

A molecular-dynamic simulation of nematic and smectic liquid crystals yields information about the characteristics of rotational and translational motion of molecules in these mesophases.

An important characteristic of the liquid-crystal state of a substance is the high mobility of its molecules with a retention of their far-range orientational ordering. However, very little is known about the dynamics of liquid crystals on the molecular level and details of the kinetic phenomena in them are still not understood [1]. Experimental values of the self-diffusion coefficients obtained by various methods [2,3] do not agree well. Values of $D_{||}$ at 398°K obtained for one of the most thoroughly studied nematics, p-azoxyanisole, vary from $2.1 \cdot 10^{-5}$ [4] to $4.1 \cdot 10^{-6}$ cm²/sec [5]. Recent theoretical estimates of the self-diffusion coefficients are based on rough approximations and require the aid of a few experimental data [6,7].

At this time one of the most promising approaches in the nonequilibrium theory of dense systems is the method of time correlation function. With these functions known, it is possible not only to determine the transport coefficients according to the theory of linear response [8] but also to gather exhaustive data on the character of molecular motion in the system. Calculation of time correlation functions is fraught with difficulties, but these can be overcome by using the method of molecular dynamics.

Molecular models of liquid crystals in this study comprised arrays of ellipsoids of revolution interacting on the basis of pair potentials, the latter accounting for anisotropic repulsion and dispersive attraction forces. For simulation of nematic crystals we use the anisotropic (12-6) potential [9]

$$\Phi(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = 4 \varepsilon_0 \varepsilon \{ (\sigma_0 \sigma / r)^{12} - (\sigma_0 \sigma / r)^6 \}. \quad (1)$$

In calculations we include only the repulsion part of potential (1)

$$\Phi_{\text{rep}}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = \begin{cases} \Phi(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) + \varepsilon_0 \varepsilon(\mathbf{u}_1, \mathbf{u}_2) & \text{for } r \leq 2^{1/6} \sigma(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}), \\ 0 & \text{for } r > 2^{1/6} \sigma(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}). \end{cases} \quad (2)$$

It has been established that the main qualitative structural and dynamic characteristics of nematic systems are determined by anisotropic repulsion forces [10]. We note that using the potential as in expression (2) reduces to a fraction the necessary computer time.

For the study of smectic crystals we use a new model, "molecule in a molecule,"

$$\Phi'(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = 4 \varepsilon_1 \varepsilon_0 \{ (\sigma_1 \sigma_0 / r)^{12} - (\sigma_2 \sigma_0 / r)^6 \}, \quad (3)$$

where ε_1 and σ_1, σ_2 correspond to different values of γ_1 and γ_2 . Here the first term represents the relatively "soft" repulsion between the outer chains and "harder" repulsion between the inner parts of molecules. The second term represents the dispersive attraction between the inner parts of molecules. According to structural data on molecules of typical smectic crystals, we select the anisotropy parameters $\gamma_1 = 3.0$ and $\gamma_2 = 2.5$.

All calculations were made in referred quantities. As reference units served the parameters of pair potentials σ_0, ε_0 and mass m of a molecule. The dimensional quantities and the corresponding referred quantities were, accordingly, in the respective relations

$$r = r^* \sigma_0; \quad \rho = \rho^* m \sigma_0^{-3}; \quad T = T^* (\varepsilon_0 / k_B); \\ t = t^* (\varepsilon_0 / m)^{-1/2} \sigma_0; \quad D = D^* \sigma_0 (\varepsilon_0 / m)^{1/2}.$$

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TABLE 1. Dynamic Characteristics of Rotational Motion of Particles with Various Asphericities but the Same Packing Factor, on the Basis of Potential (2)

η	γ	r^*	S^{OR}	D_R^*	τ_ω^*	τ_1^*	τ_2^*	τ_1/τ_2
0,530	3,5	0,75	0,81	0,007	0,006	—	—	—
	3,0	0,77	0,43	0,022	0,014	27	8,9	3,0
	2,5	0,76	0,38	0,036	0,017	16	5,3	3,0
0,550	3,0	0,65	0,55	0,010	0,008	59	19	3,1
	3,0	0,76	0,52	0,015	0,010	48	16	3,0
	2,5	0,78	0,48	0,030	0,014	19	5,9	3,2
	2,0	0,79	0,11	0,117	0,037	5,0	1,7	2,9

The method of machine "experiments" was as described earlier [10,11]. The basic specimen on which periodic boundary conditions were imposed was one containing 168 particles. The initial coordinates of all particles corresponded completely to an ordered configuration. The functions of dynamic variables were averaged over 1000 time intervals, with $\Delta t^* = 0.005$ after the equilibrium state had been reached. Reaching of the equilibrium state in the system was established on the basis of the trend of the order parameters S^{tr} and S^{OR} as functions of time (these parameters characterizing, respectively, the degree of translational ordering along the axis normal to the smectic planes [12] and the degree of orientational ordering of the system [1]), inasmuch as the dynamic characteristics had stabilized much sooner.

In the case where the thermodynamic parameters of the system (ρ and T) corresponded to the smectic phase, after the relaxation period there followed stable fluctuations of S^{tr} and S^{OR} about some mean values other than zero. In the case of the nematic phase parameter S^{tr} came close to zero. When the system parameters corresponded to an isotropic liquid, on the other hand, then during the initial transient period of the machine "experiment" there occurred a systematic drift of parameters S^{tr} and S^{OR} to zero.

The values of the order parameters were determined within the intervals $S^{tr} = 0.76-0.50$, $S^{OR} = 0.9-0.80$ for the smectic phase and $S^{OR} = 0.75-0.40$ for the nematic phase. We must note that the values obtained for S^{OR} agreed closely with experimental data on typical smectic and nematic crystals; there are experimental data available on S^{tr} in smectic crystals.

Processes of reorientation of molecules play a rather important role in physical effects occurring in liquid crystals. The orientational ordering of the structure has, moreover, an appreciable effect on the character of rotational molecular motion. The rotational motion of particles in the models was analyzed with the aid of time correlation functions for angular velocities

$$\psi_\omega(t) = \langle \omega(0) \cdot \omega(t) \rangle / \langle \omega(0) \cdot \omega(0) \rangle, \quad (4)$$

as well as vector ($l = 1$) and tensor ($l = 2$) reorientational time correlation functions

$$\psi_l(t) = \langle P_l[\mathbf{u}(0) \cdot \mathbf{u}(t)] \rangle. \quad (5)$$

Knowing these functions makes it possible to determine the character of rotational molecular motion in a system, very important in the interpretation of such physical phenomena as dielectric relaxation, infrared absorption, Rayleigh and Raman scattering of light, neutron scattering, nuclear magnetic resonance, and electron paramagnetic resonance [13]. Experimental data on time correlation functions can, in principle, be obtained from the said physical phenomena, but such data pertaining to liquid crystals are not available.

In systems under consideration here, the function ψ_ω decreases fast with time and has a range of large negative values. Such a trend of this time correlation function indicates that collisions of particles do not result in complete disordering of angular velocities but, very probably, reverse their directions of rotation. The form of the time correlation function ψ_ω and the magnitude of the correlation time τ_ω , where

$$\tau = \int_0^\infty \psi(t) dt, \quad (6)$$

depend strongly on the asphericity γ of particles. With a constant system packing factor η ,

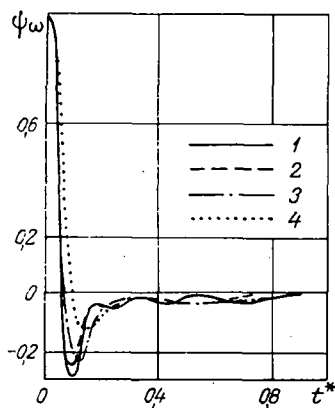


Fig. 1

Fig. 1. Time correlation function for angular velocities in systems of particles with various asphericities γ but the same packing factor $\eta = 0.550$, on the basis of potential (2); γ and T^* : 1) 3.0 and 0.65; 2) 3.0 and 0.76; 3) 2.5 and 0.78; 4) 2.0 and 0.79.

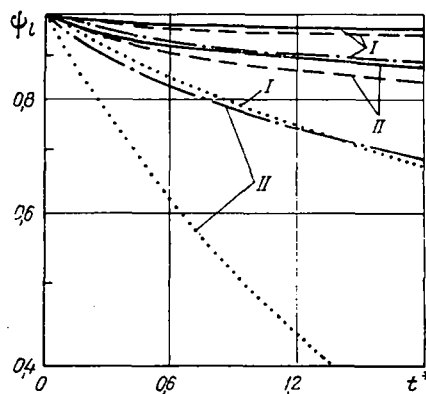


Fig. 2

Fig. 2. Reorientational time correlation functions for systems of particles with various asphericities γ but the same packing factor $\eta = 0.550$ (notation the same in Fig. 1): I) $l = 1$; II) $l = 2$.

according to the data in Fig. 1, function ψ_ω becomes less negative and less oscillatory as γ decreases, which in turn causes τ_ω to increase (Table 1).

For the known function ψ_ω one can calculate the rotational-diffusion coefficient

$$D_R = \frac{k_B T}{m} \tau_\omega. \quad (7)$$

Its magnitude depends strongly on the asphericity of particles. With $\gamma = 0.530$ and $T^* \approx 0.76$, e.g., a decrease of γ from 3.5 to 2.5 causes D_R to increase by a factor of 5.1 (Table 1). For the model of p-azoxyanisole (potential (I), $\gamma = 3$, $\sigma_0 = 5.01 \text{ \AA}$, and $\epsilon_0/k_B = 520^\circ\text{K}$)† we have found that $D_R = 0.44 \cdot 10^{10} \text{ sec}^{-1}$ at $T = 406^\circ\text{K}$, in close agreement with the experimental estimate of $10^{10} - 10^{11} \text{ sec}^{-1}$ obtained by the neutron scattering method [14].

Important information about rotation of molecules in the mesophases is contained in the time correlation function ψ_l , which determines the rate of loss of correlation in major-axes orientations. The most characteristic feature of reorientational time correlation functions for the liquid-crystal phase is their very slow decrease with time (Fig. 2). The decrease of ψ_l over the period of time during which correlations of angular velocities vanish is small. A correlation time τ_l is three orders of magnitude longer than a correlation time γ and depends strongly on the asphericity γ of particles (Table 1). This indicates that reorientation of particles in the system is difficult and explains why, among all relaxation processes in liquid crystals, those associated with reorientation of molecules are characterized by the longest time. During the initial period ($t^* < 0.1$) the ψ_l functions are Gaussian corresponding to rotation of a free rotator, later ($t^* > 0.1$) they decrease exponentially. The "free" rotation time t_f corresponds to the transition of the time correlation function ψ_l to the negative range and can be regarded as the mean time between successive "collisions" of particles. For the model of p-azoxyanisole we have $t_f^* \approx 0.06$ (or, in dimensional units, $t_f = 2.3 \cdot 10^{-13} \text{ sec}$), which corresponds to a rotation through an angle of $\approx 7^\circ$. The correlation time $\tau_2 = 0.89 \cdot 10^{-10} \text{ sec}$ for the model of p-azoxyanisole at $T = 400^\circ\text{K}$ was found to agree closely with the correlation time $\tau_2 = 0.93 \cdot 10^{-10} \text{ sec}$ obtained for real p-azoxyanisole at the same temperature by the electron-spin-resonance method [15].

Knowing the correlation times τ_1 and τ_2 makes it possible to determine the character of rotational molecular motion. In the models of liquid crystals in this study the ratio τ_1/τ_2

†The potential parameters ϵ_0 and σ_0 were selected on the basis of a comparison of computer calculation data and actual experimental data on the temperature dependence of the order parameter [21].

was always close to 3 (Table 1), indicating a diffusional rotation of particles [13].

One advantage of the method of molecular dynamics is the possibility of obtaining by it information about a system not amenable to a physical experiment. Thus, a study of the trajectories of individual particles has revealed that in the nematic phase rotational "swinging" of particles about some equilibrium orientations is accompanied by a relatively slow change of these orientations near the director orientation, while in an isotropic liquid the drift of temporary equilibrium positions is random. These results confirm the pattern intuitively arrived at by Frenkel, which describes rotational motion in liquid consisting of large complex molecules [16].

Quite many idealized models have been proposed for describing rotational motion in liquids with relatively large molecules. The method of molecular dynamics offers the possibility of checking the closeness to reality of these models so important for the study of many phenomena in liquids. Thus, an analysis of the basic premises of the "rotational diffusion" model [13], the "gaseous extended diffusion" model [17], the "extended rotational diffusion" model [18], the "inertia" model [19], the "generalized theory of gaseous rotation" [17], and also the alternative theory of rotational motion based on the quasicrystalline model of a liquid [20] has revealed that the "generalized theory of gaseous rotation" yields results closest to those of machine "experiments." This theory accounts for the existence of a negative range of the time correlation function $\psi_\omega(t)$ and for the change of the function $\psi_l(t)$ from a Gaussian to an exponential after a time of the order of t_f . The conditions of diffusional rotation in this model, viz., that $\tau_\omega < t_f \ll \tau_l$, also satisfy the simulation data.

Translational motion of particles in these systems was studied with the aid of time correlation functions for linear velocities

$$\psi_v(t) = \langle v(0) v(t) \rangle / \langle v(0) v(0) \rangle.$$

Here the difference between particles of the nematic phase and of the smectic phase in their dynamic behavior was revealed most distinctly. While the ratio of components of the self-diffusion tensor D_{\parallel}/D_{\perp} † was found to be larger than unity for nematic crystals, it was found to be smaller than unity and usually 0.4-0.5 for smectic crystals (except in the regions adjacent to the phase transitions). A comparison of results of the machine "experiments" with experimental data on the temperature dependence of the order parameters and of the self-diffusion coefficients for p-azoxyanisole shows that with the use of potential (1) and with one set of its parameters it is possible to describe the equilibrium properties as well as the transport properties (pressure, compressibility, specific heat, order parameters, self-diffusion coefficients) of liquid crystals [21].

On the basis of all this, we can conclude that the models in our study correctly reflect the fundamental structural and dynamic characteristics of nematic and smectic liquid crystals. One must keep in mind, however, that the theoretical results are based on a certain given law of pair intermolecular interaction, without introducing the concept of a mean field intensity [1] and physically meaningless adjustment parameters.

NOTATION

ϕ , ϕ_{rep} , ϕ' , anisotropic pair potentials of intermolecular interaction; \mathbf{u} , unit vector which determines the direction of the major axis in a molecule; \mathbf{r} , vector which joins the centers of mass of molecules; $\hat{\mathbf{r}} = \mathbf{r}/r$; $\epsilon = \epsilon(\mathbf{u}_1, \mathbf{u}_2)$ and $\sigma = \sigma(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}})$, functions of the mutual orientation and of the axes ratio $\gamma = \sigma_{\parallel}/\sigma_{\perp}$ of molecules; ϵ_0 and σ_0 , scale parameters which determine, respectively, the energy of pair interaction and the dimensions of molecules; m , mass of a molecule; ρ , density; $\rho^* = N/V^*$ concentration of particles; T , temperature; k_B , Boltzmann's constant; t , time; D_{\parallel} and D_{\perp} , components of the self-diffusion tensor, respectively, parallel and perpendicular to the director \mathbf{n} ; index * denotes a referred quantity; S^{tr} and S^{or} , respectively, translational and orientational order parameters; ω , (vector) angular velocity of molecules; $\psi(t)$, a time correlation function; P_l , l -degree Legendre polynomial; $\langle \dots \rangle$, averaging over particles and first instants of time; τ , correlation time (indices $\omega, l, 2$ denote the correlation times of the respective processes); $\eta = v_p N/V$, system packing factor; v_p , volume of a particle; D_R , rotational-diffusion coefficient; t_f , "free" rotation time; $v(t)$, projection of the linear velocity of a particle on some axis at instant of time t .

†The values of D_{\parallel} and D_{\perp} were determined by integration of the corresponding time correlation functions [11].

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