orientational part of the energy of the individual element, instead of (2.2), we now obtain

$$E=-{}^3/_2(\lambda\eta_{ik}+\gamma\sigma_{ik}+\alpha\Delta\eta_{ik})\nu_i\nu_k \tag{5.3}$$

(Δ is the Laplace operator).

For small deviations from equilibrium, let us write the orientation and stress tensors in the form $\eta_{ik}=\eta_{ik}^{(0)}+\epsilon_{ik}$ and $\sigma_{ik}=\sigma_{ik}^{(0)}+p_{ik}$; below we shall drop the index 0, which designates the equilibrium values of the quantities. In this notation the expression (5.3) assumes the form

$$E=E_0-{}^3/_2(\lambda\varepsilon_{ik}+\gamma p_{ik}+\alpha\Delta\varepsilon_{ik})\nu_i\nu_k, \tag{5.4}$$

where the unperturbed energy F_0 is determined by the formula (2.2).

The theory of kinetic processes in high-molecular materials is usually based on the assumption that each individual element (a segment of the macromolecule) can be regarded as a solid particle surrounded by a viscous fluid. The viscous friction thus serves as a model for the complex interparticle interactions that impede the free rotation of the selected element. We can neglect the inertia of its motion, in view of the large value of the effective internal viscosity of a polymer, and find the angular velocity ω, of the element from the equilibrium condition for the torques acting on it:

$$\boldsymbol{\omega}=b(\mathbf{M}+\mathbf{M}_f),\ \mathbf{M}=-\left[\boldsymbol{\nu}\times\frac{\partial}{\partial\boldsymbol{\nu}}\right]E,\ \mathbf{M}_f=-T\left[\boldsymbol{\nu}\times\frac{\partial}{\partial\boldsymbol{\nu}}\right]\ln W. \tag{5.5}$$

Here b is the coefficient of rotational mobility[5], $\mathbf{M}$ and $\mathbf{M}_f$ are the moments of the normal and fluctuation forces.

Using the infinitesimal-rotation operator

$$\hat{\mathbf{L}}=-i\left[\boldsymbol{\nu}\times\frac{\partial}{\partial\boldsymbol{\nu}}\right],$$

we can write Eq. (5.5) in the form

$$\boldsymbol{\omega}=-ib\hat{\mathbf{L}}(E+T\ln W), \tag{5.6}$$

where E is the energy and W is the distribution function of the orientable element. The latter should satisfy the Fokker-Planck equation:

$$\dot{W}+\frac{\partial}{\partial\nu_k}(W\dot{\nu}_k)=0. \tag{5.7}$$

The rate of rotation of the vector ν entering into this equation is connected with the angular velocity ω through kinematic relation $\dot{\nu}=\omega\times\nu$. Taking this into account, and using (5.6), we obtain from (5.7) after simple transformations the kinetic equation in the form

$$6\tau\dot{W}=-\hat{L}W\hat{L}(E/T+\ln W). \tag{5.8}$$

Here we have introduced the notation $\tau=(6bT)^{-1}$ for the Brownian rotational-diffusion time of the element. The steady-state normalized solution to (5.8) is the Gibbs distribution $W_0=Z_0^{-1}\exp(-E_0/T)$ [see (2.3)].

From the definition of the macroscopic order parameter $\eta_{ik}=\langle s_{ik}\rangle$ and the formula (1.1) for η_{ik} follows the following expression for the nonequilibrium part of the orientation tensor

$$\varepsilon_{ik}={}^3/_2(\langle\nu_i\nu_k\rangle-\langle\nu_i\nu_k\rangle_0); \tag{5.9}$$

here the angle brackets without a subscript denote averaging with the function W obtained from (5.8), while the brackets with a subscript denote averaging with the equilibrium distribution W_0. To derive the equation of motion for ϵ_{ik}, let us multiply (5.8) from the left by $\nu_i\nu_k$ and integrate over the angles (the integration is easy to perform because of the Hermitian character of the operator $\hat{L}$):

$$4\tau\dot{\varepsilon}_{ik}=-\left\langle[\nu_i\delta_{kl}+\nu_k\delta_{il}-2\nu_i\nu_k\nu_l]\frac{\partial}{\partial\nu_l}\left(\frac{E}{T}+\ln W\right)\right\rangle. \tag{5.10}$$

To make Eq. (5.10) a closed equation in the case being considered of a small deviation from the equilibrium state, let us represent the solution to the kinetic equation (5.8) in the form

$$W=W_0[1+a_{ik}(\nu_i\nu_k-\langle\nu_i\nu_k\rangle_0)], \tag{5.11}$$

where the tensor a_{ik} is assumed to be independent of ν and linear in the perturbations. For such a choice of W the derivative

$$\frac{\partial}{\partial\nu_l}\left(\frac{E}{T}+\ln W\right)=\left[2a_{lm}-\frac{3}{T}(\lambda\varepsilon_{lm}+\alpha\Delta\varepsilon_{lm}+\gamma p_{lm})\right]\nu_m, \tag{5.12}$$

which enters into (5.10), is of first order in smallness. Therefore, the averaging on the right-hand side of (5.10) should be performed with the equilibrium distribution function, i.e.,

$$2\tau\dot{\varepsilon}_{ik}=-[\langle\nu_i\nu_l\rangle_0\delta_{km}+\langle\nu_k\nu_l\rangle_0\delta_{im}-2\langle\nu_i\nu_k\nu_l\nu_m\rangle_0]\times\left[a_{lm}-\frac{3}{2T}(\lambda\varepsilon_{lm}+\alpha\Delta\varepsilon_{lm}+\gamma p_{lm})\right]. \tag{5.13}$$

The quantities ϵ_{ik} and a_{ik} are, however, not independent: computing the second moment $\langle\nu_i\nu_k\rangle$ in the formula (5.9) with the aid of the expansion (5.11), we find a linear relation between them:

$$\varepsilon_{ik}={}^3/_2N_{iklm}a_{lm},\quad N_{iklm}\equiv\langle\nu_i\nu_k\nu_l\nu_m\rangle_0-\langle\nu_i\nu_k\rangle_0\langle\nu_l\nu_m\rangle_0. \tag{5.14}$$

The substitution of (5.14) into (5.13) allows us to write down a closed equation of motion for the macroscopic-orientation tensor for the case of small deviations from equilibrium:

$$\tau\dot{\varepsilon}_{ik}=-{}^{1}/_{3}[\langle\nu_i\nu_l\rangle_0\delta_{km}+\langle\nu_k\nu_l\rangle_0\delta_{im}-2\langle\nu_i\nu_k\nu_l\nu_m\rangle_0]$$
$$\times\left[\overset{-1}{N}_{lmnj}\varepsilon_{jn}-\frac{9}{4T}(\lambda\varepsilon_{lm}+\alpha\Delta\varepsilon_{lm}+\gamma p_{lm})\right] \qquad (5.15)$$

(the exponent –1 denotes the taking of the inverse matrix).

The symmetric traceless tensor ϵ_{ik} is determined by five independent quantities, as which it is convenient to choose $\epsilon_{zz}=-(\epsilon_{xx}+\epsilon_{yy}), (\epsilon_{xx}-\epsilon_{yy}), \epsilon_{xz}, \epsilon_{yz}, \epsilon_{xy}$. If at equilibrium the polymer is uniaxially oriented, then the equations obtained from (5.15) for these quantities become uncoupled, and the computation of the equilibrium moments in (5.14) and (5.15) is elementary:

$$\langle\nu_i\nu_k\rangle_0=\frac{1}{2R}[(R-R')\delta_{ik}+(3R'-R)n_in_k], \qquad (5.16)$$

$$\langle\nu_i\nu_k\nu_l\nu_m\rangle_0=\frac{1}{8R}[(R-2R'+R'')(\delta_{ik}\delta_{lm}+\delta_{im}\delta_{kl}+\delta_{il}\delta_{km})$$
$$-(R-6R'+5\mathrm{R}'')(n_in_k\delta_{lm}+n_ln_m\delta_{ik}+\ldots)+(3R-30R'+35R'')n_in_kn_ln_m]. \qquad (5.17)$$

Owing to the high symmetry (the goup $D_{\infty h}$) of the tensor coefficients in (5.15), which are given by the formulas (5.16) and (5.17), the number of essentially different equations for the components of the ϵ_{ik} tensor reduces to three:

$$\tau\dot{\varepsilon}_{zz}=-\varkappa_1\varepsilon_{zz}+\frac{3(R'-R'')}{4TR}[3\alpha\Delta\varepsilon_{zz}+\gamma(2p_{zz}-p_{xx}-p_{yy})], \qquad (5.18)$$

$$\tau\dot{\varepsilon}_{xy}=-\varkappa_2\varepsilon_{xy}+\frac{3(R-R'')}{8TR}[\alpha\Delta\varepsilon_{xy}+\gamma p_{xy}], \qquad (5.19)$$

$$\tau\dot{\varepsilon}_{xz}=-\varkappa_3\varepsilon_{xz}+\frac{3(R-3R'+4R'')}{8TR}[\alpha\Delta\varepsilon_{xz}+\gamma p_{xz}]. \qquad (5.20)$$

Here we have introduced the following notation for the dimensionless decrements:

$$\varkappa_1=\frac{2R(R'-R'')}{3(RR''-R'^2)}f_1, \quad \varkappa_2=\frac{2(R-R'')}{3(R-2R'+R'')}f_2, \quad \varkappa_3=\frac{R-3R'+4R''}{6(R'-R'')}f_3;$$
$$f_1=\left[1-\frac{27\lambda(RR''-R'^2)}{8TR^2}\right], \quad f_2=\left[1-\frac{9\lambda(R-2R'+R'')}{16TR}\right], \qquad (5.21)$$
$$f_3=\left[1-\frac{9\lambda(R'-R'')}{4TR}\right].$$

The missing equations for the ϵ_{yz} and $(\epsilon_{xx}-\epsilon_{yy})$ normal modes can be obtained from (5.19) and (5.10): one by means of the substitutions $\epsilon_{xy}\to(\epsilon_{xx}-\epsilon_{yy})$ and $p_{xy}\to(p_{xx}-p_{yy})$ and the other by means of the substitutions $\epsilon_{xz}\to\epsilon_{yz}$ and $p_{xz}\to p_{yz}$. The first of these transformations implies a rotation of the initial coordinate system about the axis of symmetry (the z axis) through 45°; the second, a rotation through 90°. In the first case the shear stress p_{xy} amounts, as it should, to an extension along the x axis and a contraction in the direction of the y axis of the coordinate system.

§6. THE RELXATION TIMES. DYNAMIC STABILITY OF THE UNIAXIAL ORIENTATION

Let a uniformly oriented polymer, initially in equilibrium, be brought out of this state, so that the orientation tensor η_{ik} acquires an increment ϵ_{ik}. We shall assume that the perturbations are homogeneous ($\Delta\epsilon_{ik}=0$) and that there are no internal stresses ($p_{ik}=0$). Then the strictional strain, u_{ik}, that arises is also homogeneous and connected with ϵ_{ik} through the relation $u_{ik}=n\gamma\epsilon_{ik}$. In the case under consideration Eqs. (5.18)–(5.20) get simplified:

$$\tau\dot{\varepsilon}_{zz}=-\varkappa_1\varepsilon_{zz}, \quad \tau\dot{\varepsilon}_{xy}=-\varkappa_2\varepsilon_{xy}, \quad \tau\dot{\varepsilon}_{xz}=-\varkappa_3\varepsilon_{xz}; \qquad (6.1)$$

the dependence, determined by them, of the ϵ_{ik}-tensor components on time is given by the factor $\exp(-\varkappa_i t/\tau)$. Thus, the problem of the stability of the iniaxial orientation reduces to the problem of the determination of the signs of the quantities $\varkappa_i$: the equilibrium is a stable one if all the three decrements are positive. The formulas (5.21) determine the dependence $\varkappa_i(\xi)$, where the argument ξ is itself a function, (2.6), of the thermodynamic coordinates T and σ through the equation of the orientation state (2.7), (2.8). The multivaluedness of the solutions of this equation in the region $T<T_{\mathrm{cr}}$ and $\sigma<\sigma_{\mathrm{cr}}$ gives rise to a complicated dependence of the decrements on temperature and stress.

Proceeding to the investigation of this dependence, we note that the decrement $\varkappa_i$ should vanish at the boundaries of the region where the equation of state is nonunique, and where the derivative $\partial^2\Phi/\partial\eta^2$ changes its sign (the points A and B in Fig. 6): at these points the metastable orientation $\eta_{zz}=\eta$ becomes absolutely unstable against perturbations of the same symmetry (ϵ_{zz}). Let us show that not only $\varkappa_1$, but also the remaining decrements are closely related with the second derivatives of the thermodynamic potential through the corresponding components of the orientation tensor. According to the general phenomenological approach,[11] the rate of variation of the orientation tensor should be determined by the equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\varepsilon_{ik}=-\Gamma\left(\frac{\partial^2\Phi}{\partial\eta_{ik}\partial\eta_{lm}}\right)_0\varepsilon_{lm}, \qquad (6.2)$$

where Γ is a coefficient, which is assumed to have no singularities near the phase-transition point, and the subscript 0 indicates that the order parameter should be set equal to its equilibrium value after the differentiation. From the complete expression for Φ, (4.2), we find

$$\left(\frac{\partial^2\Phi}{\partial\eta_{ik}\partial\eta_{lm}}\right)_0=\lambda n\left[\delta_{il}\delta_{km}-\frac{9\lambda}{4T}N_{iklm}\right] \qquad (6.3)$$

[the tensor N_{iklm} is defined by the formula (5.14)]. After substituting (6.3) into (6.2) and computing the components of the tensor N_{iklm} with the aid of the formulas, (5.16) and (5.17), for the equilibrium moments, we obtain the equations

$$\dot{\varepsilon}_{zz}=-\Gamma f_1\varepsilon_{zz}, \quad \varepsilon_{xy}=-\Gamma f_2\varepsilon_{xy}, \quad \varepsilon_{xz}=-\Gamma f_3\varepsilon_{xz} \qquad (6.4)$$

where the f_i are found from (5.21); the factor λn in included in Γ. As can be seen from (6.2) and (6.4), the functions f_i are proportional to the second derivatives of Φ and, consequently, should change their signs at the singular points of the thermodynamic potential.

Comparing (6.4) with (6.1), we conclude that the role of the relaxation times $\tau_i=\tau/\varkappa_i$ in (6.1) is played in (6.4) by the quantities $(\Gamma f_i)^{-1}$. Thus, the simple arguments leading to Eqs. (6.4) allow us to find the function f_i, which determines the sign of the decrement $\varkappa_i$. The coefficients coupling $\varkappa_i$ and f_i in (5.21) have an appreciable influence on the magnitude of the decrement (for $\xi \gg 1$ they grow in proportion to ξ), but remain of fixed sign (positive) at all values of T and σ.

The dependence of the decrements $\varkappa_i$ on T and σ is shown qualitatively in Figs. 7 and 8. For convenience of interpretation, we show the orientation-phase diagrams $\eta(T)$ and $\eta(\sigma)$ in the same figures. Let us first consider the temperature dependence of the decrements for $\sigma=0$ (the continuous curves in Fig. 7). In Fig. 7a three solutions to the equation of the orientation state at some temperature lower than T_* are distinguished by Roman numerals. To each of the solutions corresponds its own value of the decrement $\varkappa_i$, denoted in Fig. 7, b), c), and d) by the same numeral. The decrements of the state with $\eta=0$ (the point I) are given by the general formula

$$\varkappa_{1,2,3}=(T-T_*)/T,$$

so that the isotropic phase is absolutely unstable right up to T_* and stable against weak perturbations at $T>T_*$. As has been noted above, an "easy-plane" type of orientation (the point II) is metastable. Indeed, it can be seen from Fig. 7, b) and d) that it is stable against weak perturbations of the same symmetry (ϵ_{zz}) and neutral with respect to perturbations of the form ϵ_{xz} and ϵ_{yz}. However, the state with $\eta<0$ is unstable against the normal modes ϵ_{xy} and $(\epsilon_{xx}-\epsilon_{yy})$ (see Fig. 7c, where to the point II corresponds $\varkappa_2<0$). The development of this instability should lead to the appearance of an "easy-axis" type of state with the direction of orientation lying in the xy plane. Finally, the solution with $\eta>0$ (the point III in Fig. 7a) is stable against perturbations with decrements $\varkappa_1$ and $\varkappa_2$ and neutral with respect to the ϵ_{xz} and ϵ_{yz} modes ($\varkappa_3=0$). The neutral perturbations are, in the present case, small deviations of the macroscopic-orientation vector n from the z axis (infinitesimal rotations about the x and y axes). In the absence of stresses the direction of the director is completely degenerate, and therefore such perturbations neither attenuate nor intensify in the entire existence domain of the spontaneous orientation ($T<T_c$). Out of the two positive solutions to the equation of the orientation state that exist in the temperature interval between T_* and T_c (see Fig. 7a) only the upper one is stable; the second solution, for which $\partial\eta/\partial T>0$, is unstable with respect to the ϵ_{zz} mode—the corresponding decrement, $\varkappa_1$, is negative. The distortion of the decrement spectrum under the action of a tensile stress is depicted in Fig. 7 by the dashed curves. An extension completely removes the degeneracy in the directions of the orientation axis, as a result of which the state with $\eta>0$ becomes absolutely stable; all the self-intersection points on the $\varkappa_i(T)$ graphs for $\sigma>\sigma_k$ disappear.

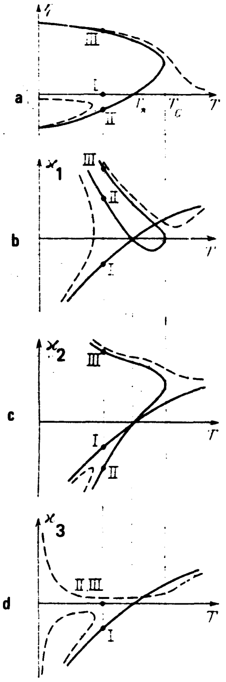

FIG. 7. Temperature dependence of the decrements $\varkappa_i$ (b, c, d) and of the order parameter η (a) for $\sigma=0$ (the continuous lines) and $\sigma>\sigma_{cr}$ (the broken lines).

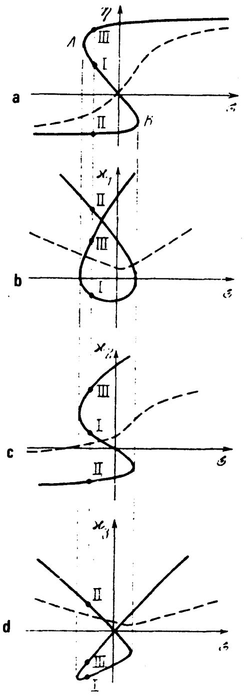

FIG. 8. Dependence of the decrements (b, c, d) and the order parameter (a) on stress for $T<T_*$ (the continuous lines) and $T>T_{cr}$ (the broken curves).

Figure 8 shows the stress dependence of the decrements for two different temperature values. The continuous lines depict isotherms corresponding to a low temperature ($T>T_*$) at which the polymer is already oriented in the absence of stresses; the broken lines depict isotherms corresponding to a high temperature, when spontaneous orientation is impossible. In the figure we have indicated the projections of the points, A and B, that delimit the nonuniqueness interval along the σ axis. The solutions ot the equation of the orientation state (Fig. 8a) within this interval and the corresponding decrements of the normal modes [Fig. 8, b), c), d)] are numbered by Roman numerals. Summarizing the information furnished by these graphs, we conclude that out of all conceivable states with a uniaxial orientation only the orientation of the "easy-axis" type (η

> 0) is stable under the action of tensile stresses ($\sigma > 0$). In the case when $\sigma = 0$ such an orientation is, as has been noted above, neutral with respect to the ϵ_{xz} and ϵ_{yz} modes, but these perturbations grow (see the point III in Fig. 8d) even in the presence of an arbitrarily small contraction ($\sigma < 0$), which indicates the tendency of the easy axis to settle in the xy plane. The state with $\eta < 0$ (the "easy-plane" type) is unstable against perturbations with the decrement $\varkappa_2$, while the section between A and B in Fig. 8a is unstable with respect to the normal modes with the decrements $\varkappa_1$ and $\varkappa_2$. As the temperature is raised, the loops in the $\varkappa_1$ and $\varkappa_3$ plots shrink and disappear at $T > T_{cr}$: the decrements become single-valued functions of the stress (the dashed lines in Fig. 8).

Let us note in conclusion that the relaxation times considered in this section determine the evolution of only small deviations from the equilibrium orientation. On the other hand, as a highly nonequilibrium process, the orientation transition itself should be characterized by times of an entirely different nature: for the kinetics of a first-order phase transition such factors as the probability of formation and the rate of growth of the nucleation centers of the new phase are important.

§7. ELASTIC VIBRATIONS OF A ROD

As shown in §4, the orientation-elastic interaction has an appreciable influence on the deformation properties of a polymer. This influence should, perhaps, manifest itself most distinctly in nonstationary deformation regimes, since the establishment of mechanical equilibrium is, in the final analysis, determined by the orientation relaxation times, which are the longest of all the solid-state times. In particular, anomalies are to be expected in the elastic properties near the orientation-transition points, with approach to which the corresponding relaxation times increase rapidly.

When the orientation effects are taken into consideration, the dynamical problems of the theory of elasticity reduce to the problem of finding simultaneous solutions to the equations of motion of the orientation tensor, (5.15), and the equations of motion of a solid

$$\rho \ddot{u}_i = \partial \sigma_{ik} / \partial x_k. \tag{7.1}$$

Here u is a displacement vector, which is connected with u_{ik} through the relation

$$u_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right);$$

from this definition and Eq. (7.1) follows the equation for the strain tensor:

$$\rho \ddot{u}_{ik} = \frac{1}{2}\frac{\partial}{\partial x_l}\left(\frac{\partial \sigma_{il}}{\partial x_k} + \frac{\partial \sigma_{kl}}{\partial x_i}\right). \tag{7.2}$$

In this and the following sections we study the propagation of weak perturbations in a homogeneously deformed polymeric solid. Retaining the previous notation, let us write the stress and orientation tensors in the form $\sigma_{ik} + p_{ik}$ and $\eta_{ik} + \epsilon_{ik}$, where

$$\sigma_{ik} = \sigma n_i n_k, \quad \eta_{ik} = {}^3/_2 \eta (n_i n_k - {}^1/_3 \delta_{ik})$$

are the constant equilibrium values of the quantities while p_{ik} and ϵ_{ik} are small changes made in them by the acoustic wave. A quantity of the same order of smallness is the strain u_{ik}, which is measured from the equilibrium strain—the latter is determined by the values of η and σ. The equations for the weak perturbations,

$$2\rho \ddot{u}_{ik} = \frac{\partial}{\partial x_l}\left(\frac{\partial p_{il}}{\partial x_k} + \frac{\partial p_{kl}}{\partial x_i}\right), \tag{7.3}$$

$$u_{ik} = \frac{1}{2\mu}\left(p_{ik} - \frac{1}{3} p_{ll} \delta_{ik}\right) + \frac{1}{9K} p_{ll} \delta_{ik} + n\gamma \varepsilon_{ik}, \tag{7.4}$$

which are obtainable from (7.2) and (4.3), together with the Eqs. (5.15) for ϵ_{ik} form a complete system.

Let us begin with the consideration of longitudinal waves in a long rod of thickness a. We shall assume that the anisotropy axis n is directed along the length of the rod (the z axis), so that the wave vector $\mathbf{k} = k\mathbf{n}$. We are now dealing with waves whose wavelength is long compared to the rod thickness ($ka \ll 1$). The opposite limiting case, when the rod can be assumed to be unbounded in all directions, will be considered in the following section.

When the condition $ka \ll 1$ is fulfilled, the longitudinal waves in the rod are simple extensions (contractions) propagating along its axis, in synchronization with which the cross section of the rod decreases (increases). If no external forces act on the lateral face, then only the p_{zz} component of the stress tensor is nonzero in such a deformation. With allowance for this we find from (7.4) and (5.18) the equations

$$u_{zz} = G^{-1} p_{zz} + n\gamma \varepsilon_{zz}, \tag{7.5}$$

$$\tau \frac{\partial \varepsilon_{zz}}{\partial t} = -\varkappa_1 \varepsilon_{zz} + \frac{3(R' - R'')}{4TR}\left(3\alpha \frac{\partial^2 \varepsilon_{zz}}{\partial z^2} + 2\gamma p_{zz}\right) \tag{7.6}$$

The substitution of u_{zz} from (7.5) into the general equation of motion (7.3) yields

$$\frac{\partial^2 p_{zz}}{\partial t^2} + n\gamma G \frac{\partial^2 \varepsilon_{zz}}{\partial t^2} = \frac{G}{\rho}\frac{\partial^2 p_{zz}}{\partial z^2}. \tag{7.7}$$

The last two equations describe plane waves in the rod. Assuming ϵ_{zz} and p_{zz} depend on the coordinates and time as $\exp[i(kz - \omega t)]$, we obtain from the condition for the consistency of the equations

$$\left(\omega^2 - \frac{G}{\rho} k^2\right)\left[\frac{2TR}{3(R' - R'')}(\varkappa_1 - i\omega\tau) + \frac{3}{2}\alpha k^2\right] + n\gamma^2 G \omega^2 = 0 \tag{7.8}$$

Upon the neglect of dissipation, to which formally corresponds $\tau = 0$,6) the last equation can easily be solved for ω:

$$\omega^2 = \frac{G}{\rho} k^2 \frac{2TR\varkappa_1/3(R' - R'') + {}^3/_2 \alpha k^2}{2TR\varkappa_1/3(R' - R'') + n\gamma^2 G + {}^3/_2 \alpha k^2}. \tag{7.9}$$

Retaining here only the leading powers of k, we have $\omega^2 = Gk^2/\rho$, i.e., the velocity of the short waves is determined by the same formula, $(G/\rho)^{1/2}$, as in the case of an isotropic solid.[10] This result is a consequence of the freezing of the equilibrium orientation in the high-frequency limit.

At low frequencies the terms with αk^2 in (7.9) can be neglected. An exception is the $\varkappa_1 = 0$ case: as indicated in §6, the decrement $\varkappa_1$ vanishes at temperatures $T < T_{cr}$ and stresses $\sigma < \sigma_{cr}$ at the boundaries of the existence domain of the metastable phase. In this case, retaining the dominant terms in (7.9), we find

$$\omega = \left(\frac{3\alpha}{2\rho n\gamma^2}\right)^{1/2} k^2,$$

from which it can be seen that the velocity of propagation of the oscillations tends to zero at low frequencies like $\omega^{1/2}$. Naturally, this should be accompanied by anomalously high absorption of the wave energy, a fact which can be verified easily by computing the damping factor $\mathrm{Im}\,\omega$ from the general dispersion equation (7.8). For long waves we obtain $\mathrm{Im}\,\omega \sim \tau k^2$, so that the ratio $\mathrm{Im}\,\omega/\mathrm{Re}\,\omega$ tends to a finite limit as $k \to 0$.

For $\varkappa_1 \neq 0$ and small k Eq. (7.9) assumes the form

$$\omega^2 = \frac{G}{\rho} k^2 \left[1 + \frac{3n\gamma^2(R' - R'')}{2\varkappa_1 TR} G\right]^{-1}.$$

Let us call the quantity

$$G_1 = 2\varkappa_1 TR/3n\gamma^2(R' - R'') \tag{7.10}$$

the modulus of orientation elasticity. Using the definition (7.10), the preceding equation can be written in the form $\omega^2 = \overline{G}k^2/\rho$, where $\overline{G}$ is a reduced modulus related with G and G_1 through

$$\overline{G} = G_1 G (G_1 + G)^{-1}.$$

To elucidate the meaning of the modulus G_1, let us note that the expression for it can be derived directly—by differentiating the strictional part of the equilibrium deformation (4.4) with respect to the equilibrium stress:

$$G_1 = \left(n\gamma \frac{d\eta}{d\sigma}\right)^{-1}. \tag{7.11}$$

The computation of the derivative

$$\frac{d\eta}{d\sigma} = \frac{d\eta}{d\xi}\frac{d\xi}{d\sigma}$$

is carried out with the aid of the self-consistency equations (2.7), (2.8), from which we have

$$\frac{d\eta}{d\xi} = \frac{3}{2}(\ln R)'', \quad \frac{d\xi}{d\sigma} = \frac{3\gamma}{2T} + \frac{9\lambda}{4T}\frac{d\eta}{d\sigma}.$$

The substitution of the expression obtained from $d\eta/d\sigma$ into (7.11) leads to the formula

$$G_1 = \frac{4T}{9n\gamma^2(\ln R)''}\left[1 - \frac{27\lambda}{8T}(\ln R)''\right],$$

which coincides with (7.10). At high temperatures ($\xi \ll 1$: the region of Mackian elasticity) we should set $(\ln R)'' = \frac{4}{45}$ in the last formula, which immediately yields $G_1 = G_{el}$ [see (4.6)]; in the low-temperature limit ($\xi \gg 1$) we have $(\ln R)'' = \xi^{-2}$ and

$$G_1 = \frac{1}{nT}\left(\frac{3\lambda}{2\gamma} + \sigma\right)^2.$$

Figure 9 shows the temperature dependence of the modulus G_1 and the relaxation time $\tau_1 = \tau\varkappa_1^{-1}$. So long as the tensile stress does not exceed the critical value, the graphs exhibit self-intersection near the equilibrium-transition temperature T_t (the curves 1). Notice that this temperature separates the regions where the polymer behaves like a vitreous ($\partial G_1/\partial T < 0$), and a hyperelastic ($\partial G_1/\partial T > 0$), material. The value of $G_1(T_t)$ determines the smallest initial slope of the deformation curves shown in Fig. 1. Therefore, if the bottom isotherm in this figure corresponds to the transition temperature, then the deformation curves should shift upwards both as the temperature is raised (the direction of increase of temperature is indicated by the arrow in Fig. 1) and as it is lowered. The extrema on the graphs of Fig. 9 become flatter and shift toward the region of higher temperatures as the stress is increased (the curves 2).

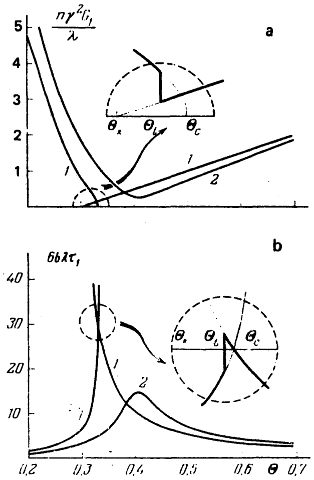

FIG. 9. Temperature dependences of the modulus G_1 (a) and the relaxation time τ_1 (b) for $\Pi = 0$ (the curves 1) and $\Pi = 0.1$ (the curves 2). The shape of the curves 1 near the transition temperature Θ_t is shown on a large scale; the heavy lines correspond to the equilibrium transition.

As the oscillation frequency ω decreases, the wavelength of the longitudinal waves can become greater than the length, l, of the rod. At frequencies corresponding to $kl \ll 1$, the rod will execute uniform (along its entire length) forced vibrations. In this regime the internal stresses $p_{zz} \sim p^{-i\omega t}$ vary in phase with the external force applied to the ends of the rod, whereas there develops between the stress and the deformation a phase difference that is due to the relaxation processes. The motion under consideration, i.e., the motion satisfying the condition $kl \ll 1$, is quasistationary. In this approximation the equation of motion of the rod, (7.7), is replaced by the equation for elastic equilibrium $\partial p_{zz}/\partial z = 0$, from which it follows that the derivative $\partial^2\epsilon_{zz}/\partial z^2$ in (7.6) is also equal to zero. Eliminating ϵ_{zz} from the Eqs. (7.5) and (7.6), we obtain in the periodic regime for the amplitude of the forced vibrations that

$$u_{zz} = \left(G^{-1} + \frac{G_1^{-1}}{1 - i\omega\tau_1}\right)p_{zz}. \tag{7.12}$$

The complex form of this formula is connected with an already noted circumstance: the deformation lags in phase behind the stress, which leads to mechanical losses (hysteresis). Separating the real and imaginary parts of u_{zz}, we find the tangent of the angle of lag:

$$\operatorname{tg}\delta=\frac{G\omega\tau_1}{G+G_1(1+\omega^2\tau_1^2)}. \tag{7.13}$$

The angle δ attains its maximum value δ_0 at the frequency ω_0; from (7.13) we obtain

$$\omega_0\tau_1=\left(1+\frac{G}{G_1}\right)^{1/2},\quad \operatorname{tg}\delta_0=\frac{G}{2[G_1(G_1+G)]^{1/2}}$$

As can be seen from Fig. 9a, the modulus G_1 increases without restriction as $T\to 0$ and $T\to\infty$ (in the first case like T^{-1}; in the second, like T). Therefore, at both of these limits the angle $\delta_0\approx G/2G_1$ tends to zero. The quantity δ_0 passes through a maximum at the temperature T_t, in the vicinity of which the relaxation processes should manifest themselves most clearly. In this region $G_1\ll G$, so that $\operatorname{tg}\delta_0\cong\frac{1}{2}(G/G_1)^{1/2}$.

The conclusions drawn about the nature of the temperature dependence of the phase shift agree with the results of Kornfel'd and Pozdnyak's experimental investigation.[12]. These authors established that the stress and the deformation coincide in phase in both the vitreous (low-temperature) and the developed hyperelastic state of the polymer, but that a phase shift occurs in the temperature region lying between these states.

In conclusion of this section, let us consider the uniform longitudinal vibrations of a rod whose length is perpendicular to the direction, n, of preferred orientation of its molecules. In the coordinate system in which the z axis is directed along n and the x axis is directed along the axis of the rod, only the component p_{xx} of the stress tensor is nonzero. The oscillation of this component excites two normal oscillatory modes of the orientation: $\epsilon_+=\epsilon_{xx}+\epsilon_{yy}$ and $\epsilon_-=\epsilon_{xx}-\epsilon_{yy}$, the equations for which follow from (5.18) and (5.19):

$$\tau\dot{\varepsilon}_+=-\varkappa_1\varepsilon_++\frac{3\gamma(R'-R'')}{4TR}p_{xx},\quad \tau\dot{\varepsilon}_-=-\varkappa_2\varepsilon_-+\frac{3\gamma(R-R'')}{8TR}p_{xx}. \tag{7.14}$$

The solution of the system (7.14) yields

$$\varepsilon_{xx}=\frac{3\gamma}{16TR}\left[\frac{2(R'-R'')}{\varkappa_1-i\omega\tau}+\frac{(R-R'')}{\varkappa_2-i\omega\tau}\right]p_{xx}.$$

Substituting this expression into the formula $u_{xx}=G^{-1}p_{xx}+\eta\gamma\epsilon_{xx}$, which is obtainable from (7.4), we find

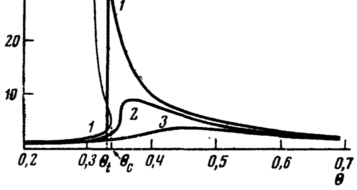

FIG. 10. Temperature dependence of the relaxation time τ_2 for $\Pi=0$ (the curve 1; the heavy lines correspond to the equilibrium transition), $\Pi=0.02$ (the curve 2), and $\Pi=0.10$ (the curve 3).

$$u_{xx}=\left[\frac{1}{G}+\frac{1}{4G_1(1-i\omega\tau_1)}+\frac{3}{4G_2(1-i\omega\tau_2)}\right]p_{xx}. \tag{7.15}$$

Here we have used for the relaxation times the notation $\tau_1=\varkappa_1^{-1}\tau$, $\tau_2=\varkappa_2^{-1}\tau$ and introduced a second orientation-elasticity modulus

$$G_2=4TR\varkappa_2/n\gamma^2(R-R''). \tag{7.16}$$

The dependence of G_2 on temperature stress is similar in many respects to the dependence of G_1 on these quantities (see Fig. 9a). The two moduli, as functions of temperature, have the same asymptotic form: $G_2=3G_1$ for $T\ll T_*$ and $G_2=G_1$ for $T\gg T_*$.

In Fig. 10 we show plots of the function $\tau_2(T)$. The main thing is that τ_2 differs from τ_1 (cf. Fig. 9b): the jump in its magnitude at the transition temperature is greater. The substantial difference between the relaxation times τ_1 and τ_2 in the vicinity of T_t leads in the case under consideration to a phase-shift dispersion that is more complicated than (7.13).

§8. SOUND IN THE UNBOUNDED MEDIUM

Let us proceed to the study of elastic waves in the unbounded medium; there are, as is well known,[10] serious differences between them and waves in rods. Let us begin with the case when a plane acoustic wave propagates along the anisotropy axis n = (0, 0, 1). In the unbounded body the displacement u produced by such a wave depends only on the coordinate z and the time. Therefore, out of the six components of the strain tensor only three—u_{zz}, u_{xz}, and u_{yz}—are nonzero; the first of them corresponds to a longitudinal wave, while the remaining two correspond to a transverse with two independent polarization directions.

Let us first consider the longitudinal wave. From (7.3) we have for it

$$\rho\ddot{u}_{zz}=\partial^2p_{zz}/\partial z^2. \tag{8.1}$$

The diagonal components of Eq. (7.4) contain along with p_{zz} the stresses, p_{xx} and p_{yy}, arising in the transverse directions. The conditions $u_{xx}=u_{yy}=0$ and $\operatorname{Sp}\epsilon_{ik}=0$ allow us to express the sum of the "transverse" stresses in terms of p_{zz} and ϵ_{zz}:

$$p_{xx}+p_{yy}=\frac{2}{3K+4\mu}[(3K-2\mu)p_{zz}+9K\mu n\gamma\varepsilon_{zz}].$$

With the aid of this relation we can express the zz-component of Eq. (7.4) in the form

$$u_{zz}=\frac{3}{3K+4\mu}(p_{zz}+2\mu n\gamma\varepsilon_{zz}).$$

Eliminating u_{zz} from (8.1) and $p_{xx}+p_{yy}$ from (5.18), we arrive at the system of linear homogeneous equations for p_{zz} and ϵ_{zz}:

$$\frac{\partial^2p_{zz}}{\partial t^2}+2\mu n\gamma\frac{\partial^2\varepsilon_{zz}}{\partial t^2}=c_l^2\frac{\partial^2p_{zz}}{\partial z^2},\quad c_l=\left(\frac{3K+4\mu}{3\rho}\right)^{1/2},$$

$$\tau\frac{\partial\varepsilon_{zz}}{\partial t}=-\left[\varkappa_1+\frac{27K\mu n\gamma^2(R'-R'')}{2TR(3K+4\mu)}\right]\varepsilon_{zz}+\frac{9\alpha(R'-R'')}{4TR}\frac{\partial^2\varepsilon_{zz}}{\partial z^2}+\frac{9\gamma(R'-R'')}{TR(3K+4\mu)}p_{zz}, \tag{8.2}$$

where c_l is the velocity of the longitudinal waves without allowance for the orientation effects.

Neglecting the dissipation ($\tau=0$), we obtain from (8.2) the dispersion equation for the plane waves:

$$\omega^2=c_l^2k^2\left[\frac{2TR\varkappa_1}{3(R'-R'')}+\frac{9K\mu n\gamma^2}{(3K+4\mu)}+\frac{3}{2}\alpha k^2\right]\Big/\left[\frac{2TR\varkappa_1}{3(R'-R'')}+3\mu n\gamma^2+\frac{3}{2}\alpha k^2\right]. \tag{8.3}$$

Let us compare this formula with (7.9). The main difference between them consists in the appearance of an additional term in the numerator of (8.3), as a result of which the longitudinal velocity, $c_\parallel(k)$, of the sound in the unbounded medium is always nonzero. Let us denote by

$$k_0=(2\mu n\gamma^2/\alpha)^{1/2} \tag{8.4}$$

the characteristic value of the wave number. For short waves ($k\gg k_0$) it follows from (8.3) that $c_\parallel=c_l$, whereas in the long-wave region ($0<k<k_0$) we obtain

$$c_\parallel=\left(c_l^2-c_t^2\frac{4\mu}{G_1+3\mu}\right)^{1/2},\quad c_t=\left(\frac{\mu}{\rho}\right)^{1/2} \tag{8.5}$$

(c_t is the transverse velocity of sound in an isotropic solid). The minimum value

$$c_\parallel=(c_l^2-{}^4/_3c_t^2)^{1/2}=(K/\rho)^{1/2}$$

is attained at $\varkappa_1=G_1=0$.

Let us now consider the transverse waves. Eliminating u_{xz} from (7.3) and (7.4), we have

$$\frac{\partial^2p_{xz}}{\partial t^2}+2\mu n\gamma\frac{\partial^2\varepsilon_{xz}}{\partial t^2}=c_t^2\frac{\partial^2p_{xz}}{\partial z^2}; \tag{8.6}$$

the same equation is obtained for the yz-component. From (8.6) and (5.20) we find (the dissipation is neglected):

$$\omega^2=c_t^2k^2\frac{4TR\varkappa_3/(R-3R'+4R'')+{}^3/_2\alpha k^2}{4TR\varkappa_3/(R-3R'+4R'')+3\mu n\gamma^2+{}^3/_2\alpha k^2}. \tag{8.7}$$

For a spontaneously oriented polymer ($\sigma=0, T<T_c$) the decrement $\varkappa_3=0$ by virtue of the degeneracy with respect to the directions of the director **n** (cf. §6). As can be seen from (8.7), the wave number k_0, (8.4), then separates the regions of normal and anomalous dispersions:

$$\omega=\begin{cases} c_tk & \text{for } k\gg k_0\\ \left(\dfrac{\alpha}{2\rho n\gamma^2}\right)^{1/2}k^2 & \text{for } k\ll k_0\end{cases}$$

Thus, the transverse sound velocity $c_\perp$ vanishes in the long-wave limit ($c_\perp\sim k$).

A tensile stress removes the degeneracy in the directions of **n**, the decrement $\varkappa_3$ becomes positive, and the formula (8.7) in the region of values of $k\ll k_0$ assumes the form

$$\omega^2=\frac{k^2}{3\rho}\left(\frac{1}{G_3}+\frac{1}{3\mu}\right)^{-1} \tag{8.8}$$

Here we have introduced the notation

$$G_3=4TR\varkappa_3/n\gamma^2(R-3R'+4R'') \tag{8.9}$$

for the third modulus of orientational elasticity.[7] The modulus G_3, as $T\to 0$, tends to the finite limit $\sigma/n\gamma$ and, at high temperatures, goes over into the Mackian-elasticity modulue (4.6).

In conclusion, let us give the results of the calculation of the longitudinal and the two transverse sound velocities for the case when the wave vector is perpendicular to the director:

$$c_\parallel=\left[c_l^2-c_t^2\left(\frac{\mu}{G_1+3\mu}+\frac{3\mu}{G_2+3\mu}\right)\right]^{1/2},$$
$$c_\perp^{(1)}=c_t\left(\frac{G_2}{G_2+3\mu}\right)^{1/2},\quad c_\perp^{(2)}=c_t\left(\frac{G_3}{G_3+3\mu}\right)^{1/2}. \tag{8.10}$$

For $T\gg T_*$, when all the $G_i\approx G_{el}\gg 3\mu$, from (8.10) follow the relations $c_\parallel\approx c_l$ and $c_\perp^{(1)}\approx c_\perp^{(2)}\approx c_t$.

[1] Generally speaking, the effective field should have been written in the form $H_{ik}=\gamma_{iklm}\sigma_{lm}+\lambda_{iklm}\eta_{llm}$ The scalar coefficients in (2.1) are the first terms of the expansions of the corresponding tensor coefficients in powers of η_{ik}—the only tensor that determines the structure of the polymer.

[2] For greater details about the asymptotic form of the function $R(\xi)$, which is related to the error integral, see the Appendix in Ref. 9.

[3] Notice that in this case $Z_0=R(\xi)e^{-3\lambda\eta/4T}$.

[4] As can be seen from Table I, $(T_{cr}-T_*)/T_*=0.153$. Thus, if T_* lies in the region of room temperatures, then the width of the indicated interval is about 50°.

[5] We assume that this coefficient is a scalar (see footnote 1).

[6] Let us recall that the bare Brownian time τ is defined as $(6bT)^{-1}$, where b^{-1} is the friction coefficient, which is proportional to the effective viscosity of the medium.

[7] Notice that the quantity 3μ in (8.8) plays the role of the Young modulus G: for the "incompressible" (transverse) perturbations under consideration we should set the bulk modulus $K=\infty$ in the definition of G, (4.4).

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