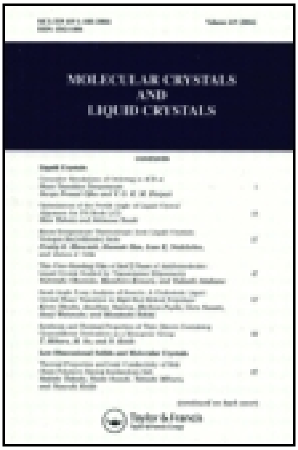

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Study of the Structure and Properties of Nematic, Smectic and Cholesteric Liquid Crystals by the Molecular Dynamics Method

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Version of record first published: 19 Oct 2010.

To cite this article: A. L. Tsykalo (1985): The Study of the Structure and Properties of Nematic, Smectic and Cholesteric Liquid Crystals by the Molecular Dynamics Method, Molecular Crystals and Liquid Crystals, 129:4, 409-421

To link to this article: http://dx.doi.org/10.1080/00268948508085040

Mol. Cryst. Liq. Cryst., 1985, Vol. 129, pp. 409–421
0026-8941/85/1294–0409/$20.00/0

The Study of the Structure and Properties of Nematic, Smectic and Cholesteric Liquid Crystals by the Molecular Dynamics Method

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(*Received June 29, 1984*)

Methods of computer experiments which were successfully used to study isotropic liquids are rather promising for the investigation of properties of different liquid crystals. This paper discussed the main results of studying anisotropic systems by methods of computer experiments (the molecular dynamics method and that of Monte Carlo). It gives the description of the molecular dynamic model and the technique of molecular dynamic modeling liquid crystals of different types (nematic, smectic, cholesteric, as well as films of liquid crystals). Special attention is paid to the choice of the pair potential of interaction which takes into account anisotropic of the dispersion attraction and form peculiarities of molecules as well as specific contributions to the interaction energy (which result in the formation of twisted cholesteric structures, smectic layers, etc.) The model of "a molecule in a molecule" is suggested to describe the smectic state.

According to the results of computer experiments some values were calculated such as structure characteristics of different liquid crystals and films of liquid crystals (order parameters, orientational and translational distribution functions, coordination numbers), characteristics of dynamic behaviour of particles (mean square displacements, time correlation function, time of correlation and that of relaxation), as well as physical and chemical properties (pressure, energy, heat capacity, sound velocity, coefficients of compressibility, coefficients of selfdiffusion).

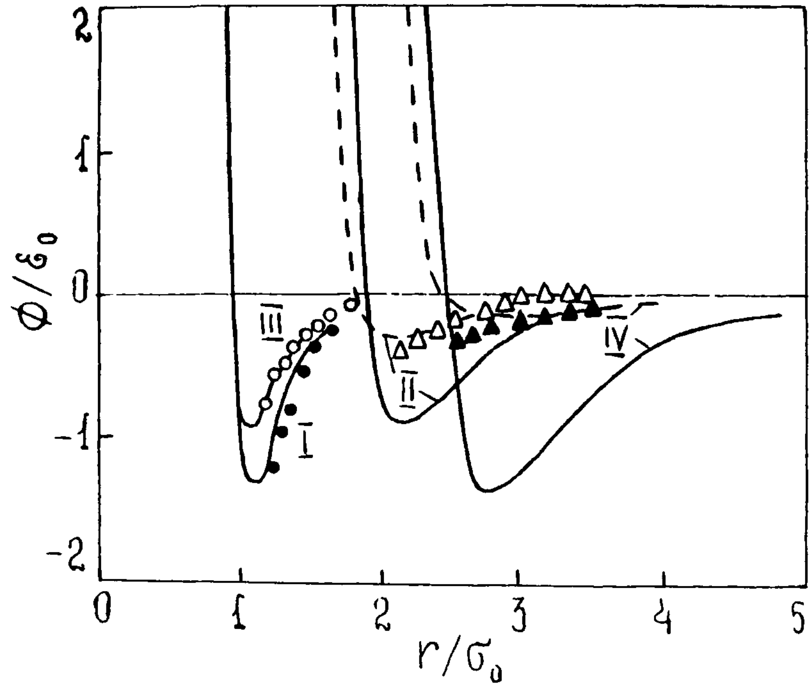

FIGURE 1 Comparison of potentials ϕ, $\gamma = 2.5$, $n = 0$ (solid lines) and $N = 2$ (dashed lines) for characteristic mutual orientations of molecules with results of calculations performed by the Lifshitz-McLakhlan theory[9] for the five-centred model of *p*-azoxyanisole (PAA) (figures): I-||; II-|—; III-|·; IV----.

The data obtained by molecular dynamic modelling were compared with experimental ones. The results of this comparison were discussed and a good agreement between calculated and experimental data was found.

Peculiarities of structure thermodynamic and transport properties of liquid crystals, their wide application in practice and their role in biological systems resulted in thorough studies of these substances during recent years. However theoretical methods of investigation are not fully developed and their use is impossible without approximations and assumptions lowering the reliability of results. Data on dynamics of particles of liquid crystals systems are very scarce.

To study a variety of properties of different kinds of liquid crystals it is reasonable to use the molecular dynamics method which was successfully applied for investigating isotropic liquids. This method is based on numerical integration of equation systems for the motion of particles composing the substance, and it allows strictly in principle

TABLE I

The pressures (P), configuration internal energy (U), thermal coefficients of pressure (γ_v) of PAA obtained with molecular dynamics method and comparison with experiment

T, K	ρ g/cm^3	P, bars	U, 10^3 J/Mole	γ_v, bar · K^{-1}	
				MD method	experiment
371	1.169	142	−24.3	10.0	13 [14]
394	1.169	372	−23.9	10.5	13 [15][a]
414	1.169	581	−23.4		

[a] For 1.282 g/cm^3

to solve the statistic problem of the system of a great number of interacting particles. As a result one can get rather complete information about properties of a system which helps determine characteristics of particles dynamic behaviour (time correlation functions of linear and angular velocities, reorientational functions; etc.), structure (orientational and translational ordering parameters, distribution functions), thermodynamic properties (pressure, energy, heat capacity, thermodynamic velocity of sound, coefficients of compressibility, etc.), transport properties (selfdiffusion, viscosity, thermal conductivity, etc.).

In this paper liquid crystals of three types—nematic (NLC), smectic (SLC), cholesteric (CLC) were studied by the molecular dynamics method. Special attention was paid to the pair potential of interaction.

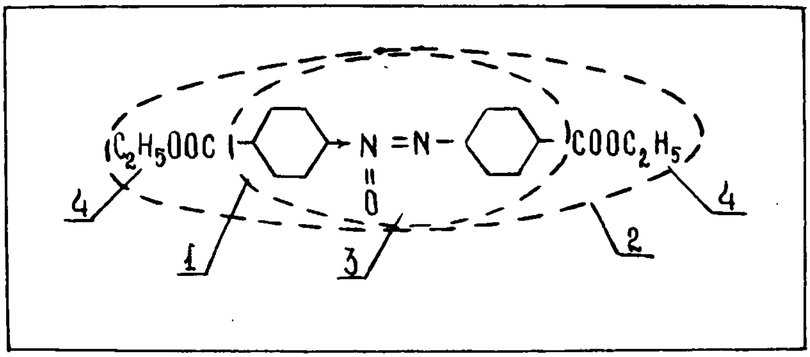

FIGURE 2 Schematic representation of the typical smectic molecular model (ethyl ether of p-azoxybenzoic acid): 1—inner (smaller) ellipsoid, 2—outer (larger) ellipsoid, 3—central part of molecule, 4—end-"chains." The rotation axis of an ellipsoid molecule is horizontal and lies in the plane of the drawing.

We tried to use a simple molecular model, when it was possible, which reflect the main kinds of molecular interactions and resulted in the qualitative description of the most important properties of the above types of liquid crystals. The applied general form of the intermolecular potential of interaction for ellipsoid molecules was as follows:

$$\phi = \frac{4\epsilon_0\epsilon_1(\mathbf{u}_i, \mathbf{u}_j)}{\sigma_1^n(\mathbf{u}_i, \mathbf{u}_j, \mathbf{r})}\left[\frac{\sigma_\perp\sigma_1(\mathbf{u}_i, \mathbf{u}_j, \mathbf{r})}{r}\right]^{12} - \frac{4\epsilon_0\epsilon_2(\mathbf{u}_i, \mathbf{u}_j)}{\sigma_2^n(\mathbf{u}_i, \mathbf{u}_j, \mathbf{r})}\left[\frac{\sigma_\perp\sigma_2(\mathbf{u}_i, \mathbf{u}_j, \mathbf{r})}{r}\right]^{6} - 4\epsilon_0 m(\mathbf{u}_i \times \mathbf{u}_j \cdot \mathbf{r})(\mathbf{u}_i, \mathbf{u}_j)\left(\frac{\sigma_\perp}{r}\right)^7,$$

where r is the distance between centres of particle masses, $\mathbf{u}_i$ and $\mathbf{u}_j$ are unit vectors, directed along the long axes of ellipsoids, $\mathbf{r}$ is the unit vector directed along the line connecting molecules centres, ϵ is the energy parameter of the potential, $\sigma_\perp$ is the length of the ellipsoid short axis. Functions $\epsilon(\mathbf{u}_i, \mathbf{u}_j)$ and $\sigma(\mathbf{u}_i, \mathbf{u}_j, \mathbf{r})$ have the form suggested by B. J. Berne and P. Pechukas.[1]

The first two addenda of the potential take into account interaction forces: anisotropic forces of repulsion and dispersive attraction. The account of these addenda is enough for modeling NLC and SLC. Thus, in case of $\sigma_1 = \sigma_2$ and $\epsilon_1 = \epsilon_2$ this potential corresponds to

TABLE II

The adiabatic compressibility (β_S) and thermodynamic velocity of sound (w) of PAA and MBBA obtained with molecular dynamics method and comparison with experiment

			β_S, 10^{-12} cm · c/g		w, 10^5 cm/c	
Substance	T, K	ρ, g/cm^3	MD method	Experiment	MD method	Experiment
PAA	400	1.194	37.1	54.3 [16][a]	1.50	1.26 [16][a]
	407	1.173	42.1	65.3 [16]	1.42	1.15 [16]
MBBA	308	1.044	56.8	42.4 [17][b]	1.30	1.55 [17][b]
	314	1.026	64.6	49.2 [17][c]	1.23	1.44 [17][c]

[a] For 399 K
[b] For 309 K
[c] For 312 K

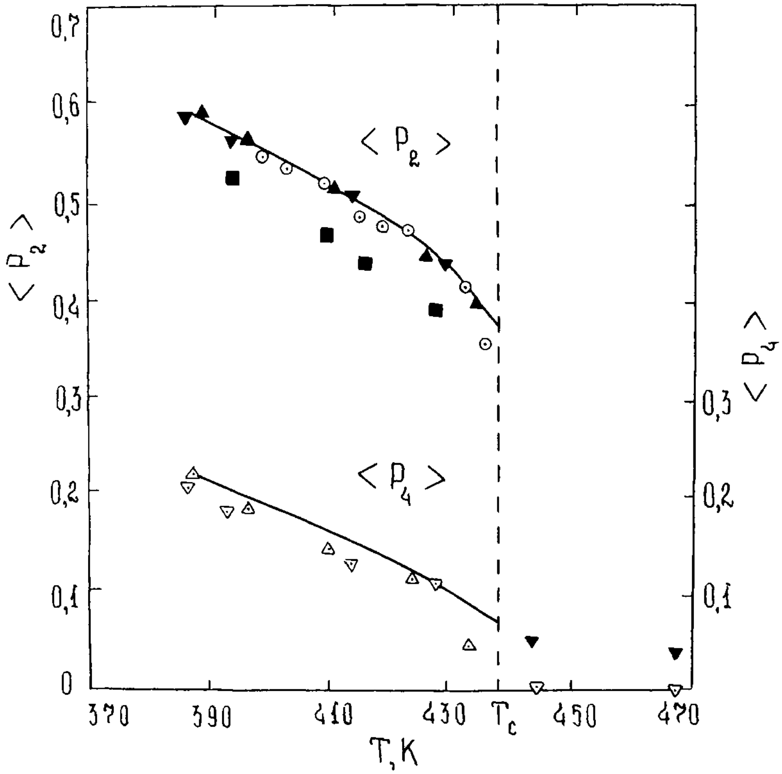

FIGURE 3 Temperature dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at constant density: ▲, ▼ are modeling, $\langle P_2 \rangle$ at 1.169 g/cm^3 for $N = 108$ and 168 respectively (N—number of particles in the based box), $n = 2$, $\gamma = 2.5$, $\sigma_0 = 5.36$ Å, $\epsilon_0/k = 535$ K; △ and ▽ are the same for $\langle P_4 \rangle$; ■ are the same for $\langle P_2 \rangle$ at 1.116 g/cm^3; ○ is experimental data (NMR) for PAA at 1.169 g/cm^3.[10] The solid line corresponds to the Chandrasekhar-Madhusudana theory.[11]

the one previously used by us for studying NLC.[2] (Figure 1). Supposing that $\sigma_1 \neq \sigma_2$ and $\epsilon_1 \neq \epsilon_2$ it is possible to successfully simulate SLC. In the latter case the model of a "molecule in a molecule" is used.[3] A smaller ellipsoid is located in every large elongated ellipsoid. Large ellipsoids interact with one another according to the law of power repulsion (the first addendum of the potential takes into account relatively "soft" repulsion of endchains of smectics molecules and more "rigid" repulsion of central parts of these molecules). Smaller ellipsoids attract each other (the second addendum of the potential takes into account dispersive attraction of benzene ring of molecules central parts) (Figure 2). The last member of the potential describes dipole-quadrupole interaction, with parameter m characterizing the relative value of this interaction and being connected with the dis-

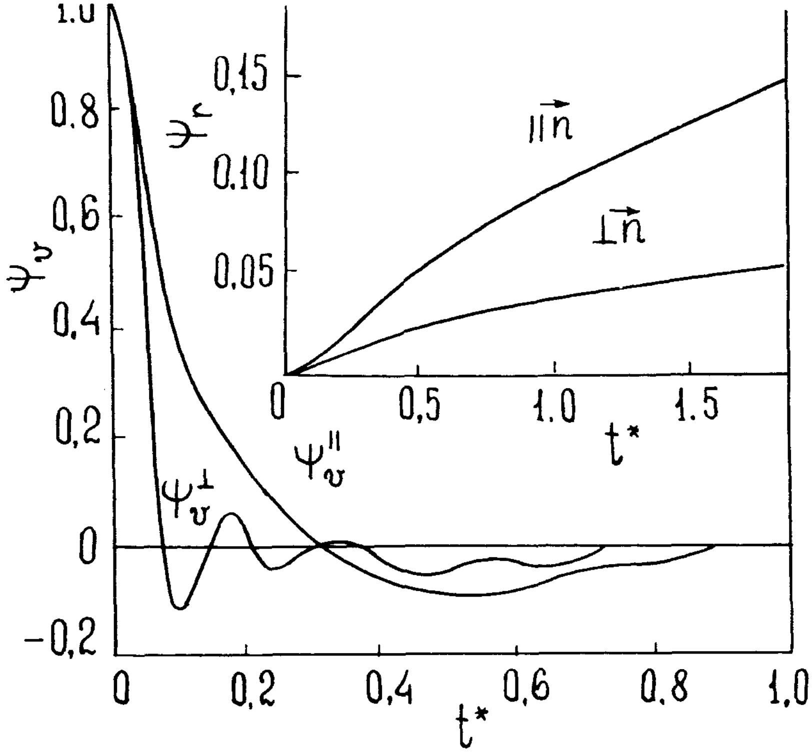

FIGURE 4 Time correlation functions (TCF) of linear velocities ψ_v and square-mean displacements ψ, of NLC, found by the method of modeling ($\gamma = 3.0$, $\rho^* = 0.350$, $n = 0$, $T^* = 0.77$).

tribution of electronic density of molecules. According to Goossens theory[4] which is widely used in recent years, it is the contribution of dipole-quadrupole interactions that determines peculiar features of CLC in the first place.

The statistical problem was solved by numerical integrating the system of motion equations for 108, 168 or 256 ellipsoidal particles (each of which had five powers of freedom) placed into the basic sample which had the form of a cube or a rectangular parallelepiped. Periodical boundary conditions were imposed on the planes of the basic sample, which presented the possibility to simulate an infinitely large system with translational periodicity. In modeling liquid crystals films the basic sample from the side of two opposing planes was limited by energetically homogeneous flat walls, with molecules interacting with these walls according to anisotropic potential Mi (9-3).

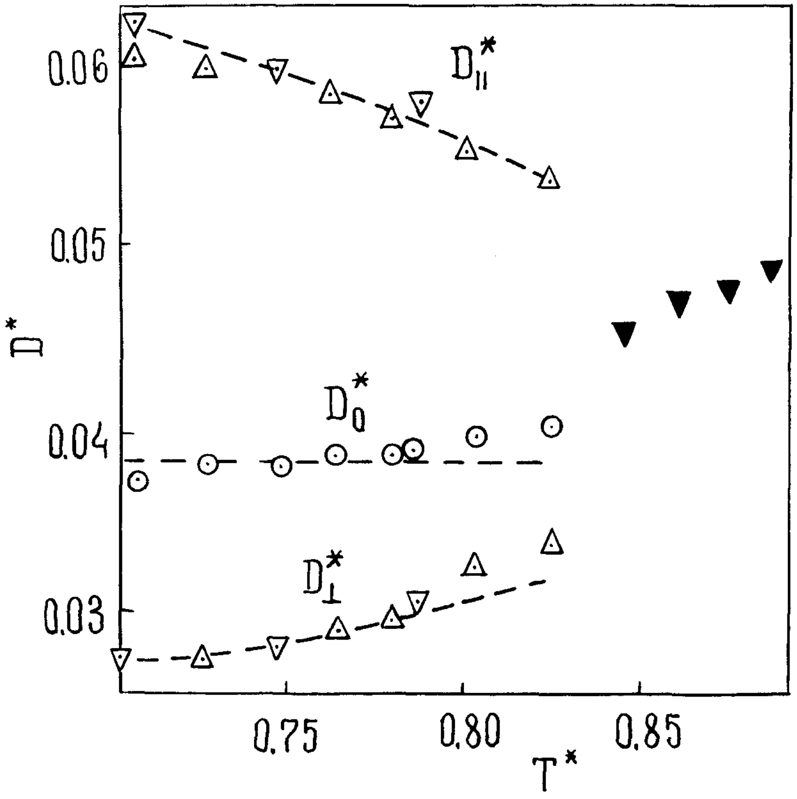

FIGURE 5 Temperature dependences of the self-diffusion coefficients ($D_{\parallel}$, $D_{\perp}$ and D_0) of the molecular dynamic model in the range of existing of NLC and IL (γ = 2.5, n = 2, ρ^* = 0.420): △—NLC, N = 108; ▽ is the same, N = 168; ▼—IL, ⊙—D_0. Dashed lines correspond to approximate relationships.[12]

During each molecular-dynamic "experiment" the transition from initial state (nonequilibrium for given conditions) to equilibrium one characteristic of nematic, smectic, cholesteric mesophases or an isotropic liquid took place (depending on the character and parameters of a potential of molecular interactions as well as on the system temperature and density).

Figure 3 shows the temperature dependences of order parameters (coefficients of series expansion in Legendre's polynomials for orientational distribution function) $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for the most thoroughly studied NLC of *p*-azoxyanisole. The agreement with experimental data in $\langle P_2 \rangle$ is very good, but experimental data in $\langle P_4 \rangle$ are up to now scarce and contradictory. The molecular dynamics method enables us to find not only any order parameters ($\langle P_4 \rangle$, $\langle P_6 \rangle$, etc.) but to determine complete orientational distribution function, as well as to estimate how many expansion terms are necessary to describe it reliably depending on temperature, pressure, external field, etc. We found that for states of high ordering knowledge of $\langle P_2 \rangle$ was required as well as $\langle P_4 \rangle$ and $\langle P_6 \rangle$.

Time correlation functions of linear velocities in directions parallel and perpendicular to the director (Figure 4) show the considerably easier movement of NLC molecules in the former direction. In this connection the ratio of the selfdiffusion tensor components $D_\parallel/D_\perp$ for NLC calculated applying the molecular dynamics method is more than unit according to experimental data. Temperature dependences $D_\parallel$ and $D_\perp$ for NLC are also in reasonable agreement with experi-

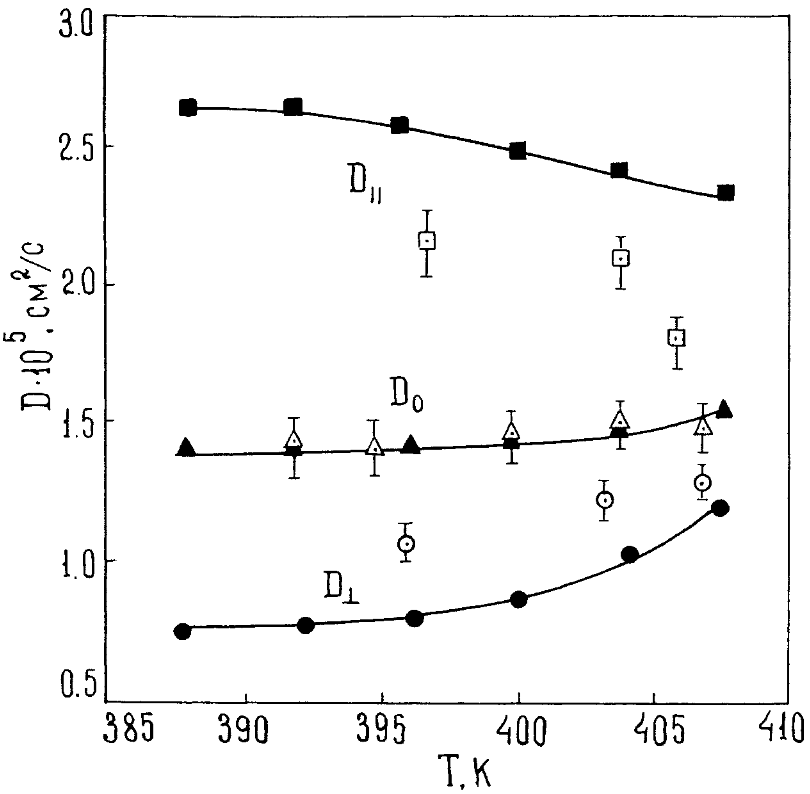

FIGURE 6 Temperature dependences of $D_\parallel$, $D_\perp$ and D_0 for PAA: ■, ● and ▲ are the results of modeling ($\gamma = 3.0$, $\eta = 0$, $\sigma_0 = 5.01$ Å, $\epsilon_0/k = 520$ K), □, ○, △ are experimental data on the neutron diffraction.[13]

TABLE III

Reduced values of some properties and structure characteristics of SLC and NLC obtained with molecular dynamics method

NN	1	2	3	4	5	6
Properties[a,b]	SLC	SLC	SLC	SLC	NLC	SLC
ρ^*	0.234	0.236	0.245	0.245	0.245	0.255
T^*	0.38	0.36	0.42	0.46	0.57	0.44
η_1	0.81	0.93	0.87	0.85	0.77	0.91
η_2	0.75	0.76	0.63	0.58	0.45	0.72
τ_1	0.55	0.57	0.73	0.48	0.12	0.76
τ_2	0.12	0.14	0.29	0.05	0.00	0.33
σ	0.50	0.55	0.64	0.47	0.10	0.69
$\tau^*_{\parallel}$			0.013	0.015	0.0281	0.0072
$\tau^*_{\perp}$			0.026	0.027	0.044	0.018
τ^*_{ω}			0.0050	0.0071	0.0137	
$D^*_{\parallel}$	0.029		0.0055		0.110	0.021
$D^*_{\perp}$	0.037		0.0110		0.025	0.009
$D_{\parallel}/D_{\perp}$	0.78		0.50		4.4	2.3
D^*_R			0.0042	0.0081	0.0156	

[a] $\rho^* = \rho N \sigma_0^3$; $T^* = T/\frac{\epsilon_0}{k}$; $\tau^* = t/(\epsilon_0/m)^{-1/2}\sigma_0$; $D^* = D/\sigma_0(\epsilon_0/m)^{1/2}$;

[b] η_n, τ_n and σ are orientational, transitional and mixed order parameters respectively and expansion coefficients of partition function $f(x)$:

$$f(x) = \frac{1}{d} + \frac{2}{d}\sum_{n=1} \langle\cos\left(\frac{2\pi nx}{d}\right)\rangle \cos\left(\frac{2\pi n}{d}\right),$$

$$\tau_n = \langle\cos\left(\frac{2\pi nx}{d}\right)\rangle;$$

$$\eta_n = \langle P_{2n}(\cos\theta)\rangle;$$

$$\sigma = \langle\cos(2\pi x/d)\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)\rangle$$

mental data (Figure 6). Time correlation functions of angular velocities and reorientational function found by the molecular-dynamic method give the possibility to calculate rotational diffusion coefficients for NLC and corresponding correlation time steps. The results of molecular dynamics simulation show that the most adequate model out of idealized ones suggested for describing rotational motion is the generalized theory of gas-like rotation.[5]

The character of distribution function $\varphi(x/\sigma_0)$ for the density of molecules mass centres along the director (given in Figure 7) shows the presence of molecule layers typical for SLC (the presence of distinct periodical maxima).

In the case of SLC the value $\psi^{\parallel}_{u}$ in the point of the first minimum

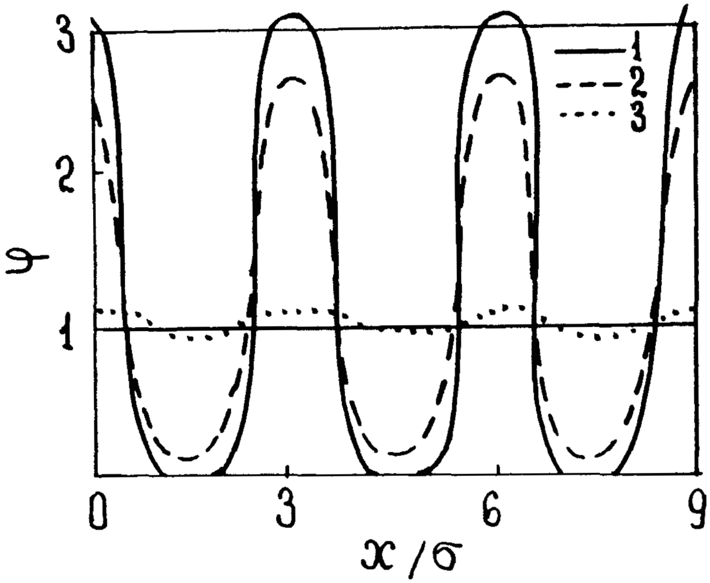

FIGURE 7 Distribution function of particle mass centres for SLC along the axis parallel to the director, according to data of modeling: 1 and 2—for SLC, 3—for NLC.

is approximately three times as large as the similar value $\psi_v^{\perp}$ (Figure 8), which is the evidence of availability of ordered oscillations in the direction perpendicular to smectic layers and of difficulty of molecules motion in this direction as compared to the motion in the plane of a smectic layer. Thus, according to molecular dynamic data for SLC $D_{\parallel}/D_{\perp} < 1$ which corresponds to experimental data for the larger part of the range where SLC exist (small parts adjoining the phase transition lines can serve as exceptions).

Peculiarities of molecules locations in smectic layers can be described by the binary distribution functions $g(r/\sigma_0)$. Their forms give the possibility to distinguish SLC A (the comparatively smaller first maxima and attenuation of oscillations at large distances) from SLC B (the higher first maximum and availability of long-range ordering which shows itself in the existence of oscillation even at large distances). The molecular dynamics method for SLC was used to determine not only orientational order parameters, but also translational and mixed order parameters.[6]

In case of CLC one can observe spontaneous twisting of conditionally chosen molecular layers so that the directors for such layers composed a typical cholesteric spiral. Figure 9 illustrates it. With

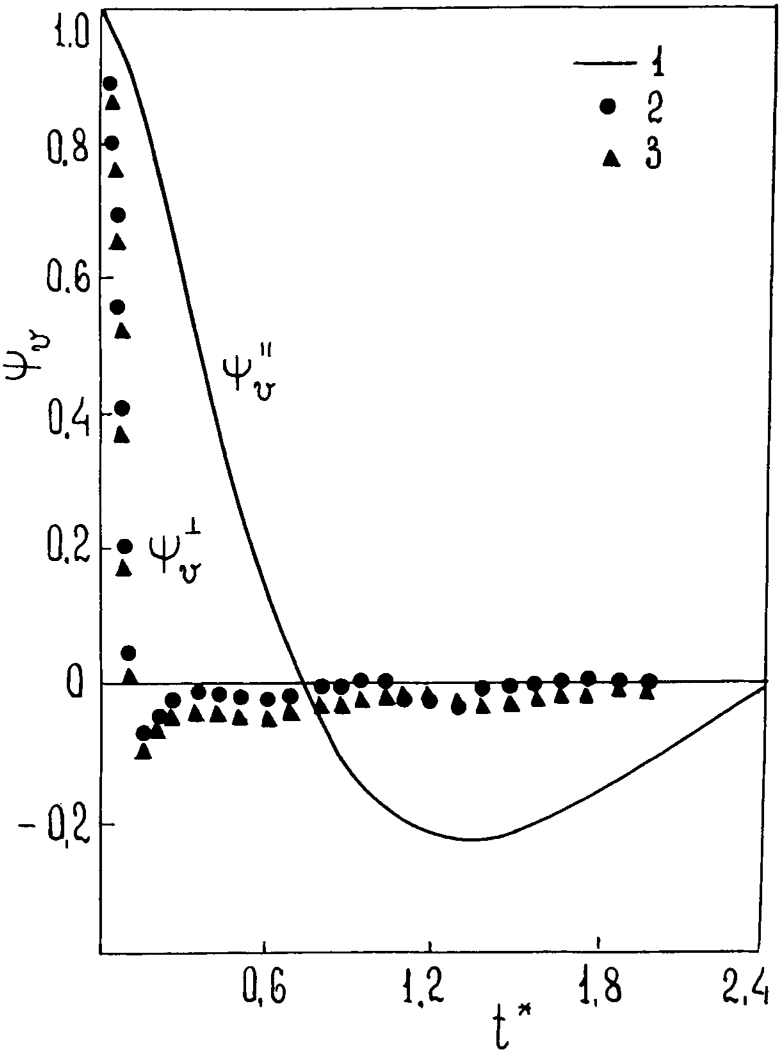

FIGURE 8 TCF of linear velocities of SLC molecules according to modeling data: 1 is parallel to x-axis (to the director), 2 is parallel to y-axis, 3 is parallel to Z-axis.

increasing the temperature the spiral pitch decreased as was the case with the majority of experimentally studied cholesteric liquid crystals that are cholesterine derivatives.[7] Obtained temperature dependences for orientational molecule order parameters in conditionally chosen CLC layers correspond qualitatively to experimental data available.[8]

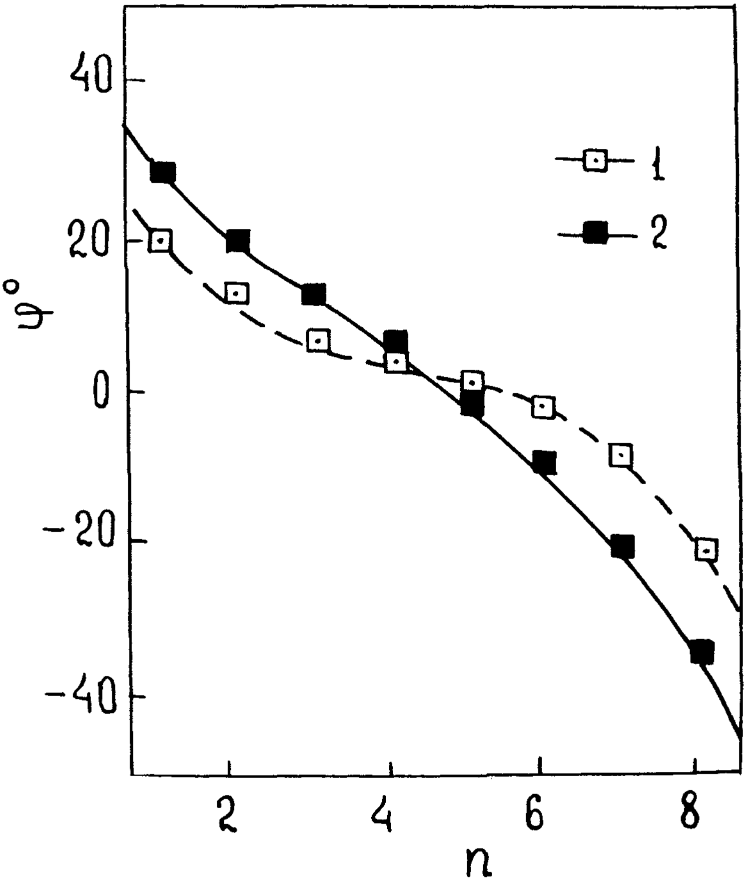

FIGURE 9 Angle dependences of director projections for CLC model layers on the plane *x*-*y* with the axis *x* on the layer numbers in equilibrium states according to modeling data: 1—T^* = 0.39, 2—T^* = 0.75.

The results of performed research are the evidence of great possibilities exhibited by the molecular dynamics method in studying liquid crystals. In this case information on molecular characteristics of substances is only used (molecular sizes and form, intermolecular interaction, etc.) which permits to establish the relation between structure, macro- and microscopic properties as well as to obtain information on the molecular level (for example, data on the character of separate molecules motion), which is impossible to do experimentally or is connected with great difficulties. The development of electronic digital computers and determination of interaction energies for complicated molecules present the basis for a wider application of the molecular dynamic method.

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