Contribution to the theory of relaxation processes in molecular liquids and liquid crystals

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We describe a molecular liquid schematically in the single-molecule approximation as a suspension of rigid axisymmetric particles in an anisotropic viscous fluid. We determine a relaxation equation for the average orientation of polar molecules in the liquid crystal phase; it contains two relaxation times that depend on the anisotropy of the medium and the interaction of a molecule with its neighbors. We determine relaxation equations for the average orientation of non-polar molecules in the isotropic and liquid crystal phases. We consider the behavior of a liquid crystal in a rotating field.

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1. INTRODUCTION

Of all the relaxation processes which are possible in liquids, consisting of prolate polyatomic molecules, the relaxation processes which are connected with the disorientation of molecules and which appear when fields which orient separate molecules act upon the liquid are characterized by the longest relaxation times.[1] The relaxation time in the liquid-crystal phase exceeds by several orders of magnitude the relaxation time of the corresponding processes in the isotropic phase,[2–4] a fact initially attributed to the presence of "swarms" of molecules which when fields or velocity gradients are applied behave as rigid particles in a viscous fluid. The idea of "swarms" is inconsistent, as was already pointed out by Frenkel',[1] but "swarms" are used even up to the present time to explain the behavior of molecular liquids and liquid crystals.[5] In what follows the relaxation phenomena in the isotropic and liquid crystal phases are considered on the basis of the concept that a separate molecule is the kinetic unit.

We assume that each molecule is an axisymmetric rigid particle, the orientation of which in space is determined by a unit vector **e** directed along the symmetry axis of the particle. The components of the vector **e** are connected through the relation

$$e^2=1, \tag{1.1}$$

by virtue of which we need two variables for the description of the orientation of the particle in space. The average orientation of the molecules can be described by an infinite set of quantities—the moments of the distribution function, which are defined as follows

$$\langle e_i\rangle=\int w(\mathbf{e})\,e_i\delta(1-\mathbf{e}^2)\,d\mathbf{e},$$
$$\langle e_ie_j\rangle=\int w(\mathbf{e})\,e_ie_j\delta(1-\mathbf{e}^2)\,d\mathbf{e} \tag{1.2}$$

and so on. The odd-order moments are non-vanishing only for polar molecules in a field.

It is convenient to describe the average orientation also by the anisotropy tensors which are connected with the above mentioned moments of the distribution function and are defined such that when the orientations of the molecules are all equally probable all anisotropy tensors vanish. For instance,

$$S_{js}=\langle e_je_s\rangle-{}^1/_3\delta_{js},$$
$$S_{jsik}=\langle e_je_se_ie_k\rangle-{}^1/_{15}(\delta_{js}\delta_{ik}+\delta_{ji}\delta_{sk}+\delta_{jk}\delta_{si}). \tag{1.3}$$

One normally uses the second-rank anisotropy tensor for the description of the anisotropy of liquid crystals.[6]

In the single-molecule approximation, when the system is considered to be a collection of molecules each of which is in some average field produced by the other molecules, one can, in correspondence with well known results,[7] express the average dipole moment per unit volume in terms of the first and second order moments,

$$P_i=n\mu\langle e_i\rangle+n(\alpha^{\parallel}-\alpha^{\perp})\langle e_ie_j\rangle E_j, \tag{1.4}$$

and express the permittivity tensor for the optical frequency region or for non-polar molecules in terms of the anisotropy tensor,

$$\varepsilon_{ik}=\varepsilon_0\delta_{ik}+4\pi n(\alpha^{\parallel}-\alpha^{\perp})S_{ik}. \tag{1.5}$$

It is convenient to assume that the conversion factor from the internal field to the applied field **E** is included in the constant dipole moment of the molecule μ, which by assumption is directed along the symmetry axis of the molecule, and in the coefficient $\alpha^{\parallel}-\alpha^{\perp}$ which determines the induced dipole moment of the molecule. In Eqs. (1.4) and (1.5), n is the number of molecules per unit volume and ε_0 is the permittivity of the liquid in the isotropic state.

One can write down similar formulae for the magnetic moment and the magnetic permeability. Usually the constant magnetic moment of the molecules of interest to us is equal to zero, and molecular liquids which form liquid crystals are characterized by an anisotropic magnetic susceptibility[7]

$$\chi_{ij}=\chi_0\delta_{ij}+n(m^{\parallel}-m^{\perp})S_{ij}, \tag{1.6}$$

where $m^{\parallel}-m^{\perp}$ is the difference between the values of the magnetic susceptibility of a single molecule.

The potential energy of a molecule in the anisotropic average field of its neighbors can be written in the form of an expansion in terms of invariants that are formed from the vector **e** and the tensors (1.3). In the simplest approximation (see[8,9]) which takes into account also the energy of the interaction of the molecule with the field[10] we write

$$U(\mathrm{e}) = -T[\varkappa e_j h_j + {}^1/_2 \sigma (e_j h_j)^2 + {}^1/_2 \nu e_j e_k S_{jk}], \tag{1.7}$$

where T is the temperature in energy units, $\varkappa = \mu E/T$, $\sigma = (\alpha^{\parallel} - \alpha^{\perp}) E^2/T$, **h** is a unit vector in the direction of the field strength, and ν is a phenomenological constant that depends on the density and the temperature. If we demand that the molecule is oriented along the symmetry axis determined by the tensor S_{jk}, then $\nu > 0$.

The given approximation (1.7) successfully describes the main features in the behavior of liquid crystals, and in particular it describes the isotropic liquid–nematic liquid crystal transition; however, it is insufficient for a description of the details of the thermodynamic behavior,[11] and the potential energy of a molecule must apparently contain also other invariants. Besides it is possible that for a more complete description it will be necessary to forgo first of all the idea of a molecule as an axisymmetric rigid particle.

In the present paper we use the single-molecule approximation to determine relaxation equations for the moments of the distribution function which allows us by virtue of Eqs. (1.4) to (1.6) above to consider the kinetics of the polarization, the optical anisotropy, and the magnetization of molecular crystals in the isotropic and the liquid-crystal phases.

2. EQUILIBRIUM ORIENTATION OF MOLECULES IN A UNIAXIAL LIQUID CRYSTAL IN A FIELD

The values of the parameters $\varkappa$ and σ in Eq. (1.7) are small for all reasonable values of the field, so that we can write the equilibrium distribution function in the form

$$w_e = [1 + \varkappa e_j h_j + {}^1/_2 (\sigma + \varkappa^2)(e_j e_s - \langle e_j e_s \rangle_0) h_j h_s] w_0, \tag{2.1}$$

where w_0 is the normalized distribution function for the orientations of the molecules for the case when the field is zero. Bearing in mind that the anisotropy tensor of a liquid with the symmetry of a uniaxial crystal can be written in the form

$$S_{jk} = S(n_j n_k - {}^1/_3 \delta_{jk}), \tag{2.2}$$

where S is the magnitude of the anisotropy and **n** a unit vector in the direction of the axis of macroscopic symmetry of the substance (in a field **n** coincides with the direction of the field), we determine the normalization constant and write

$$w_0 = \frac{1}{4\pi} \sqrt{\frac{\nu S}{2}} \frac{1}{F(\sqrt{\nu S/2})} \exp\{{}^1/_2 \nu S (e_j n_j)^2\}. \tag{2.3}$$

The function $F(z) = \int_0^z e^{x^2} dx$ in Eq. (2.3) is tabulated in[12].

The odd moments of the distribution function (2.3) vanish and the first even moments have the form

$$\langle e_i e_k \rangle_0 = {}^1/_2 (1 - M_2) \delta_{ik} + {}^1/_2 (3M_2 - 1) n_i n_k, \tag{2.4}$$

$$\begin{aligned} \langle e_i e_k e_l e_m \rangle_0 = {}& {}^1/_8 (1 - 2M_2 + M_4)(\delta_{ik}\delta_{lm} + \delta_{il}\delta_{km} \\ & + \delta_{im}\delta_{kl}) + {}^1/_8 (-1 + 6M_2 - 5M_4)(n_i n_k \delta_{lm} \\ & + n_l n_m \delta_{ik} + n_i n_l \delta_{km} + n_k n_m \delta_{il} + n_i n_m \delta_{kl} \\ & + n_k n_l \delta_{im}) + {}^1/_8 (3 - 30M_2 + 35M_4) n_i n_k n_l n_m, \end{aligned} \tag{2.5}$$

where M_2 and M_4 are functions of νS and defined by the relations

$$M_2(x) = \frac{1}{\sqrt{2x}} \frac{e^{x/2}}{F(\sqrt{x/2})} - \frac{1}{x}, \quad M_4(x) = \frac{1}{x} + \left(1 - \frac{3}{x}\right) M_2(x). \tag{2.6}$$

For small and large values of the argument, the functions (2.6) have the form

$$\begin{aligned} M_2 &= \frac{1}{3} + \frac{2}{45} x + \dots, & M_2 &= 1 - \frac{2}{x} + \dots, \\ M_4 &= \frac{1}{5} + \frac{4}{105} x + \dots, & M_4 &= 1 - \frac{4}{x} + \dots. \end{aligned} \tag{2.7}$$

We now find the moments of the distribution function (2.1), which determine the average orientation of the molecules in the field

$$\langle e_i \rangle_e = \varkappa \langle e_i e_j \rangle_0 h_j, \tag{2.8}$$

$$\langle e_i e_k \rangle_e = \langle e_i e_k \rangle_0 + {}^1/_2 (\sigma + \varkappa^2)(\langle e_i e_k e_j e_s \rangle_0 - \langle e_i e_k \rangle_0 \langle e_j e_s \rangle_0) h_j h_s, \tag{2.9}$$

$$\langle e_i e_k e_l \rangle_e = \varkappa \langle e_i e_k e_l e_j \rangle_0 h_j, \tag{2.10}$$

$$\begin{aligned} \langle e_i e_k e_l e_m \rangle_e = {}& \langle e_i e_k e_l e_m \rangle_0 + {}^1/_2 (\sigma + \varkappa^2)(\langle e_i e_k e_l e_m e_s e_j \rangle_0 \\ & - \langle e_i e_k e_l e_m \rangle_0 \langle e_j e_s \rangle_0) h_j h_s. \end{aligned} \tag{2.11}$$

The equilibrium values of the polarization, the optical anisotropy, and the magnetization of a molecular liquid are determined by the moments (2.8) and (2.9), which we now rewrite using Eqs. (2.2), (2.3), and (2.5). Using the fact that **n** coincides with **h** when there is a field, we have

$$\langle e_i \rangle_e = \varkappa M_2(\nu S) h_i, \tag{2.12}$$

$$\langle e_i e_k \rangle_e = S h_i h_k + {}^1/_3 (1 - S) \delta_{ik}, \tag{2.13}$$

where M_2 is defined by Eq. (2.6) while S satisfies an equation which follows from Eq. (2.9),

$$3M_2 - 1 + {}^3/_2 (\sigma + \varkappa^2)(M_4 - M_2^2) = 2S. \tag{2.14}$$

When the field vanishes we get from Eq. (2.14) an equation which has been derived before.[8,9]

For large values of ν when Eqs. (2.7) are valid it follows from Eq. (2.14) that

$$S = 1 - 3/\nu. \tag{2.15}$$

In this approximation the magnitude of the anisotropy is independent of the field.

3. DYNAMICS OF A PARTICLE IN AN ANISOTROPIC LIQUID

On each molecule of the liquid there acts a torque which is determined by the potential energy (1.7)

$$\begin{aligned} L_{js} = T[& (\varkappa + \sigma e_l h_l)(e_s h_j - e_j h_s) \\ & + \nu (S_{ji} e_s - S_{si} e_j) e_i]. \end{aligned} \tag{3.1}$$

Under the action of the torque the molecule, as a rigid axisymmetric particle, moves in some anisotropic medium which is formed by the other molecules and which has an equation of motion that contains the moments of the distribution function[13]1) in the approximation linear in the velocity gradients, i.e., the second-order moments. Therefore, when considering the simplest approximation, we assume that the anisotropic medium is additionally characterized by an internal variable, the symmetric tensor S_{jl}. The equations of motion of such a medium which were written down in general form by Hand[14] contain several phenomenological constants which have the meaning of viscosity coefficients.

Under the action of torques a particle in an anisotropic viscous liquid performs a regular rotation with a velocity that can be written in the form

$$\Omega_i = M_{ij}L_j, \quad \text{or} \quad \Omega_{kl} = {}^1/_2 e_{kli} M_{ij} e_{jms} L_{ms}. \tag{3.2}$$

The symmetric rotational mobility tensor M_{ij} is a function of the vector **e** and of the symmetric tensor S_{jl}. Taking into account the terms of first order in the anisotropy tensor S_{jl} we write

$$M_{ij} = \frac{D}{T}\left[\delta_{ij} + \chi_0 e_i e_j + \chi_1 S_{ij} + \chi_2 S_{ks} e_k e_s \delta_{ij} + \chi_3 (S_{js} e_s e_i + S_{is} e_s e_j) + \chi_4 S_{ks} e_k e_s e_i e_j\right]. \tag{3.3}$$

In Eq. (3.3), D and χ_α are phenomenological constants such that for an isotropic liquid the coefficient D is the rotational diffusion coefficient of the molecules which, for instance, for an ellipsoid of rotation has the form[13]

$$D = \frac{T}{6\eta\Omega}\frac{1}{\delta} \tag{3.4}$$

where η is the viscosity coefficient of an isotropic liquid, Ω the volume of a molecule, and δ a form factor ($\delta = 1$ for a spherical particle, $\delta \approx 3$ for an ellipsoid semi-axis ratio $a/b \approx 4$, which is typical for molecules in a liquid crystal). The dimensionless coefficients χ_α depend on the shape of the particle and on the "viscosity coefficients" of the medium.

We now find from (3.2) and (3.3) the rotational speed of a particle in an anisotropic liquid under the action of the torque (3.1)

$$\Omega_{lm} = \frac{D}{T}\left[L_{lm} + \chi_1 (L_{mj} S_{jl} - L_{lj} S_{jm}) + \chi_2 S_{ji} e_j e_i L_{lm} + \chi_3 (L_{mi} S_{jl} - L_{li} S_{jm}) e_i e_j\right]. \tag{3.5}$$

The condition that the work done by the torques must be positive imposes some limitations on the values of the phenomenological constants. In particular,

$$D > 0, \quad -3/2S < \chi_1 < 3/S. \tag{3.6}$$

Positive values of χ_1 correspond to a braking of the rotation around an axis perpendicular to the axis of symmetry of the liquid crystal. The coefficient χ_2 does not affect the anisotropy of the mobility and we shall therefore omit it in what follows.

4. ROTATIONAL DIFFUSION EQUATION AND MOMENTS OF THE DISTRIBUTION FUNCTION

A particle in a liquid performs a Brownian motion and the rotational velocity of a particle can be written in the form

$$\tilde{\Omega}_k = \Omega_k(\mathrm{e}) + \psi_k(\mathrm{e}, t), \tag{4.1}$$

where $\Omega_k = -\frac{1}{2} e_{kjs} \Omega_{js}$ is the regular component of the velocity connected with the action of constant torques and determined, for instance, by Eq. (3.5) and ψ_k is the random component of the velocity which is by assumption a Gaussian random function, the statistical properties of which are determined by the relations

$$\overline{\psi_k(\mathrm{e}, t)} = 0, \quad \overline{\psi_k(\mathrm{e}, t)\psi_m(\mathrm{e}', t')} = 2D_{km}(\mathrm{e}, \mathrm{e}')\delta(t - t'). \tag{4.2}$$

The averaging in Eqs. (4.2) is over an ensemble of realizations of the random functions.

From Eq. (4.1) there follows an equation for the rate of change of the orientation vector which, when we add the reaction forces with an undetermined multiplier L, has the form

$$\frac{de_j}{dt} = e_{jks}\Omega_k e_s - {}^1/_2 L e_j + \Phi_j, \tag{4.3}$$

where the random component Φ_j has three independent components and only after the determination of the undetermined multiplier takes the form $\Phi_j = e_{jks}\psi_k e_s$.

We introduce next the distribution function

$$w(\mathrm{e}, t) = \overline{\delta(\mathrm{e} - \mathrm{e}(t))\delta(1 - \mathrm{e}^2(t))} \tag{4.4}$$

and, following the method expounded in Klyatskin's monograph,[15] we find the rotational diffusion equation which after evaluating the undetermined multiplier takes the form

$$\frac{\partial w}{\partial t} + e_s \frac{\partial(\Omega_{js} w)}{\partial e_j} = e_{jks} e_{mlp} \frac{\partial}{\partial e_j} D_{kl} e_p e_s \frac{\partial w}{\partial e_m}. \tag{4.5}$$

When completing the operations in (4.5) we must assume the components of the vector **e** to be independent, since condition (1.1) is satisfied automatically.2)

In the case considered the antisymmetric angular velocity tensor is given by Eq. (3.5). The symmetric rotational diffusion tensor D_{kl} can, as can be checked easily, be written in the form

$$D_{ij} = TM_{ij}, \tag{4.6}$$

where M_{ij} is given by Eq. (3.3).

We have earlier considered[13,16] particular cases of Eq. (4.5) for an isotropic liquid.

The equations for the moments of the distribution function are determined by multiplying Eq. (4.5) by combinations of orientation vectors and integrating over all orientations. We then use the averaging rule

$$\int B \frac{\partial F}{\partial e_j}\delta(1 - \mathrm{e}^2)\,d\mathrm{e} = 2\int e_j BF\delta(1 - \mathrm{e}^2)\,d\mathrm{e} - \int \frac{\partial B}{\partial e_j} F\delta(1 - \mathrm{e}^2)\,d\mathrm{e}. \tag{4.7}$$

The equations for the first moments have the form

$$\frac{d\langle e_i\rangle}{dt} - \langle\Omega_{is} e_s\rangle = e_{iks} e_{mlp}\left(\delta_{sm}\langle e_p D_{kl}\rangle + \left\langle e_p e_s \frac{\partial D_{kl}}{\partial e_m}\right\rangle\right), \tag{4.8}$$

$$\frac{d\langle e_i e_j\rangle}{dt} - \langle\Omega_{is} e_s e_j\rangle - \langle\Omega_{js} e_s e_i\rangle = e_{jks} e_{mlp}\left(\delta_{im}\langle e_p e_s D_{kl}\rangle\right.$$

$$+\delta_{sm}\langle e_i e_p D_{kl}\rangle + \left\langle e_i e_p e_s \frac{\partial D_{kl}}{\partial e_m}\right\rangle\Big) + e_{iks}e_{mlp}\Big(\delta_{jm}\langle e_p e_s D_{kl}\rangle + \delta_{sm}\langle e_j e_p D_{kl}\rangle + \left\langle e_j e_p e_s \frac{\partial D_{kl}}{\partial e_m}\right\rangle\Big). \tag{4.9}$$

By virtue of Eqs. (1.4) to (1.6), Eqs. (4.8) and (4.9) determine the kinetics of the polarization, the magnetization, and the optical anisotropy of a molecular liquid.

Equations (4.8) and (4.9) contain not only the first- and second-order moments, but also higher-order moments, and the set of equations is, generally speaking, not closed. When the deviation from equilibrium of the system is small we can use the method[17] proposed by Leontovich to determine the higher-order moments in terms of the first- and second-order moments; the gist of this method is that one assumes for a non-equilibrium state the existence of some fictitious field such that at a given time the distribution function in the actual field is the same as the equilibrium distribution function in the fictitious field. The non-equilibrium moments of the distribution function are then determined by Eqs. (2.8) to (2.11), in which the actual values of the field are replaced by the fictitious ones. This approach was recently applied to a study of the kinetics of the orientation of dipole particles in a field[18] and is used in the following sections.

5. KINETICS OF THE ORIENTATION OF POLAR MOLECULES IN THE LIQUID CRYSTAL PHASE

We consider the uniform liquid crystal phase consisting of molecules with a constant dipole moment μ which is directed along the symmetry axis of the molecule. We assume that the uniformity of the sample is maintained, for instance, by a sufficiently strong constant magnetic field. We determine now the relaxation equation for the average dipole moment of a molecule, assuming that a variable electric field of strength **E** acts upon the system.

For the case considered there follows from Eqs. (4.8), (4.6), and (3.5) the equation

$$\frac{1}{D}\frac{d\langle e_i\rangle}{dt} = -2\langle e_i\rangle + (\nu+\chi_1)S_{ij}\langle e_j\rangle - \nu S_{jl}\langle e_j e_l e_i\rangle + \nu\chi_1(S_{jk}S_{jl}\langle e_l e_k e_i\rangle - S_{ij}S_{jl}\langle e_l\rangle) + \frac{\mu}{T}\left[\frac{2}{3}\delta_{ij} - S_{ij} + \chi_1\left(2S_{il}S_{lj} - \frac{1}{3}S_{ij} - S_{lk}S_{lk}\delta_{ij}\right)\right]E_j. \tag{5.1}$$

Apart from the required first-order moments, Eq. (5.1) also contains second- and third-order moments which we must express in terms of the first-order moments.

Furthermore, we shall consider a uniaxial liquid crystal when we can write the anisotropy tensor in the form

$$S_{ij} = S(n_i n_j - {}^1\!/_3\delta_{ij}), \tag{5.2}$$

where **n** is a unit vector determining the orientation of the symmetry axis of the crystal. As we take only effects into account of first order in the variable field **E** only the direction of the unit vector **n** can change in the field.

Using the method mentioned in the preceding section we assume that there exists some fictitious addition to the field $\delta\mathbf{E}$ with which we can connect the deviation of the distribution function and its moments from their equilibrium values. The first-order moment in which we are interested has the equilibrium value

$$\langle e_i\rangle_e = \frac{\mu}{T}\left[Sn_i^0 n_j^0 + \frac{1}{3}(1-S)\delta_{ij}\right]E_j, \tag{5.3}$$

and the deviation from the equilibrium value is

$$\xi_i = \langle e_i\rangle - \langle e_i\rangle_e = \frac{\mu}{T}\left[Sn_i^0 n_j^0 + \frac{1}{3}(1-S)\delta_{ij}\right]\delta E_j, \tag{5.4}$$

where n_i^0 is the unit vector determining the initial (field-free) orientation of the symmetry axis of the liquid crystal.

Considering Eq. (5.1) up to terms of first order in the field strength we replace the anisotropy tensor by its zeroth order value

$$S_{ij} = S\left(n_i^0 n_j^0 - \frac{1}{3}\delta_{ij}\right).$$

Further, the third-order moments can be expressed by means of Eqs. (2.9), (2.10), and (5.4) in terms of the quantities ξ_i. After some simple calculations we determined the relaxation equation

$$\frac{d\xi_i}{dt} = -\frac{1}{\tau^\perp}(\xi_i - n_i^0 n_j^0 \xi_j) - \frac{1}{\tau^\parallel} n_i^0 n_j^0 \xi_j - \frac{\mu}{T}\left[Sn_i^0 n_j^0 + \frac{1}{3}(1-S)\delta_{ij}\right]\frac{dE_j}{dt}. \tag{5.5}$$

There occur two relaxation times in Eq. (5.5); they are defined by the relations

$$\frac{1}{\tau^\perp} = D\left[3 + \frac{4S-1}{3(1-S)}(3 - S\chi_1)\right], \tag{5.6}$$

$$\frac{1}{\tau^\parallel} = D\frac{2(1-S)}{3(1+2S)}(3 - S\chi_1). \tag{5.7}$$

The values of the relaxation times as functions of S are given in Fig. 1 for the value $3 - S\chi_1 = 1$. When the quantity $3 - S\chi_1$ decreases to zero $\tau^\perp$ increases to $1/3D$, remaining smaller than the value $1/2D$ of the relaxation time in an isotropic medium, while $\tau^\parallel$ increases without bounds for all values of S. As $S \to 1$ it follows from Eqs. (5.6) and (5.7), using (2.15), that $\tau^\perp \to 0$ and $\tau^\parallel \to \infty$ regardless of the value of χ_1.

We consider the cases where an oscillating field $E \propto e^{-i\omega t}$ is applied parallel or at right angles to the symmetry axis of the liquid crystal. One can then easily determine ξ_i from Eq. (5.5) and after that, using Eqs. (1.4), (2.8) and the general definitions in[10], write down expressions for the permittivity in the two cases mentioned

$$\varepsilon^\parallel = \varepsilon_0 + \frac{8\pi}{3}n(\alpha^\parallel - \alpha^\perp)S + \frac{4\pi}{3}n\frac{\mu^2}{T}(1+2S)\left[1 + \frac{i\omega\tau^\parallel - (\omega\tau^\parallel)^2}{1+(\omega\tau^\parallel)^2}\right], \tag{5.8}$$

$$\varepsilon^\perp = \varepsilon_0 - \frac{4\pi}{3}n(\alpha^\parallel - \alpha^\perp)S + \frac{4\pi}{3}n\frac{\mu^2}{T}(1-S)\left[1 + \frac{i\omega\tau^\perp - (\omega\tau^\perp)^2}{1+(\omega\tau^\perp)^2}\right]. \tag{5.9}$$

Since the relaxation times $\tau^\parallel$ and $\tau^\perp$ are different, the frequency dependences of $\varepsilon^\parallel$ and $\varepsilon^\perp$ are different, and

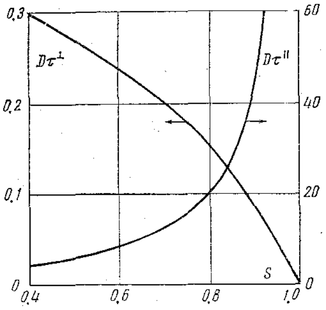

FIG. 1. The transverse and longitudinal relaxation times and functions of the order parameter of the liquid crystal phase for $3-S\chi_1=1$.

this has been observed experimentally for the liquid-crystal phase.[2,3] The results of the paper in which the case was studied where the dipole moment was directed along the axis of the molecule[2] can be compared with Eqs. (5.8) and (5.9) obtained here.

In the cited investigation[2] it was observed that the value of $\tau^{\parallel}$ reaches 10^{-8} to 10^{-6} s, whereas the value of $\tau^{\perp}$ could not be measured by the methods used, i.e., it was less than 10^{-7} s. We find from Eqs. (5.6) and (5.7) that this difference is possible, if the effect of the parameter χ_1 is considerable, i.e., if its value is close to $3/S$. For a typical value $S\approx 0.6$ the value of χ_1 approaches 5. The values of Eq. (3.3) then determine an appreciable anisotropy of the mobility which cannot be neglected.

6. KINETICS OF THE ORIENTATION OF NON-POLAR MOLECULES IN THE ISOTROPIC PHASE

We now consider the isotropic phase of a molecular liquid in a field, assuming that the molecules do not have constant dipole moments. The normalized equilibrium distribution function is in this case given by a formula similar to Eq. (2.3)

$$w_e=\frac{1}{4\pi}\sqrt{\frac{\sigma}{2}}\frac{1}{F(\sqrt{\sigma/2})}\exp\{{}^1/_2\sigma e_jh_j\}, \qquad (6.1)$$

where **h** is a unit vector indicating the direction of the electric field strength. The equilibrium moments of the distribution function (6.1) are given by Eqs. (2.4) and (2.5) in which M_2 and M_4 are now functions of σ and given by Eqs. (2.6) and (2.7).

The value of the parameter σ is small for molecular liquids and we can therefore restrict ourselves in those cases to the first terms in the expansion of the function (6.1); bearing, however, in mind possible applications to dilute macromolecular mixtures and suspensions, we determine the relaxation equation without assuming σ to be small.

In the case considered the first-order moments vanish identically. It follows from (4.9), (4.6), and (3.5) that the equation for the required second-order moments has the form

$$\frac{1}{D}\frac{d\langle e_ie_k\rangle}{dt}=-6\left(\langle e_ie_k\rangle-\frac{1}{3}\delta_{ik}\right)$$
$$+\sigma(\langle e_ke_j\rangle h_jh_i+\langle e_ie_j\rangle h_jh_k-2\langle e_ie_ke_je_s\rangle h_jh_s). \qquad (6.2)$$

The fourth-order moment occurs in Eq. (6.2). To express it in terms of the second-order moments we use the method mentioned in Sec. 4. We assume that we can find for each non-equilibrium value of the distribution function some fictitious field $\mathbf{E}+\delta\mathbf{E}$ such that the distribution function at that time in the actual field is the same as the equilibrium distribution function in the fictitious field. The non-equilibrium moments of the distribution function are then given by Eqs. (2.4) and (2.5) in which the actual value of the field is replaced by the fictitious one.

Assuming that the deviation from equilibrium is small and thus that $\delta E/E\ll 1$, we can express the values of the fictitious field in terms of the second-order moment. Using Eq. (2.4) and expanding the quantity M_2 in a series we find up to second-order terms the equation

$$\xi_{ik}=\sigma\frac{\partial M_2}{\partial\sigma}(3h_ih_k-\delta_{ik})\frac{E_j}{E^2}\delta E_j+\frac{1}{2}(3M_2-1)\frac{1}{E^2}$$
$$(E_i\delta E_k+E_k\delta E_i-2h_ih_kE_j\delta E_j). \qquad (6.3)$$

We have introduced here the notation $\xi_{ik}=\langle e_ie_k\rangle-\langle e_ie_k\rangle_e$ for the deviation of the second-order moment from its equilibrium value.

We can now use Eq. (2.5) to express the fourth-order moments in Eq. (6.2) in terms of the second-order moment, after which we determine the relaxation equation for the second-order moments

$$\frac{d\xi_{ik}}{dt}=-D\nu_1\xi_{ik}-D\nu_2(h_ih_j\xi_{jk}+h_kh_j\xi_{ji}-2h_ih_kh_jh_s\xi_{js})$$
$$-\frac{1}{2}D\nu_3(3h_ih_k-\delta_{ik})h_jh_s\xi_{js}-\left[\sigma\frac{\partial M_2}{\partial\sigma}(3h_ih_k-\delta_{ik})\right.$$
$$\left.-(3M_2-1)h_ih_k\right]\frac{E_j}{E^2}\frac{dE_j}{dt}-\frac{1}{2}(3M_2-1)\frac{1}{E^2}\left(E_i\frac{dE_k}{dt}+E_k\frac{dE_i}{dt}\right). \qquad (6.4)$$

The three constants in Eq. (6.4)

$$\nu_1=\sigma\frac{1-M_4}{3M_2-1},\quad \nu_2=\sigma\frac{5M_4-3M_2}{3M_2-1},\quad \nu_3=4\frac{M_2-M_4}{M_4-M_2^2}-\sigma\frac{1-M_4}{3M_2-1} \qquad (6.5)$$

determine three independent relaxation times

$$\tau_1^{-1}=D\nu_1,\quad \tau_2^{-1}=D(\nu_1+\nu_3),\quad \tau_3^{-1}=D(\nu_1+\nu_2). \qquad (6.6)$$

Substituting the values of M_2 and M_4 for $\sigma\ll 1$ into (6.5) we get

$$\nu_1\approx 6-{}^3/_7\sigma,\quad \nu_2\approx{}^3/_7\sigma,\quad \nu_3\approx{}^2/_7\sigma. \qquad (6.7)$$

For large σ the main terms in the expansion of the ν_α in terms of $1/\sigma$ have the form

$$\nu_1\approx 2+\frac{6}{\sigma},\quad \nu_2\approx\sigma+3,\quad \nu_3\approx\sigma-2. \qquad (6.8)$$

The first terms in the expansions for the relaxation times (6.6) thus have the form

$$\tau_1\approx\frac{1}{6D}\left(1+\frac{1}{14}\sigma\right),\quad \tau_2\approx\frac{1}{6D}\left(1+\frac{1}{42}\sigma\right),\quad \tau_3\approx\frac{1}{6D}+O(\sigma^2), \qquad (6.9)$$

$$\tau_1\approx\frac{1}{2D}\left(1-\frac{3}{\sigma}\right),\quad \tau_2\approx\frac{1}{D\sigma},\quad \tau_3\approx\frac{1}{D\sigma}. \qquad (6.10)$$

The values of the relaxation times for arbitrary values of σ are shown in Fig. 2.

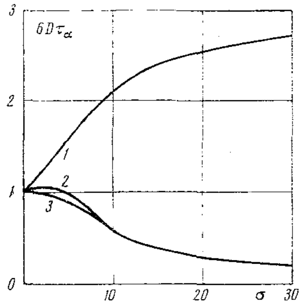

FIG. 2. Relaxation times as functions of the field strength. The numbers at the curves denote the numbers of the relaxation times according to Eqs. (6.6).

By virtue of Eq. (1.5), Eq. (6.4) describes effects which are connected with the change in the anisotropy of the permittivity of molecular liquids in variables fields, for instance, the relaxation of the Kerr effect; when this was studied relaxation times $\tau = 1/6D$ having values 10^{-11} to 10^{-10} s were determined.[19]

7. OPTICAL ANISOTROPY OF A LIQUID CRYSTAL IN A ROTATING FIELD

In the case where the constant magnetic moment of the molecule is equal to zero the average orientation of the molecules is described by the even moments of the distribution function and first of all by the second-order moment which in the equilibrium state has the form

$$\langle e_i e_j \rangle_e = S h_i h_j + {}^1/_3 (1-S)\delta_{ij}, \qquad (7.1)$$

where h_i is a unit vector determining the direction of the field strength. The value of S is here a function of σ and given by Eq. (2.14).

When considering this case we can obtain by the same method as in the preceding sections the relaxation equation for the quantities $\xi_{ij} = \langle e_i e_j \rangle - \langle e_i e_j \rangle_e$ which has, clearly, the form

$$\begin{aligned}\frac{d\xi_{ij}}{dt} &= -D\mu_1\xi_{ij} - D\mu_2(h_i h_s \xi_{sj} + h_j h_s \xi_{si} - 2h_i h_j h_l h_s \xi_{ls}) \\ &- \frac{1}{2}D\mu_3(3h_i h_j - \delta_{ij})h_l h_s \xi_{ls} - \frac{2}{3}\sigma\frac{\partial S}{\partial\sigma}(3h_i h_j - \delta_{ij})\frac{H_k}{H^2}\frac{dH_k}{dt} \\ &- \frac{S}{H^2}\left(H_i\frac{dH_j}{dt} + H_j\frac{dH_i}{dt} - 2h_i h_j H_k\frac{dH_k}{dt}\right). \qquad (7.2)\end{aligned}$$

The quantities μ_α are some functions of σ, S, and χ_1 and, as $S \to 0$ go over into the functions (6.5)

$$\lim_{S\to 0}\mu_\alpha(\sigma, S, \chi_1) = \nu_\alpha(\sigma). \qquad (7.3)$$

We do not give here the explicit form of the functions μ_α.

Equation (7.2) describes the kinetics of the average orientation of non-polar molecules in the liquid crystal phase and by virtue of Eq. (1.5) it determines the change in the optical anisotropy of the liquid crystal in variable fields.

We now consider a liquid crystal in a rotating magnetic field

$$h_1 = \cos\omega t, \quad h_2 = \sin\omega t, \quad h_3 = 0. \qquad (7.4)$$

By virtue of Eq. (1.5) we can express[16] the angle between the optical axis of the suspension and the 1-axis, which is denoted by χ, in terms of the moments of the distribution function

$$\operatorname{tg} 2\chi = \frac{2\langle e_1 e_2\rangle}{\langle e_1^2\rangle - \langle e_2^2\rangle}. \qquad (7.5)$$

One may expect that in the rotating field (7.4) the optical axis of the suspension rotates with the same velocity, but with a phase lag of an angle α, the expression for which can be found from the relaxation Eq. (7.2). In accordance with our assumptions we write the unknown moments in the form

$$2\langle e_1 e_2\rangle = A\sin 2(\omega t - \alpha), \quad \langle e_1^2\rangle - \langle e_2^2\rangle = A\cos 2(\omega t - \alpha). \qquad (7.6)$$

The corresponding equilibrium values of the second-order moments are simply determined through Eqs. (7.1). For the moments considered we have

$$2\langle e_1 e_2\rangle_e = S\sin 2\omega t, \quad \langle e_1^2\rangle_e - \langle e_2^2\rangle_e = S\cos 2\omega t. \qquad (7.7)$$

We now use Eq. (7.2), bear in mind (7.6) and (7.7), and find without any further approximations after some simple calculations that

$$\operatorname{tg} 2\alpha = 2\tau\omega, \qquad (7.8)$$

where the relaxation time τ is given by the relation

$$\frac{1}{\tau} = D(\mu_1 + \mu_2). \qquad (7.9)$$

The quantities μ_1 and μ_2 can be expanded in a power series in σ. Up to first-order terms we write

$$\frac{1}{\tau} = 6D[\alpha(S_0, \chi_1) + \beta(S_0, \chi_1)\sigma], \qquad (7.10)$$

where S_0 is the value of the order parameter for zero field.

By virtue of Eq. (7.3) it follows from Eq. (7.9) that in the isotropic phase τ is the same as the relaxation time τ_3 given by Eq. (6.6).

For measurements[20] performed for the liquid crystal phase under conditions where the constant angular velocity of the rotating field ω is less than some critical value while the magnetic field strength H is sufficiently large that the macroscopic uniformity of the orientation in the whole of the volume is guaranteed we find the relation

$$\sin 2\alpha = \text{const}\,\frac{\omega}{H^2}, \qquad (7.11)$$

which for small α is the same as Eq. (7.8), provided $\tau \propto 1/H^2$. For this it is necessary to assume that the kinetic element is a separate molecule in order that in Eq. (7.10) the last term dominates the first one; β does not need to be small here as the measured relaxation times are appreciably larger than the relaxation time $1/6D$ in the isotropic liquid.

8. CONCLUSION

Taking into account the anisotropy of the medium and the interaction of the molecules with their neighbors leads thus to an explanation of the large values of the

relaxation times in the liquid crystal phase. Each of these facts is necessary although the form in which they are taken into account for calculations can be made more precise. One may hope that in the framework of the concepts given here the kinetic phenomena in liquid crystals can be connected with the sizes and shape of molecules in as far as this can allow the single molecule approximation used here.

1)The values of the stress tensor of a suspension of ellipsoids given in our paper[13] are erroneously understated by the amount $2\mu\varphi\gamma_{ik}$ which must be added to the appropriate expressions. This reduces to the fact that the value of ω in the definition (4.9) (see[13]) must be increased by unity. The remaining expressions then remain valid. The numerical values of the quantities ω and V in Figs. 1 and 3 must be increased by unity. In Eqs. (7.5), in the equation that follows, and in (9.3) one should read 2.5 instead of 1.5.

2)In a similar manner we can establish the form of the rotational diffusion equation for a particle of arbitrary shape, the oreintation of which is determined by two mutually perpendicular unit vectors **e** and **c**

$$\frac{\partial w}{\partial t}+e_s\frac{\partial(\Omega_{js}w)}{\partial e_j}+c_s\frac{\partial(\Omega_{js}w)}{\partial c_j}=e_{jks}e_{lin}\left\{\frac{\partial}{\partial e_j}\left[D_{ki}\left(e_se_n\frac{\partial w}{\partial e_l}+e_sc_n\frac{\partial w}{\partial c_l}\right)\right]\right.$$
$$\left.+\frac{\partial}{\partial c_j}\left[D_{ki}\left(c_sc_n\frac{\partial w}{\partial c_l}+c_se_n\frac{\partial w}{\partial e_l}\right)\right]\right\}.$$

The antisymmetric angular velocity tensor Ω_{js} and the symmetric diffusion tensor D_{ki} are here functions of the vectors **e** and **c** and of the tensor S_{jk}.

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