When a one-component liquid boils, the heat is transported away from the hot surface mainly by the vapor in the bubbles [4]. For example, for water at atmospheric pressure and $q = 200 \cdot 10^3$ W/m², the proportion q_r/p of the heat transported by the vapor is about 50%. It is therefore important in elucidating the transfer mechanism to determine the heat transport by the vapor in the boiling of gasoil, which is a multicomponent liquid with a relatively low latent heat of evaporation (the overall value for the mixture is taken as 250 kJ/kg).

The amount of heat carried by the bubbles at the instant of detachment can be determined from the local characteristics via

$$q_r = \frac{\pi}{6} \overline{d}_0^3 f r \rho'' n. \qquad (3)$$

Figure 3 shows q_r calculated from (3); it clearly increases with the heat flux, although the proportion in the total heat removed is small. For example, q_r/q is about 6% at $q = 0.4q_{cr}$.

The data show that heat transport by the vapor does not make a substantial contribution to the total heat flux in the boiling of gasoil, which is a difference from a one-component liquid.

NOTATION

α, heat-transfer coefficient; q, specific heat flux; q_{cr}, critical heat flux; q_r, specific heat flux transferred by vapor bubbles; T, temperature; P, pressure; d_0, detachment diameter of bubbles; f, frequency of bubble detachment; n, density of nucleation sites; r, latent heat of evaporation; ρ'', vapor density.

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EFFECT OF A MAGNETIC FIELD ON A LIQUID CRYSTAL FILM AND STUDY OF THE FREDERIKS TRANSITION USING MOLECULAR DYNAMICS

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UDC 532.783.548-14

We discuss the results of a molecular-dynamics study of the lattice model of a liquid crystal.

The effect of bounding surfaces and external fields on the properties of liquid crystal films is of significant theoretical interest, and is also important in applications because of the wide use of various magnetooptical and electrooptical effects in liquid crystals. The traditional theoretical methods of dealing with problems of this kind have series difficulties, and therefore computer simulations of the problem are of great interest [1, 2].

Several interesting results were obtained in [3] in a study of the effect of a magnetic field on the phase transition in the lattice model of a liquid crystal by the Monte Carlo method. In particular, it was established that the well-known molecular field theory was in satisfactory agreement with the computer results. In the present paper we study a more complicated situation, which is of greater importance in practice. We consider the case when the liquid-crystal system experiences the competing effect of bounding surfaces and an external

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field [4]. In other words, we consider the computer simulation of the Frederiks effect. We use the method of molecular dynamics, since in the Monte Carlo method important aspects of the problem involving the dynamical behavior of the system cannot be studied.

Model and Simulation Methods. We used the lattice modification of the Maier–Saupe model of a liquid crystal [5]. In this model particles are localized at the sites of a simple cubic lattice and hence the problem simplifies considerably. The anisotropic pair potential, describing the interaction between particles, has the form

$$U_{ij} = -\varepsilon_{ij} P_2(\cos\beta_{ij}). \quad (1)$$

The magnitude of the interaction is determined by the positive parameter ε_{ij}, which is taken to be equal to ε for nearest neighbors and zero otherwise.

This simple model was chosen for two reasons. First, as shown by a Monte Carlo study of the bulk lattice model with the interaction potential (1), an orientational phase transition takes place which qualitatively describes real nematic liquid crystals. According to the data of [6], the inclusion of the translational degrees of freedom does not lead to a significant change in the results. Second, even in this simple model, the study of the Frederiks transition requires an order of magnitude increase in the execution time, as compared with the study of usual liquid-crystal systems. In order to obtain sufficiently reliable results it is necessary to study phase trajectories of the system of $3 \cdot 10^4$ to $6 \cdot 10^4$ steps with a reduced time step of $\Delta t^* = 0.005$, whereas in the usual case trajectories with a few thousand steps are sufficient [1, 7].

In integrating the equations of motion of the particles in the two directions lying in the plane of the bounding surfaces, the usual periodic boundary conditions were used. The sample was bounded by two surfaces with the third coordinate axis taken to be perpendicular to these surfaces. The number of particles of the sample for which the equations of motion were solved was 1000 (a system of 10 × 10 × 10 particles). The number of particles chosen is a compromise between the necessity of studying a sufficiently large system, and the execution time of the simulation. In addition, the Lebwohl–Lasher result for the reduced temperature of the nematic–isotropic liquid orientational phase transition is known for a bulk system of 10 × 10 × 10 particles in the field-free case ($T^* = 1.145$ [7]).

The bounding surfaces ensure the required orientation of the director of the liquid-crystal system along one of the coordinate axes, where the orientation at the surfaces depends on the geometry of the Frederiks effect being considered. The effect of the surfaces is modeled as a field which acts on the first layer of particles closest to the surface. The energy of a particle in the surface field has the form

$$U_i^s = -\varepsilon P_2(\cos\alpha_i). \quad (2)$$

The effect of the surface forces, as given by (2), is equivalent to adding a layer of particles on either side of the ten layers in the direction of the axis perpendicular to the orienting surfaces, such that the particles in the two added layers are completely oriented parallel or perpendicular to the surfaces.

The interaction of a molecule with the external field has the form

$$U_i^f = -\varepsilon\chi P_2(\cos\gamma_i). \quad (3)$$

For real systems interacting with a magnetic field, the parameter χ is proportional to the anisotropy $\Delta\chi$ of the diamagnetic susceptibility and to the square of the magnetic flux density.

The Frederiks effect was simulated in the following way. First the director was oriented by the surface forces either parallel or perpendicular to the surfaces. Then a magnetic field was applied to the system in a direction creating a competition with the surface orientations. As the magnetic field is increased, the initial orientation remains unchanged up to a certain critical field H_c. For fields greater than the critical field, the director begins to change.

The magnitude of the critical field $H_{c,i}$ for a deformation of type i is proportional to the corresponding elastic modulus K_i [8, 9]:

$$H_{c,i} = \frac{\pi}{d}\left(\frac{K_i}{\Delta\chi}\right)^{1/2}, \quad i = 1,\ 2,\ 3.$$

The values of $H_{c,i}$ can be found directly from the simulation in terms of the maximum angle between the director in the central layer of the sample and the magnetic field. Hence from the critical fields for bend, twist, and splay deformations, one can obtain the corresponding elastic constants, which determine the behavior of the liquid crystal in an external field.

Obviously in order to determine the critical fields and the dependence of the orientational characteristics of the model on the magnetic field strength, it is important to be able to simulate system at constant temperature. The classical scheme used in the method of molecular dynamics is equivalent to a micro-canonical ensemble average, and is unsatisfactory in this respect. Therefore we simulated the Frederiks effect using both the classical scheme and also a method which is equivalent to an average in the canonical ensemble (the basis of this method has been given by Anderson [10]). The essence of the latter method is as follows. The particles of the system exchange energy with the particles of the surroundings and thereby maintain a constant temperature of the system.† In all other respects, the techniques of carrying out the simulation are analogous to those described earlier [1, 11].

Since the director of the system varies in space in the Frederiks transition, it is important to correctly determine the orientational characteristics of the model. It is convenient to use an orientation tensor of the second rank for this purpose:

$$Q_{\alpha\beta}=\frac{1}{N}\Big(\sum_{i=1}^{N}u_{\alpha_i}u_{\beta_i}\Big)-\frac{\delta_{\alpha\beta}}{3},\quad \alpha,\ \beta=x,\ y,\ z.$$

The orientation tensor averaged over a time interval (during which the director remains fixed) was diagonalized. Its eigenvalues λ_1, λ_2, λ_3 and corresponding eigenvectors n_1, n_2, n_3 were determined. The orientational order parameter is proportional to the largest eigenvalue

$$\langle P_2\rangle=\frac{3}{2}\lambda,$$

and the director n is the eigenvector corresponding to this eigenvalue.

The time required for the system to reach equilibrium depended mainly on the ratio of the competing forces (magnetic field and orienting surfaces). The relaxation time was particularly large for $H \simeq H_c$. However in all cases the duration of the transient period did not exceed $5\cdot10^3$ to $6\cdot10^3$ time steps. The averaging time in all of the runs was at least an order of magnitude larger. The initial state was significantly less of an effect on the transition time to equilibrium than the ratio of the completing fields.

The maximum error for the order parameter was ±0.02 and for the internal energy was ±0.01. In the calculations using the classical scheme the error in the temperature did not exceed ±0.005. The computer program used in the simulation was tested by comparing its results for bulk systems with the Monte Carlo data [5, 7], where periodic boundary conditions were used along all three coordinates axes in performing this test. Four runs were done at four different temperatures. In all runs there was complete agreement of the data to within the accuracy of the simulation. The results obtained using molecular dynamics with T = const were randomly checked by numerically integrating the equations of motion according to the well-accepted method based on the condition of constant total energy of the system. Complete confirmation of the results was found in this case as well.

Results and Discussion. We first consider the data obtained for $\chi = 0$. This problem was solved earlier by the present authors for a more complicated system [1]. However now it is of interest to compare this system with the characteristics of the lattice model of a liquid crystal without bounding surfaces.

Figure 1 shows the temperature dependence of the order parameter $\langle P_2\rangle$ in different layers of the liquid-crystal film parallel to the orienting surfaces. The first layer is the closest layer to the wall, while the fifth layer is farthest from the wall. This simulation indicates that the orienting effect of the walls is large only for the first layer closest to the wall, which remains orientationally ordered even at the relatively high temperature $T^* = 1.57$. The degree of order for the layer farthest from the wall falls off much more rapidly with increasing temperature and has the form characteristic of the phase transition in bulk nematics. Comparison with the Monte-Carlo results for the analogous lattice system (10 × 10 × 10) without orienting surfaces [7] shows that the degree of order of the fifth layer (farthest from the wall) approximately corresponds to that of the bulk lattice

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†A detailed description of the computational scheme will be published in a separate paper.

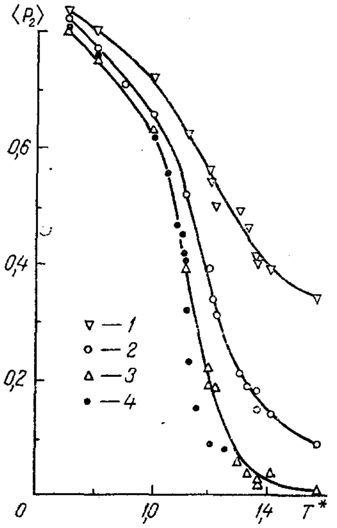

Fig. 1

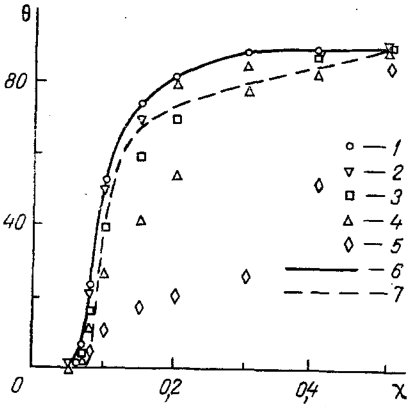

Fig. 2

Fig. 1. Temperature dependence of the order parameter $\langle P_2 \rangle$ in different layers of the liquid-crystal film ($\chi = 0$): 1) first layer (closest to wall); 2) second layer; 3) fifth layer (farthest from wall); 4) Monte Carlo data for the bulk system 10 × 10 × 10 [7].

Fig. 2. Angle between the director and the easy axis of orientation as a function of the magnetic field strength for different layers of the liquid-crystal film: 1), 2), 3), 4), 5) band deformation ($T^* = 1.0$) for the fifth, fourth, third, second, and first layers, respectively; 6) twist deformation ($T^* = 1.0$), fifth layer; 7) twist deformation ($T^* = 0.7$), fifth layer.

system. The somewhat large "blurring" effect of the transition in the layer can be interpreted as due to the relatively small number of particles, since the same effect occurs when one compares data on the temperature dependence of $\langle P_2 \rangle$ for systems with 10^3 and 20^3 particles [7].

Comparison of our results for the temperature dependence of the internal energy of the system with the Monte Carlo data for a bulk system [3] shows that the surface forces are insignificant in this respect. Hence in the model studied here, the effect of the walls appears mainly in the orientation of the director along a given direction, and does not change significantly the orientational order of the layers far from the wall or the properties of the system as a whole.

We consider now the effect of applying a field to the liquid-crystal film, which creates an orientational effect that competes with the effect of the bounding surfaces of the liquid crystal. For fields which are strong enough to overcome the elastic forces of the liquid crystal, there will be a reorientation of the director, and a new equilibrium director distribution will be established.

In Fig. 2 the dependence of the angle between the director and the magnetic field is shown for different layers of the liquid-crystal film for the case of band and twist deformations. In agreement with experiment, we find that for fields less than the critical field $H < H_c$ the director is determined by the orienting action of the surfaces. When the field is increased above the critical field, we see from Fig. 2 that the original equilibrium director field gradually changes, and for $H \gg H_c$ the angle θ reaches 90°, which means that the director in all of the layers is along the direction of the field. The variation of the angle θ for the layers far from the wall is qualitatively the same: a sharp jump upon reaching the critical field and a subsequent slow increase up to 90°. However the situation is different in the layer closest to the wall. Here the angle θ initially increases slowly up to about 25° and only upon reaching a relatively high field strength does the director rapidly align with the external field.

The maximum angle between the director and the axis of easy orientation takes place in the middle layer of the sample (the fifth layer) when $H > H_c$. As seen from Fig. 2, the angle

θ_{max} depends significantly on the temperature of the system. For $T^* = 1.0$, θ_{max} reaches saturation for $\chi = 0.3$ (curve 6), but for $T^* = 0.7$, θ_{max} is close to 90° only when $\chi = 0.5$ (curve 7). Hence an increase in the temperture facilitates the reorientation of the system under the action of the field.

Comparison of the maximum angles between the director and the field for bend and twist deformations at $T^* = 1.0$ (Fig. 2, curves 1 and 6) shows that these curves coincide with each other to within the error of the simulation. This result is not unexpected. It follows from the symmetry of the interaction potential (1). It is obvious that the same curve would also be obtained for a splay deformation.

It is interesting to follow the deviation of the director from the direction specified by the walls in different layers of the liquid-crystal film. This dependence is shown in Fig. 3 for different values of the magnetic field at $T^* = 1.0$ for the case of a twist deformation. We see that for small values of χ, the dependence of the angle θ on the number of the layer is smooth and the deflection of the director from the direction of easy orientation is relatively small. However as the field increases the angle θ rapidly reaches saturation and the director is lined up along the field (this occurs when $\chi = 0.5$, even in the second layer). The dependence obtained in the simulation qualitatively agrees with experiment.

Curves 8 and 9 in Fig. 3 show the results of the continuum theory, obtained for a plane layer with a homeotropic orientation and strong coupling with the surfaces. For near-critical fields, the theory predicts a sinusoidal variation of the angle θ, and for large fields this dependence is significantly distorted [12]. The maximum angle θ is about 80° for $H = 2H_c$ and 90° for $H = 4H_c$. Comparison of the theory with the simulation results shows that they agree qualitatively for small ($H \simeq H_c$) and large ($H >> H_c$) fields (in our model the critical field corresponds to the value $\chi \simeq 0.07$ at $T^* = 1.0$). However the maximum angle of 80° was observed in the simulation for $H \simeq 1.7H_c$ and 90° was observed for $H \simeq 2.4H_c$.

Figure 4 shows the dependence of the order parameter $\langle P_2 \rangle$ on the number of the layer for the same set of runs as in Fig. 2. When $H < H_c$ the quantity $\langle P_2 \rangle$ smoothly decreases as the distance of the layer from the orienting surface increases. However when χ is relatively large, the order parameter $\langle P_2 \rangle$ decreases sharply at first, and then rapidly increases up to a value ~0.7 (curves 5 and 6). This behavior can be explained by noting the competing effects of the magnetic field and the orienting surfaces. It is interesting that the order parameter $\langle P_2 \rangle$ of the fifth layer (farthest from the wall) for $\chi \approx 0.40$ approximately corresponds to $\langle P_2 \rangle$ of the first layer for $\chi \approx 0$. This indicates that an external field which reorients the director does not significantly change the degree of orientational order of the system (at least for the field strengths studied here). Figure 4 also shows molecular dynamics data for a more realistic model of a nematic film, consisting of ellipsoidal particles with five degrees of freedom (curve 1, for $\chi = 0$). Curves 1 and 2 are qualitatively similar, and correspond to zero field.

We compare our results with the experimental data on the Frederiks transition. When a magnetic field acts on a liquid crystal, reorientation of the director is observed for fields of order $H_c \sim 10^4$ Oe [8]. Quantum-mechanical calculations show that in this case the interaction energy of a molecule with the field is a quantity of the order of 10^{-5}°K, which is much smaller than the thermal energy. However for macroscopic volumes the interaction energy (which is proportional to the number of molecules) is much larger than the thermal energy, and a collective rotation of the molecules under the action of the field is observed. The value of the energy constant ε of the model potential can be estimated from the value of the molecular field constant A in the Maier–Saupe potential: $\varepsilon \sim A \sim 4.5\ T_c$, where T_c is the temperature of the nematic–isotropic liquid phase transition. It is known that for many nematics T_c is about 300°K, and hence we obtain a value of order 10^3°K for ε. Therefore the parameter χ must be of order 10^{-8}, whereas the simulations show that the critical field corresponds to $\chi \sim 10^{-1}$.

This significant difference can be explained by noting that the Frederiks effect is a macroscopic phenomenon and involves a collective rotation of the molecules. The external field does not significantly affect the relative orientation of neighboring molecules or the order parameter. Hence when we compare the simulation results with data for real nematics, we must interpret the term "particle" not as an individual molecule, but as a molecular cluster consisting of a large number of molecules. Then in calculating the quantity χ we must take into account the number of molecules in a cluster.

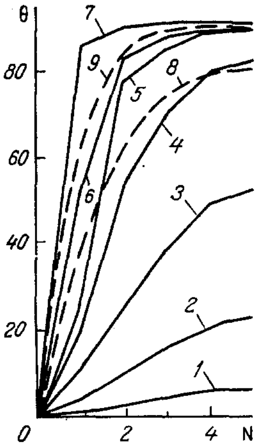

Fig. 3

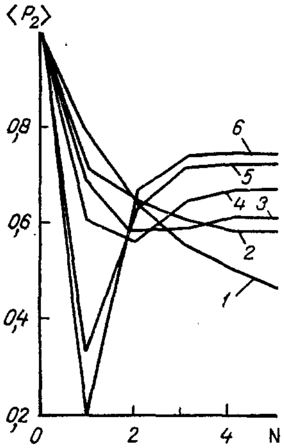

Fig. 4

Fig. 3. Angle between the director and the easy axis of orientation as a function of the distance from the bounding surfaces for different values of the external field (bend deformation, $T^* = 1.0$): 1) $\chi = 0.07$; 2) 0.08; 3) 0.10; 4) 0.20; 5) 0.30; 6) 0.40; 7) 0.50; 8), 9) continuum theory for $H = 2H_c$ and $4H_c$, respectively.

Fig. 4. Dependence of the orientational order parameter on the layer number for different values of the external field (bend deformation, $T^* = 1.0$); 1) molecular dynamics data for a model of a nematic film consisting of ellipsoidal particles ($\chi = 0$) [1]; 2) $\chi = 0$; 3) 0.10; 4) 0.20; 5) 0.40; 6) 0.50.

This approach is in correspondence with the modern interpretation of the Maier–Saupe theory, which considers only the long-range attractive forces. It successfully describes the orientational phase transition in nematics, even though it is known that short-range repulsive forces play an important role in liquid crystals. This contradiction has been explained by proposing the existence of highly ordered clusters in nematics. These clusters also exist near the transition into the nematic phase [13]. The clusters, whose structure is determined by the repulsive forces, are less anisotropic than individual molecules, and so the short-range anisotropic respulsive forces are less significant for the orientational phase transition. Hence the pair potential used in the Maier–Saupe theory describes the interaction between clusters of molecules, and not between individual molecules. An indirect demonstration of the correctness of this approach is the success of the Maier–Saupe theory. There is also more direct support of the existence of clusters from the data of x-ray and neutron scattering experiments [13].

NOTATION

U_{ij}, pair interaction potential; ε_{ij}, energy parameter of the potential; P_2, second-order Legendre polynomial; β_{ij}, angle between the symmetry axes of particles i and j; Δt^*, reduced time step; T^*, reduced temperature; U_i^s, energy of a particle in the surface field; α_i, angle between the symmetry axis of a particle and one of the coordinate axes; U_i^f, energy of a particle in the external field; γ_i, angle between the field direction and the molecular symmetry axis; χ, dimensionless parameter determining the strength of the interaction of a particle with the field; $\Delta\chi$, anisotropy of the diamagnetic susceptibility of the particle; H, magnetic field; K, elastic constant; d, thickness of the liquid crystal film; $Q_{\alpha,\beta}$, second rank orientation tensor; $u_{\alpha i}$, $u_{\beta i}$, components of a unit vector determining the symmetry axis of a molecule; $\delta_{\alpha\beta}$, Kronecker delta; λ_1, λ_2, λ_3, n_1, n_2, n_3, eigenvalues and corresponding eigenvectors of the orientation tensor; $\langle P_2\rangle$, orientational order parameter; θ, angle between the director and the axis of easy orientation; $H_{c,i}$, critical field corresponding to the i-th elastic constant (K_i); N, number of the layer.

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PRECRITICAL NUCLEUS FORMATION IN A LIQUID WITH SURFACTANT

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Equilibrium states of a liquid containing dissolved gas and a surfactant are considered. It is shown that the presence of the surfactant makes possible appearance of stable gas (and vapor) bubbles at pressures exceeding the saturation pressure.

Many Newtonian liquids and their mixtures with a dispersed heavy impurity have significantly non-Newtonian relaxation properties. Thus, after sudden compression of a mixture of glycerine containing a dissolved gas with a quartz filament a significant reduction in pressure at constant mixture volume can be observed, with the characteristic time of this process comprising tens of minutes [1]. On the other hand, after a sudden volume extension isochoric pressure increase occurs in the mixture. Similar volume creep properties appear in multicomponent liquid mixtures, for example, heavy petroleums with a high paraffin content and asphaltene-resin fractions [2-4]. Pressure processing of homogeneous and inhomogeneous media, in particular, petroleums, also leads to changes in their rheologic properties [5]. Relaxation phenomena of this type are also met in studies of the thermodynamic properties of various gas—liquid systems [6, 7]. In the latter case one can clearly distinguish two relaxation processes having different time scales. The first of these, with a characteristic time of the order of seconds or minutes, is related to conventional liberation or absorption of the free gas phase, while the second, with a characteristic time sometimes reaching several hours, is apparently of the same nature as the volume relaxation of gas—liquid solutions mentioned above. These phenomena usually prove to be more strongly expressed if the system has a well-developed liquid—solid boundary surface. Such conditions can be produced not only by introducing solid particles into the liquid, but also when a liquid saturates a porous body, which latter case is of greater practical importance [8].

On the whole the situation appears as though formation of macroscopic vapor or gas bubbles occurs even in the precritical region, i.e., in region of stable existence of the degasified liquid phase or at pressures above the saturation pressure for liquids containing dissolved gases. Although the physical cause and corresponding mechanisms of such precritical development of new phase volumes remain unclear at present, the phenomenon itself has been used effectively in technology, especially in the petroleum industry [4, 8]. In the present study it will be assumed that liquid media manifesting these effects contain all possible impurities, and a model will be proposed to explain the origin of these effects, thus defining paths for their further study and practical application. As follows from the model,

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