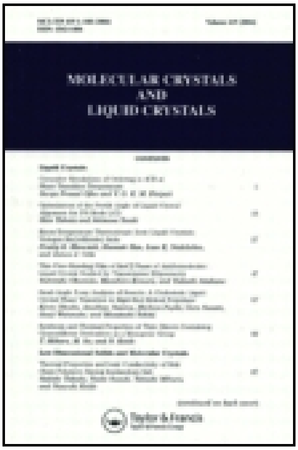

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Molecular Dynamic Investigation of Liquid Crystals Consisting of Disc-Like Molecules

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Molecular Dynamic Investigation of Liquid Crystals Consisting of Disc-Like Molecules

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The results of first-made molecular-dynamic investigation of liquid crystals formed by disc-like molecules are given. The proposed molecular model is based on the representation of molecules in the form of flattened ellipsoids of rotation in the centres of which spherical centres of repulsion and/or attraction are located in some cases. Besides steric factors related to the form of molecules the potential of the pair interaction takes into account anisotropy of forces of dispersive attraction. In some cases this potential also included dipole-quadrupole interaction causing the effect of cholesteric twisting. The statistic problem was solved by the molecular dynamics method, i.e. by way of solving the system of equations for the movement of particles interacting with one another, which were placed in the basic sample with periodic boundary conditions. The numbers of particles in the main sample were 168 or 256.

The data obtained in the process of modeling (after the transition of the system into the equilibrium state) permitted to judge about the structure of the system (translational and orientational distribution functions, order parameters, coordinational numbers), equilibrium properties (pressure, energy, compressibility, heat capacity, thermodynamic velocity of sound) and transport characteristics (time correlation functions, coefficients of self-diffusion). The contribution of molecular interaction energy to structure characteristics was found as well as dynamic behaviour of particles and physicochemical properties. The analysis of results obtained allowed to admit the possibility of existence in certain intervals of temperature and density of some liquid crystalline mesophases many of which have not been observed experimentally up to now. The method of molecular dynamics gave the possibility to predict many properties of such systems and to judge about the peculiarities of phase transitions between similar mesophases.

The ability of some substances composed by disc-like molecules to form liquid crystals attracted great attention to such systems.[1–3] However, the characteristics of orientational and translational orderings of molecules, peculiarities of their motion, physical and chemical properties of these substances as well as some other important properties are not sufficiently studied though available data show the wide variety of possible types of liquid crystalline mesophases in such systems. To solve these problems it is reasonable to use the molecular dynamics method, which has recently been used successfully for the investigation of particles dynamics, the structure and properties of nematic, smectic and cholesteric liquid crystals, as well as their thin films.[4-6]

In this paper the method of molecular dynamics is used to study models for systems of disc-like molecules; peculiarities of their structure; thermo-dynamic and transport properties are determined. New liquid-crystalline structures which can exist in certain temperature ranges in substances composed by disc-like molecules are predicted on the basis of the result obtained.

Systems consisting of flattened ellipsoids of rotation are used as the molecular dynamic model. The basic sample had a form of a rectangular parallelepiped ($L_x = 4{,}70\ \sigma_0$, $L_y = 3{,}37\ \sigma_0$, $L_z = 3{,}89\ \sigma_0$) and contained 168 or 256 particles. On the basis of X-ray structural investigations the length ratios for short and long axes were equalled to 0.3. To lessen the influence of surface effects periodical boundary conditions were superimposed on the fins of the basic sample. Initial conditions were chosen in such a way that the rotation axes should be directed along the x-fin of the main sample,† while the mass centres form a regular lattice.

For the purposes of modelling and determining properties of disc-like molecules systems a series of molecular computer "experiments" were carried out for different pair potentials of interaction (interactions of homogeneous flattened rotation ellipsoids; interactions of ellipsoids in which centres of attraction and repulsion are located (Figure 1), interactions of ellipsoids with dipole-quadrupole forces taken into account), their general form is given in [4]. The potentials take into account the principal components of molecular interaction energy-anisotropic forces of repulsion and attraction, as well as the dipole-quadrupole contribution, which according to Goossens theory[7] determines the appearance of spiral twisting typical for cholesteric liquid crystals.

The structure where short axes of ellipsoid molecules (rotation axes) are approximately parallel to one another, long-range translational ordering is absent and distinct "columns" (or "threads") formed by molecules do not arise, is characteristic of the molecular model of homogeneous flattened ellipsoids (this model corresponds

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†As refers to the systems of disc-like molecules, it is convenient to determine the director as the axis of the principal direction of short axes (axes of ellipsoids rotation).

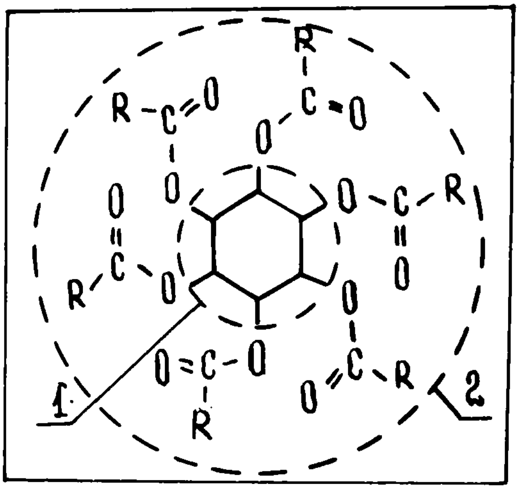

FIGURE 1 The model of a characteristic disc-like molecule with the centre of attraction (R from n-C_5H_{11} to n-C_8H_{17}: 1—the attraction centre, 2—the outer ellipsoid. The axis of rotation of the flattened ellipsoidal molecule is perpendicular to the plane of the drawing and crosses its centre.

to the uniform distribution of force centres of interaction) (Figure 2). The projection of molecules on the plane parallel to the principal direction of rotation axes (director) resembles the similar projection of usual NLC. Such a type of the system can be called a nematic liquid crystal of disc-like molecules (NLC-D or N_D). Some properties of this liquid crystal are given in Table I.

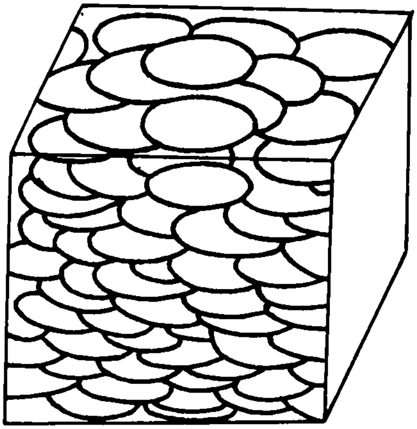

FIGURE 2 The configuration of disc-like particles, forming NLC-D (N_D).

TABLE I

Some results of molecular dynamic modelling of liquid-crystal systems of disc-like molecules with the use of potential[4] for $\eta^* = 0,427$

State, No	1	2	3	4	5
The retained terms of the right parts[a]	1	1	1 and 3	1 and 3	1 and 3
T^*	0,68	0,78	0,79	1,32	1,75
u^*/N	$-$ 9,767	$-9{,}536$	$-19{,}98$	$-17{,}20$	$-14{,}15$
$\langle P_2\rangle$	0,743	0,631	0,972	0,909	0,791
$D^*_\parallel$	0,009	0,013	0,005	0,006	0,018
$D^*_\perp$	0,047	0,046	0,011	0,013	0,028
$D_\parallel/D_\perp$	0,19	0,28	0,45	0,46	0,64
D^*_0	0,034	0,035	0,009	0,011	0,025
D^*_R	—	—	0,000	0,048	0,103
τ^*_1	16,8	9,53	55,8	38,5	20,6
τ^*_2	5,8	3,12	19,4	13,8	7,6
τ_1/τ_2	2,9	3,1	2,9	2,9	2,9
Type of the mesophase	NLC-D (or N_D)	NLC-D (or N_D)	SLCB-D (or D_B)	SLCB-D (or D_B)	NLC-D (or N_D)

[a] u^*—reduced configurational inner energy; D^*_0—reduced average coefficient of self-diffusion; $D^*_0 = \frac{1}{3}(2D^*_\perp + D^*_\parallel)$; η^*-packing parameter

When one uses the molecular model with the centre of attraction (in this way the interaction of benzol rings located in the centres of disc-like molecules is simulated) it is more profitable from the energy point of view to use the structure characterized by the availability of "columns" or "threads," with the long-range translational ordering of the location of molecules mass centres of each "column" being absent. The projection of a "column" on the plane parallel to the principal direction of rotation axes (the director) is similar to the projection of molecules of SLC layer. The distribution of molecules on a plate perpendicular to the "column" axes can correspond to a two-dimensional liquid or a two-dimensional crystal (Figure 3). In the first case one can speak about smectic crystals A of disc-like molecules (SLCA-D or D_A), in the second one—about smectic B of disc-like molecules (SLCB-D or D_B). Structures of the last type were observed experimentally for the case of hexagonal ordering of molecules on a plane perpendicular to "columns" axes.[1]

The molecular model of "ellipsoid in ellipsoid,"[4] describing the interaction of flattened rotation ellipsoids with the thickened central part, in which the force centre of interaction is located, allows to

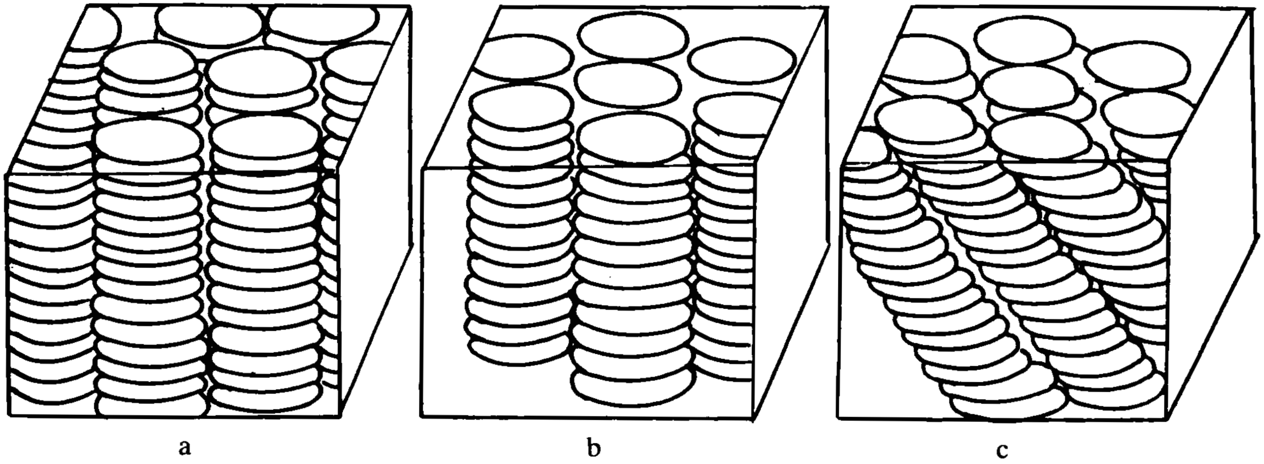

FIGURE 3 Typical configurations of disc-like particles, forming SLC A-D (D_A) (a), SLC B-D (D_B) (b) and SLC H-D (D_H) (c).

predict the inclined thread-like structure (Figure 3), which is more profitable from the energy view-point. Depending on the availability of ordering for projections of "columns" axes on the plane perpendicular to them we can speak about smectic liquid crystals C of disc-like molecules (SLCC-D or D_C) or about smectics H of disc-like molecules (SLCH-D or D_H). Molecular dynamics simulation with a similar model to be used permits to predict the formation of "screw columns" (each disc-like molecule in a "column" is somewhat displaced with respect to the neighbouring one so that a screw structure is formed). Such a displacement can be caused by weak long-range forces or peculiarities of the molecular structure. In this case the geometrical place of molecular centres of each "column" is a spiral (Figure 4a). Depending on the relative ordering of screw columns and the slope of molecules to the principal direction of a "column" we can speak about liquid crystals SLCSA-D (D_{SA}), SLC SB-D (D_{SB}), SLC SC-D (D_{SC}), or SLC SH-D (D_{SH}).

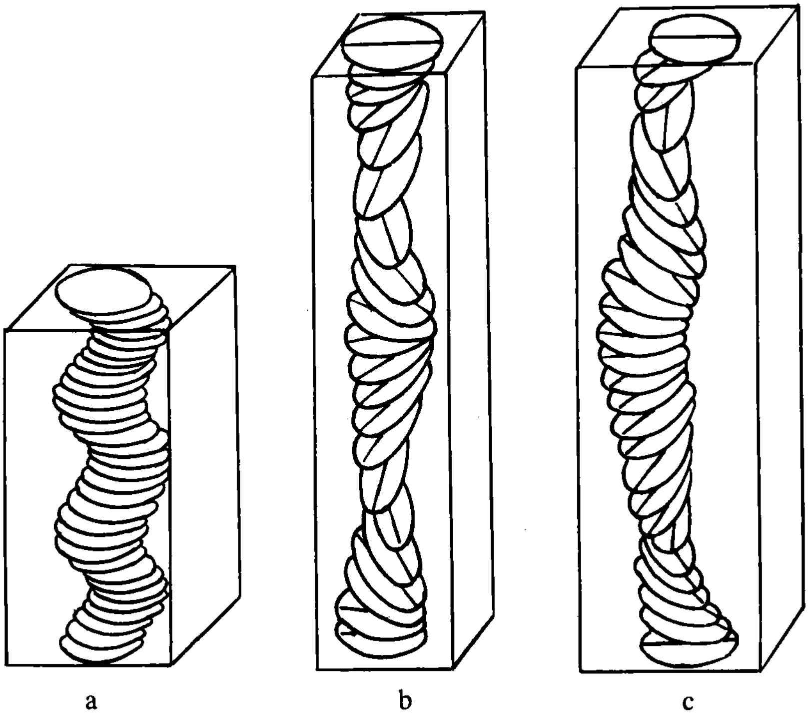

FIGURE 4 Configurations of disc-like particles, forming "columns": a—SLC S-D (D_S); b—CLC (A or B) -D ($N^*_{A \text{ or } B}$); c—CLC S (A or B) -D ($N^*_{SA \text{ or } SB}$).

Rather interesting new structures are predicted in molecular dynamics modelling on the basis of the molecular model of flattened homogeneous three-axis ellipsoid. The discrepancy between the form of a molecule and that of a normal rotation ellipsoid is connected with the nature of a molecular structure (for example, for polymer mesophases).[8] In this case the formation of structures similar to usual CLC of elongated molecules is possible. The angle between two neighbouring molecules can be caused by the same reason as for usual CLC (for example, dipole-quadrupole interaction);[7] in this case the planes containing two large molecule axes are perpendicular to the axis of spiral twisting. Such liquid crystals can be called cholesteric liquid crystals of disc-like molecules (CLC-D or N*) (Figure 5). For molecular systems, described by a similar molecular model, but additionally characterized by the availability of force attraction centres (for example, located in central parts of molecules) the combination of spiral twisting and "columns" is possible (Figure 4b). If "columns" axes are perpendicular to planes, containing two large axes of molecules and their centres are located similarly the centres of particles of a "two-dimensional" liquid, one can speak about CLC A-D (or N_A^*). Contrary to the structure of screw columns, the centers of molecules forming columns are on the same straight line in this case (Figure 4b). If the centres are located in the plane perpendicular to "columns" axes in an orderly way ("two-dimensional" crystal), we have CLC B-D (or N_B^*). In some cases the formation of inclined structures of CLC C-D (or N_C^*) and CLC H-D (or N_H^*) is possible: in the first case the axes of inclined "columns" form a "two-dimensional" liquid, in the second one—"a two-dimensional" crystal. Such structures predict the model of flattened three-axes ellipsoids with

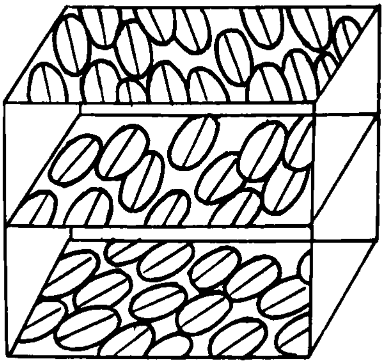

FIGURE 5 The configuration of disc-like particles, forming CLC-D (N*).

the central parts widened—the model of "ellipsoid (or sphere) in ellipsoid."

Some more complicated structures correspond to a case when the cholesteric twisting combines with the screw-like form of the line connecting the centres which form molecular "columns" (Figure 4c). Here we can speak about liquid crystals CLC SA-D (N^*_{SA}), CLC SB-D (N^*_{SB}), CLC SC-D (N^*_{SC}) and CLC SH-D (N^*_{SH}) (Table II).

Out of the above mentioned liquid crystals properties of disc-like molecules systems predicted by the method of molecular dynamics only the structure of SLC B-D (D_B)[1–3] was observed and studied relatively well, though some peculiarities of the mesophase, considered in paper,[9] permit to refer it to NLC-D (N_D). The theoretical analysis of the phase transition from SLC-D (D) to NLC-D (N_D) is given in.[10] The remarkable characteristic of the SLCA-D (D_A) system is the absence of ordering of column axes. The possible existence of such structures is confirmed by experimental data.[11] As for cholesteric systems (CLC-D or N*, CLCS-D or N^*_S) their existence is probably confirmed by the results of experimental observations described in.[12] The authors of this study compared these spiral "columns" with spiral columns of St. Peter's high altar in the Vatican City (see Figure 4). However such an interpretation is not up to now single as the results of observations[12] could be affected by peculiar chiral packing on the surface of the mesomorphic droplets.

As an example let us consider some properties of NLC-D (N_D), found by the method of molecular dynamics. The analysis of trajectories of particles motion shows that the original correct packing of particles is soon disturbed and in the equilibrium state one can observe the character of centres location for particles masses typical for ordinary NLC. Orientational ordering however, is more distinct ($\langle P_2 \rangle$ ranged from 0.63 to 0.75 and $\langle P_4 \rangle$ - from 0.26 to 0.41), which is connected with the difficulty of reorientation of disc-like particles as compared with elongated ones (Table I). Orientational distribution functions of NLC-D (N_D)$f(\cos \theta)$ (Figure 6) were sharply descending curves, qualitatively similar to NLC functions.[6]

Time correlation functions (TCF) of linear velocities, perpendicular to director $\psi_v^{\perp}$ had a distinct negative region of NLC typical for a liquid (Figure 7). However TCF of linear velocities parallel to director $\psi_v^{\parallel}$ had a peculiar feature: a minimum and a small maximum in the positive region ($T^* = 0.67$), which disappeared with increasing the temperature ($T^* = 0.78$).

The components of the translational selfdiffusion tensor at temperatures $T^* = 0.67–0.78$ ranged in the intervals: $D_{\parallel}$ from 0.010 to

TABLE II

The peculiarities of structure of liquid crystals mesophases of disc-like molecules

The type of liquid crystal mesophase	The peculiarities of structure					
	Presence of advantageous orientation of short axes (the axes of rotation) of molecules	Presence of "columns"	The direction of the director coincides with the direction of "columns"	Presence of two-dimensional lattice	The axes of "columns" are straight line	Presence of the angle between neighbouring molecules leading to form cholesteric spiral
NLC-D (N_D)	+	−		−		−
SLCA-D (D_A)	+	+	+	−	+	−
SLCB-D (D_B)	+	+	+	+	+	−
SLCC-D (D_C)	+	+	−	−	+	−
SLCH-D (D_H)	+	+	−	+	+	−
SLCSA-D (D_{SA})	+	+	+	−	−	−
SLCSB-D (D_{SB})	+	+	+	+	−	−
SLCSC-D (D_{SC})	+	+	−	−	−	−
SLCSH-D (D_{SH})	+	+	−	+	−	−
CLC-D (N^*)	+	−		−		+
CLCA-D (N^*_A)	+	+	+	−	+	+
CLCB-D (N^*_B)	+	+	+	+	+	+
CLCC-D (N^*_C)	+	+	−	−	+	+
CLCH-D (N^*_H)	+	+	−	+	+	+
CLCSA-D (N^*_{SA})	+	+	+	−	−	+
CLCSB-D (N^*_{SB})	+	+	+	+	−	+
CLCSC-D (N^*_{SC})	+	+	−	−	−	+
CLCSH-D (N^*_{SH})	+	+	−	+	−	+

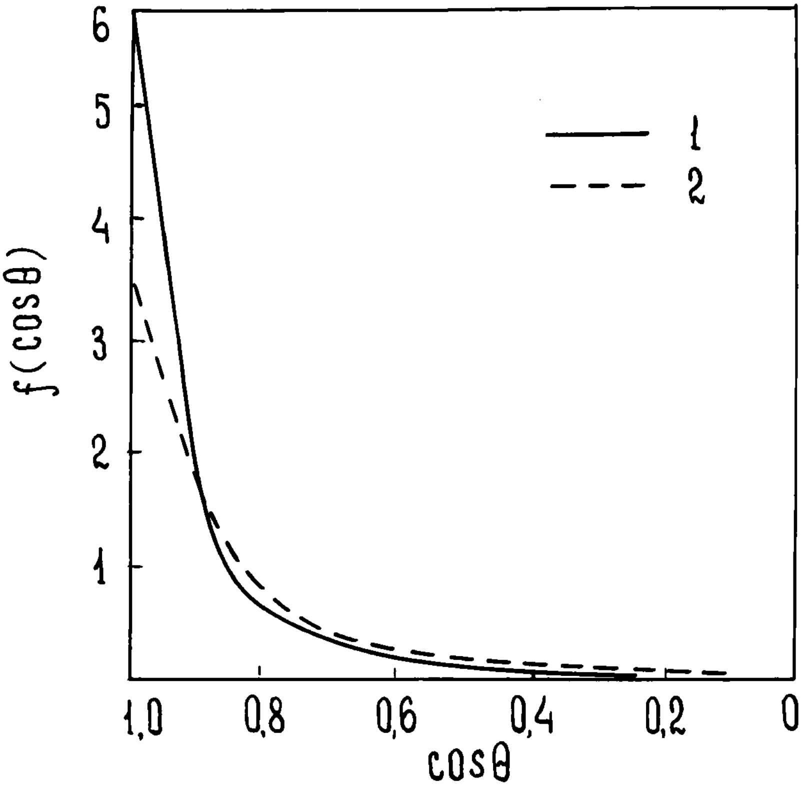

FIGURE 6 Orientational distribution functions f (cosθ) of NLC-D (N_D) particles: 1—$T^* = 0.68$; $\langle P_2 \rangle = 0.743$; 2—$T^* = 0.78$; $\langle P_2 \rangle = 0.631$.

0.015, $D_\perp$ from 0.050 to 0.046. The ratio of $D^*_\perp/D^*_\parallel$ was 5.0–3.5 and the effective selfdiffusion coefficient D_0 remained almost constant (0.036). The coefficient of the rotational diffusion in all cases was close to zero, which is explained by the difficulty of revolving flattened ellipsoids around the large axis.

Peculiar features were found for systems with molecular "columns" (or "threads") for example, for SLC A-D (D_A). Such "columns" exhibit stability and exist even very close to elevated temperatures ($T^* = 1.3$). Function f (cos θ) has a higher maximum. In spite of high order state the translational ordering of particles masses centres in a "column" has a "liquid" character (quick attenuation of oscillations of binary distribution function for mass centres along the axis of a "column"). If in the case of NLC-D (N_D) the function take zero values rather quickly one can observe for SLC A-D (D_A) compara-

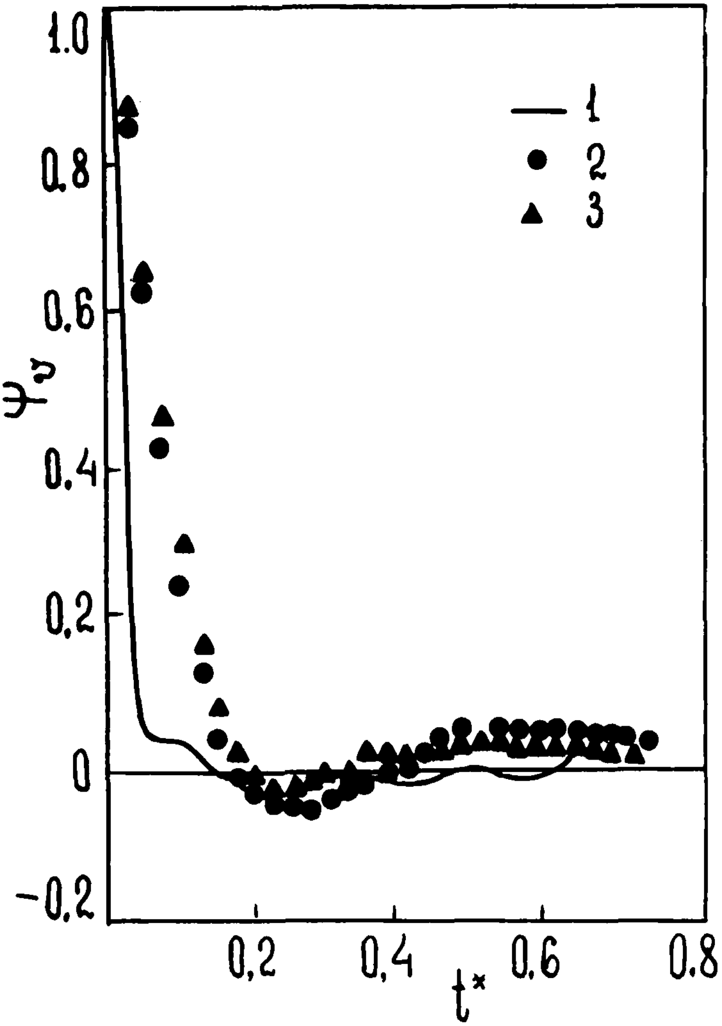

FIGURE 7 Time correlation functions of linear velocities of NLC-D (N_D) particles (state 1, Table 1): 1—along the x-axis (parallel to the director); 2—along the y-axis; 3—along the Z-axis.

tively slow attenuation and distinct oscillations $\psi_v^{\perp}$, which is connected with high correlations in particles motion and reminds the motion of particles of a solid. While functions ψ_ℓ (ℓ = 1.2) for NLC-D (N_D) are similar to corresponding functions of NLC, the character of ψ_ℓ for SLC A-D (D_A) reminds the character of such functions for ordinary SLC. Thus, in both cases qualitative agreement with the systems of elongated molecules is observed.

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