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Molecular Dynamics Study of the Nematic Liquid Crystals

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Since nematic liquid crystals have found a wide use for solving a number of practical problems, the theoretical prediction of thermodynamic and transport properties of liquid crystal systems, as well as an explanation of the structure and dynamic characteristics on the basis of reasonable molecular models have become a point of great importance. The modern molecular-statistical theories, e.g. Maier-Saupe theory and its modifications, use rough approximations (mean field approximations for example) and therefore may lead to wrong conclusions.

To solve the problem “machine experiments” seem to be quite promising since they enable the statistical problem of determining the properties of systems consisting of a large number of particles to be solved accurately. Unfortunately, in the first investigations of the systems of hard spherocylinders, with the use of the Monte-Carlo method^{1,2} there have been serious difficulties and the opposite conclusions have been obtained. Kushick and Berne^{3,4} have examined the nematic stability and the diffusion in the nematic liquid crystal model by the molecular dynamics method, but only one state was investigated for a three dimensional system.

Our work on the molecular dynamics method, which enables one to calculate static and dynamic properties of model systems from a solution of Newton’s equations of motion, is used for exploring models of the nematic liquids. The computer model consists of a basic box with periodical boundary conditions containing 168 or 108 ellipsoidal particles.

The interaction potential is taken to be of the pair-wise additive Lennard-Jones form with a strength parameter ϵ and a range parameter σ dependent upon the major to minor ellipsoidal axis ratio $\sigma_{\parallel}/\sigma_{\perp}$ and the relative

position and orientation of the two particles⁵ (Figure 1):

$$\begin{aligned}\phi(r, \mathbf{u}_i, \mathbf{u}_j) &= 4\epsilon_0 \varepsilon(\mathbf{u}_i, \mathbf{u}_j) \left\{ \left[\frac{\sigma_{\perp} \sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}})}{r} \right]^{12} - \left[\frac{\sigma_{\perp} \sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}})}{r} \right]^6 \right\}, \\ \varepsilon(\mathbf{u}_i, \mathbf{u}_j) &= [1 - f^2(\mathbf{u}_i \cdot \mathbf{u}_j)^2]^{-1/2}, \\ \sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) &= \left\{ 1 - \frac{1}{2} f \left[\frac{(\hat{\mathbf{r}} \cdot \mathbf{u}_i + \hat{\mathbf{r}} \cdot \mathbf{u}_j)^2}{1 + f(\mathbf{u}_i \cdot \mathbf{u}_j)} + \frac{(\hat{\mathbf{r}} \cdot \mathbf{u}_i - \hat{\mathbf{r}} \cdot \mathbf{u}_j)^2}{1 - f(\mathbf{u}_i \cdot \mathbf{u}_j)} \right] \right\}^{-1/2}, \\ f &= \frac{\sigma_{\parallel}^2 - \sigma_{\perp}^2}{\sigma_{\parallel}^2 + \sigma_{\perp}^2},\end{aligned}\quad (1)$$

where \mathbf{u}_i and \mathbf{u}_j are the unit vectors parallel to the molecule's major axis, \mathbf{r} is a vector joining the centers of the two ellipsoids, and ϵ_0 and σ_{\perp} are scaling parameters. The potential ϕ takes into account the main contributions into the liquid crystal molecular interaction energy: anisotropic, short-range repulsion and long-range dispersion attraction.⁶ To determine the relative contributions made by the attractive and repulsive forces some "machine experiments" are performed on the basis of the repulsive potential ϕ_R which is the first addend of the right-hand part of Eq. (1). The range of the potential ϕ was $r/\sigma_{\perp} \leq 2.5\sigma$ and the range of the potential ϕ_R was $r/\sigma_{\perp} \leq 2^{1/6}\sigma$.

Some molecular dynamics simulations were performed with the modified form of the potential (1):

$$\phi_1 = \frac{\phi}{\sigma^2(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}})}. \quad (2)$$

The well depth of the potential (1) depends upon the relative orientation of the interacting molecules comparatively slightly (the orientation significantly effects only the maximum attraction distance). For the potential (2) the orientation of the molecules has a great influence on both the potential well depth and the maximum attraction distance which conforms to the results of the Lifshiz-Mc-Lahlan theory⁷ (Figure 1).

Simulating has been carried out with 3 translational and 2 rotational degrees of freedom taken into account. The Hamiltonian of the system is

$$H = \sum_{i=1}^{3N} \frac{P_i^2}{2m} + \sum_{i=1}^N \frac{1}{2\mathcal{J}} (P_{\theta_i}^2 + P_{\phi_i}^2 / \sin^2 \theta_i) + \sum_{i=1}^N \sum_{i < j} \phi_{ij},$$

where P_i , P_{θ_i} , P_{ϕ_i} are the impulses corresponding to the translational and rotational degrees of freedom; θ_i and ϕ_i are the polar angles defining the orientation of the vector \mathbf{u}_i ; m , \mathcal{J} are the mass and inertia moment of the ellipsoid respectively, N is a number of molecules in the system.

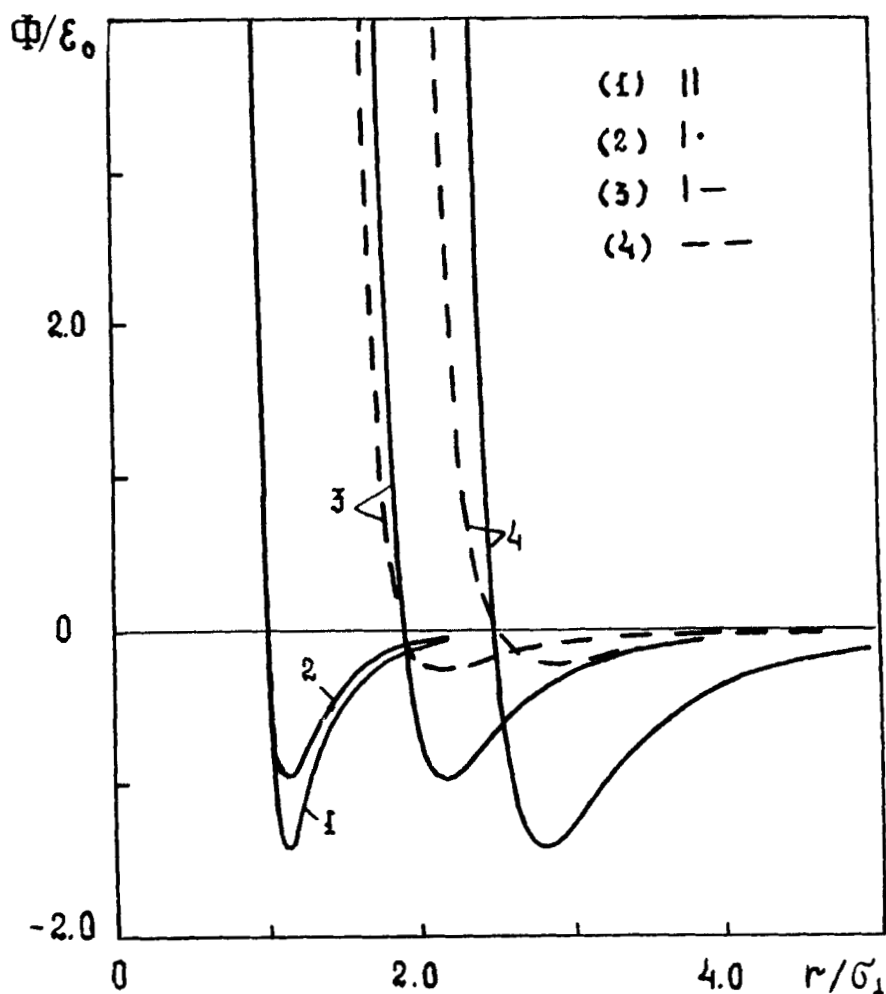


FIGURE 1 The reduced potential energy of two ellipsoidal particles ($\sigma_{||}/\sigma_{\perp} = 2.5$) for some specific orientations. Solid lines correspond to the nonspherical potential ϕ ; dashed lines correspond to the potential ϕ_1 . The potentials ϕ and ϕ_1 are the same for orientations 1 and 2.

The calculations proceeded from a perfect crystal state with order parameter

$$S_1 = \frac{3}{2} N^{-1} \left[\sum_{i=1}^N (\mathbf{u}_i \cdot \mathbf{n})^2 \right] - \frac{1}{2}$$

being equal to 1, where \mathbf{n} is the direction of preferential alignment (the director). Transition from the initial nonequilibrium state to equilibrium

one continued for several thousands time steps. The distributions obtained from previous simulations were taken as initial distributions for every next experiments. All simulations were carried out with a reduced time increment of $\Delta t^* = 0.005$ and were continued for 1000 time steps after equilibrium. At the parameters of potential ϕ_1 were $\varepsilon_0/k = 525$ K; $\sigma_{\perp} = 5.36$ Å and $m = 428.9 \times 10^{-24}$ g (for para-azoxyanisole) the time step was

$$\Delta t \equiv \sigma_{\perp}(\varepsilon_0/m)^{-1/2} \Delta t^* \approx 2 \cdot 10^{-14} \text{ s.}$$

The calculations were carried out for the major to minor axis ratios $\sigma_{\parallel}/\sigma_{\perp}$ equal to 2.0; 2.5; 3.0; 3.5; packing fractions η equal to 0.500; 0.530; 0.550 ($\eta = \rho V_{\text{ell}}$ where ρ is a number density and V_{ell} is an ellipsoidal volume) and for the reduced temperatures T^* in the range of 0.7 to 0.9 (see Table I).

TABLE I

Molecular dynamic simulations of the nematic liquid crystals
All quantities are given in reduced units: $T = (\varepsilon_0/k)T^*$; $D = \sigma_{\perp}(\varepsilon_0/m)^{1/2}D^*$

No.	Potential	$\sigma_{\parallel}/\sigma_{\perp}$	η	T^*	S_1	D_{\parallel}^*	D_{\perp}^*	$D_{\parallel}^*/D_{\perp}^*$
1	ϕ_R	3.5	0.53	0.76	0.81	0.130	0.019	6.8
2	ϕ_R	3.0	0.53	0.77	0.44	0.067	0.022	3.0
3	ϕ_R	3.0	0.55	0.76	0.52	0.042	0.016	2.6
4	ϕ	3.0	0.55	0.77	0.54	0.038	0.013	2.9
5	ϕ_R	2.0	0.50	0.84	0.05	0.057	0.051	1.1
6	ϕ_R	2.5	0.55	0.78	0.48	0.041	0.021	2.0
7	ϕ	2.5	0.55	0.76	0.52	0.026	0.012	2.2
8	ϕ_R	2.0	0.55	0.80	0.11	0.029	0.026	1.1
9	ϕ_1	2.5	0.55	0.71	0.63	0.059	0.026	2.3
10	ϕ_1	2.5	0.55	0.78	0.52	0.057	0.030	1.9
11	ϕ_1	2.5	0.55	0.83	0.40	0.053	0.034	1.6
12	ϕ_1	2.5	0.55	0.89	0.04	0.049	0.049	1.0

For each of these molecular dynamic simulations the orientational order parameter S_1 and

$$S_2 = \frac{5}{4} N^{-1} \left[\sum_{i=1}^N (\mathbf{u}_i \cdot \mathbf{n})^4 \right] - \frac{1}{4},$$

the equilibrium distribution functions, the autocorrelation functions (ACF) of linear velocities parallel (ψ_{\parallel}) and perpendicular (ψ_{\perp}) to the director, the angular velocity ACF (ψ_{ω}) were determined. The reorientational ACF

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

where P_l is a Legendre polynomial, $l = 1, 2$ and the components of the self-diffusion tensor D_{\parallel} , D_{\perp} obtained by integrating $\psi_{\parallel}(t)$ and $\psi_{\perp}(t)$ respectively were also determined.

It was found that at sufficiently high densities and suitable temperature values these systems formed orientational ordered fluids corresponding to nematic liquid crystals. The time dependence of the linear velocity ACF $\psi_{\parallel}(t)$ and $\psi_{\perp}(t)$ has a great difference: $\psi_{\parallel}(t)$ decays more slowly than $\psi_{\perp}(t)$. This indicates that the particle movements perpendicular to the nematic order direction are more hindered than those along this direction (Figure 2). At sufficiently high density and low temperature the velocity ACF $\psi_{\parallel}(t)$ and

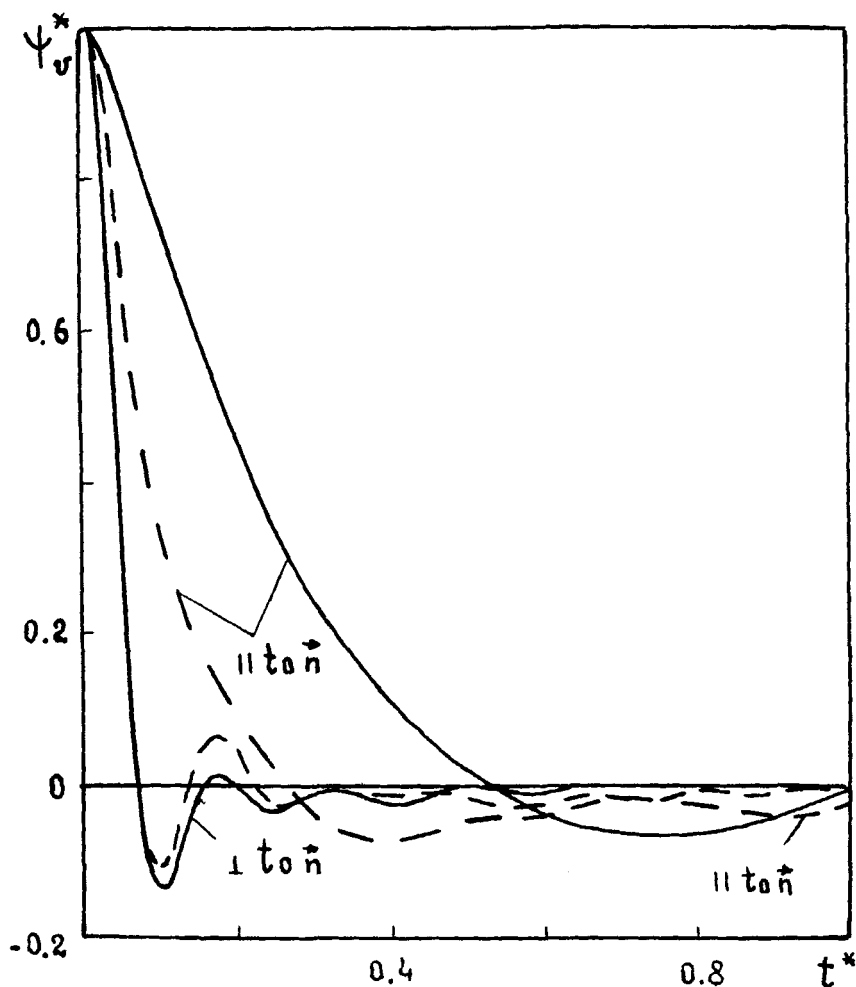


FIGURE 2 The normalized linear velocity autocorrelation functions $\psi_v^*(t) = \langle v(0) \cdot v(t) \rangle / \langle v(0) \cdot v(0) \rangle$ parallel and perpendicular to the direction of preferential alignment \mathbf{n} . Solid lines correspond to state number 1 (see Table I); $\sigma_{\parallel}/\sigma_{\perp} = 3.5$; dashed lines correspond to state number 6, $\sigma_{\parallel}/\sigma_{\perp} = 2.5$. $t = \sigma_1(\epsilon_0/m)^{-1/2}t^* \approx 4 \cdot 10^{-12}t^*$ s.

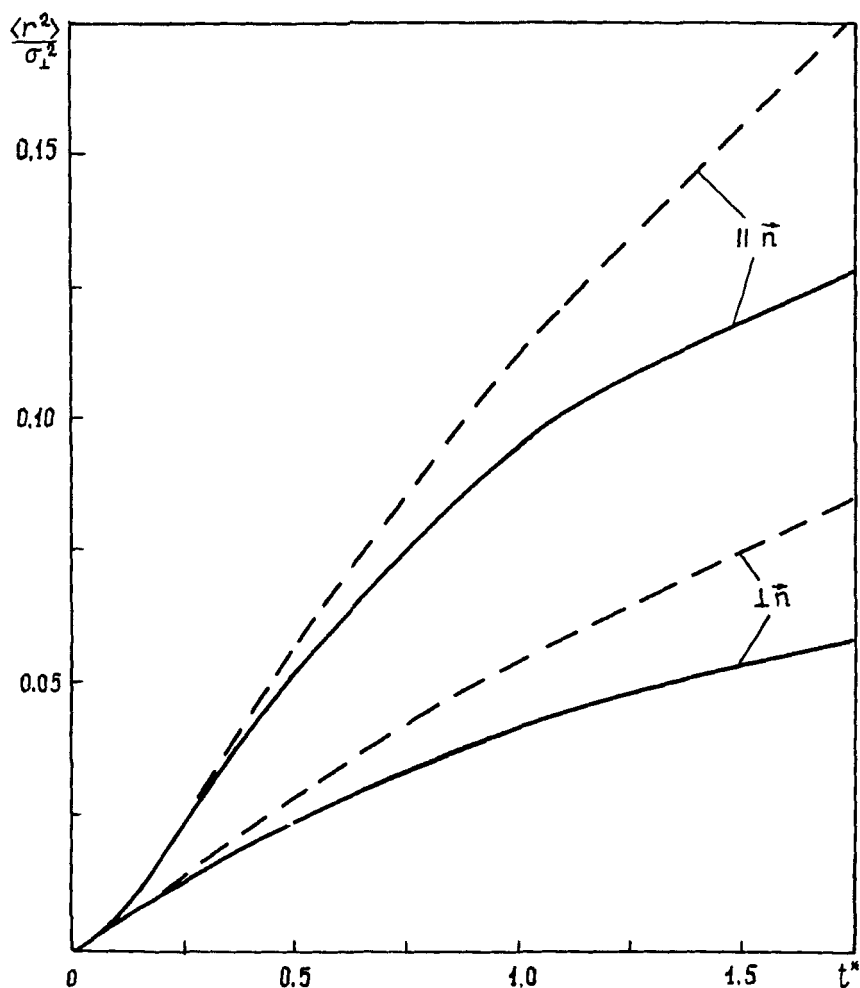


FIGURE 3 The mean-square displacements of the ellipsoidal particles vs time parallel and perpendicular to the director \mathbf{n} . Solid lines correspond to the potential ϕ (state number 7); dashed lines correspond to the potential ϕ_R (state number 6).

$\psi_{\perp}(t)$ have a negative region; the angular velocity ACF ψ_{ω} (Figure 4) has a pronounced negative region in all simulations. This indicates that a fluid particle's angular velocity is on the average reversed by a collision with the "cage" of neighbouring molecules.

The reorientational ACF $\psi_1(t)$ and $\psi_2(t)$ decay very slowly (Figure 4). This shows the fact that the rotational motion in the anisotropic liquid is strongly hindered. For reduced times $t^* > 1.0$ both ACF decay exponentially. For the simulation number 6 (see Table I) the relaxation times

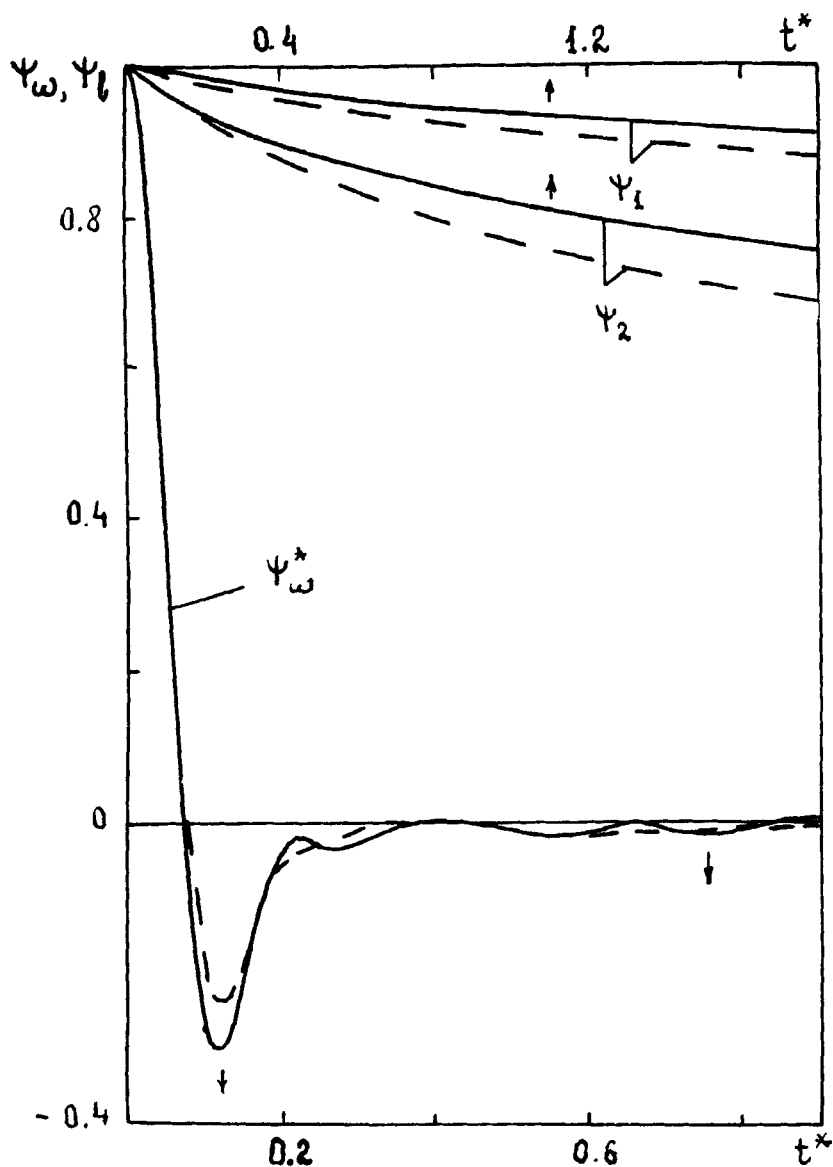


FIGURE 4 The normalized angular velocity autocorrelation functions

$$\phi_\omega^*(t) = \langle \omega(0) \cdot \omega(t) \rangle / \langle \omega(0) \cdot \omega(0) \rangle$$

and the reorientational autocorrelation functions $\psi_l = \langle P_l[\mathbf{u}(0) \cdot \mathbf{u}(t)] \rangle$ for the states shown in Figure 3.

$\tau_i^* = \int_0^\infty \psi_i dt^*$ are $\tau_1^* \simeq 21$ and $\tau_2^* \simeq 7$. The ratio τ_1/τ_2 for all "experiments" was about 3. These results suggest that for our models of nematic liquids the rotational motion is diffusive.⁸ It should be noted that ratio $\sigma_{\parallel}/\sigma_{\perp}$ had a great influence on the shape of ACF.

The qualitative form of ACF for the potentials ϕ and ϕ_R is quite identical; the values of the order parameters are close to each other. The main qualitative regularities in behavior of nematic liquid crystal systems are thought to be predicted on the basis of investigations of the repulsive particle models, since the anisotropic repulsive forces play the leading role in the nematic order setting. However, to predict the main properties quantitatively, the attractive forces should be taken into account as well.

By varying the form and parameters of the interaction potential a good agreement for the temperature dependence of the order parameter between the calculated ($\phi_1: \sigma_{\parallel}/\sigma_{\perp} = 2.5$; $\eta = 0.55$; $\sigma_{\perp} = 5.36 \text{ \AA}$; $\epsilon_0/k = 525 \text{ K}$) and experimental data of para-azoxyanisole was obtained (Figure 5). The experiments carried out with 108 and 168 particles in the basic box correlate well with each other. A special experiment performed at higher temperature $T^* = 0.89$ showed that the system was transferred into the isotropic state, however the transition process was very long.

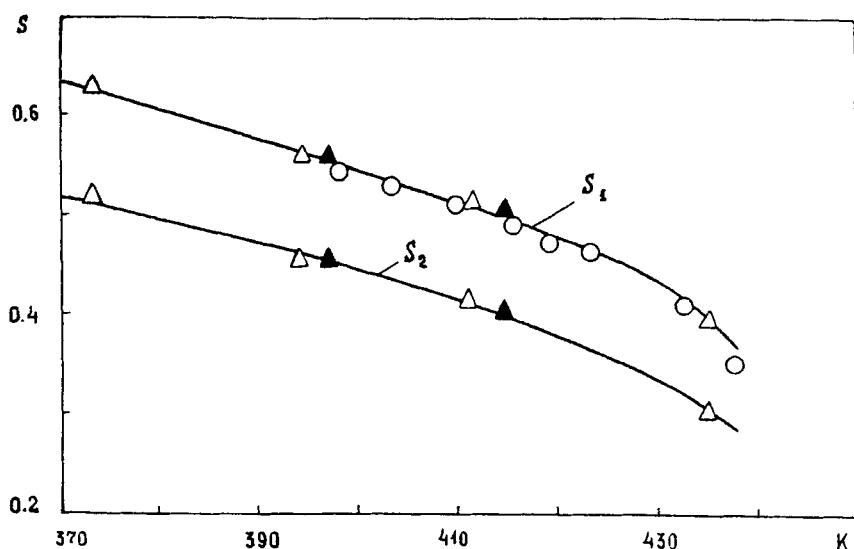


FIGURE 5 The orientational order parameters S_1 and S_2 vs temperature at the constant volume ($221 \text{ cm}^3/\text{mole}$): \triangle and \blacktriangle correspond to the molecular dynamics results for 108 and 168 particles respectively (potential $\phi_1: \sigma_{\parallel}/\sigma_{\perp} = 2.5$; $\eta = 0.55$; $\sigma_{\perp} = 5.36 \text{ \AA}$; $\epsilon_0/k = 525 \text{ K}$); \circ corresponds to the experimental data.⁶ Curves represent theoretical value.¹⁰

The values of the self-diffusion tensor components D_{\parallel} and D_{\perp} calculated for potential ϕ_1 exceed the experimental data⁹ nearly two times. Nevertheless the temperature dependence character and ratio D_{\parallel}/D_{\perp} are similar to the experimental results. The values of D_{\parallel} and D_{\perp} calculated for the potential ϕ are considerably lower than for the potential ϕ_1 since the repulsive branch of the potential ϕ is rather steep and are in good agreement with the experimental data.⁹

We have compared our results of the "machine experiments" with those of Kushick and Berne,^{3,4} who explored one state of the system composed of ellipsoids of rotation. The agreement has been found to be rather good (within the tolerance limits for the computed values), in spite of the difference in the number of particles in the basic box.

In conclusion it should be noted that a rather simple nematic liquid model used in this work gives a proper character of the order-parameter temperature-dependence in the nematic phase and shows transition of the system into the isotropic state as the temperature rises. The self-diffusion tensor components of the model are also in reasonable agreement with the experimental data. The molecular dynamics method is, undoubtedly, promising for the investigation of anisotropic systems though there is some difficulty in comparison with isotropic liquids which also takes place in actual experiment, i.e. too slow transition of the system to equilibrium.

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