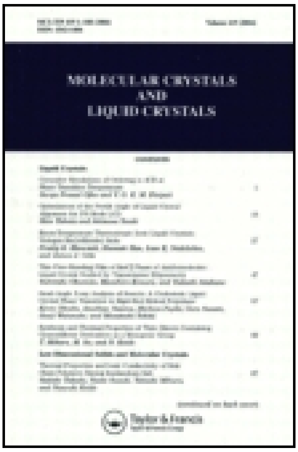

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Statistical-Mechanical Model for Calculating Equilibrium Properties of Systems Composed of Interacting Ellipsoidal Molecules at a Solid Surface

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Statistical-Mechanical Model for Calculating Equilibrium Properties of Systems Composed of Interacting Ellipsoidal Molecules at a Solid Surface

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We have proposed a statistical-mechanical theory of a nematic liquid crystal composed of ellipsoidal molecules interacting through angle-dependent nonseparable potentials in contact with a solid interacting surface. The theory takes into account pair intermolecular correlations. Within the framework of the theory the concept of an average force potential is used to develop a truncation procedure for arbitrary equation of the chain. The closed system of integral equations for average force potential is similar to that used by Brook-Levinson and Zakharov for uniform nematic phase. These equations are solved numerically and results are given for the cubic closed packing ellipsoidal molecules interacting through Berne–Pechukas potentials. Although the calculations have been made for the nematic liquid crystal, the general approach can be applied to any liquid crystalline phase.

Keywords: Mean force potentials, system of the nonlinear integral equations

1 INTRODUCTION

A solid crystalline surface would be able to induce the additional orientational ordering or disordering in the liquid crystals (LCs) which close to the one. Surface effects in LCs have mainly been studied in nematic liquid crystals (NLCs). The question how long can promoting perturbation be propagated into the bulk has been a long-standing one.[1–3] In recent years extensive experimental work has been devoted to the understanding of the microstructure of LCs close to the surface.[2–3] From theoretical viewpoint the first attempt to account for these results was made by de Gennes[4] who developed the phenomenological a Landau-type theory of NLCs for describing the perturbations induced by the nematic-isotropic and nematic-vapour interfaces. Another series of theoretical studies has been made with molecular models.[5–9] The first molecular model for the nematic-isotropic and nematic-wall interfaces have been developed by Telo da Gama[5] who have used simple anisotropic hard core interactions between elongated molecules. The more realistic Gay-Berne model potential in the framework of the generalized mean-field theory has been used by Tijpto-Margo and Sullivan.[9] In that theories the orientational intermolecular correlations are neglected everywhere except for the excluded volume region in which the molecules penetrate into each other. On the other hand, an alternative approach based on the assumption that the probability density of the distribution of a selected group of molecules was considered under some restriction on the distribution of the other molecules. A first step toward such an approach was recently taken by Osipov and Hess.[8] In order to study strong orientational correlations they employed the approximation of perfect local orientational order which implies that long molecular axes are approximately parallel with group of neighbor molecules. It should be noted, however, that this approximation can be applied only to systems composed of molecules interacting through nonspecific short-range potentials. There is another microscopic approach to the description of the system composed of interacting ellipsoidal molecules[11] based on the method of conditional distribution (MCD) originally proposed by Rott.[12] This is a kind of self-consistent field theory which is based on the model structures (cells, cell clusters, holes). In the first approximation all the states of the system, where each molecular cell is occupied by a molecule are taken into account. In each approximation, reduced distribution functions can be introduced. They obey infinite chains of integro-differential equations. The problem of truncation of these chains was specifically solved within the framework of the method.[11] The initial chains of integro-differential equations were initially transformed to the form of integral equations with respect to the so-called average-force potentials. Then truncation at the lowest-order equation preserved binary correlations. It should be emphasized that the MCD is quite different from the variational self-consistent field method first applied by Kirkwood to the cell method. The essence of the former approximation is that one considers two cells and averages over the states of one to determine the self-consistent field. Further, the method takes exact account of a wide range of many-body correlations. The remaining correlations can, at least in principle, be taken into account by means of the following approximations of the method. In this paper, using only statistical-mechanics and a series of well-defined approximations we present a theory for the equilibrium nematic phase composed of interacting ellipsoidal molecules near the interacting solid wall.

2 METHOD

We consider a one-component fluid consisting of ellipsoidal molecules with coordinates $i \equiv (q_i, e_i)$ describing molecular positions q_i and orientations $e_i(|e_i| = 1)$ of prolite ellipsoids of revolution, of major semiaxis $\sigma_\parallel$ and minor semiaxis $\sigma_\perp$, in contact with the solid planar wall. The x-axis of the coordinate frame is chosen to be normal to the wall and nematic molecules occupy the half-space $x > 0$, and the space-fixed z-axis chosen so that the nematic director lies in the YZ plane.

One use the statistical scheme in which the total volume V of the system of N molecules is divided into N equal cells, $v = V/N$, every cell being occupied by a molecule. The nature of these cells can, in principle, be chosen arbitrarily; in practice, it would be most satisfactory to choose cells sufficiently small so that the probability of two molecules occupying a single cell is negligible. By integration of the Gibbs canonical distribution, a set of functions $F_i(\mathrm{i}), F_{ij}(\mathrm{ij})$, etc., is introduced in order to define the densities of the probability for the molecules to be found about the positions

$m = W_m$ ($W_m = v_m \otimes \alpha_m, \alpha_m$ is the volume associated with orientations $m = (i,j)$. Using mean-force potentials (MFP)[12,13] we can present the above mentioned functions the form

$$F_i(i) = Q^{-1} \exp\{-\beta \varphi_i(i)\}, \tag{1}$$

$$F_{ij}(ij) = Q^{-2} \exp\{-\beta(\Phi(ij) + \varphi_{ij}(ij)\} \tag{2}$$

where $Q = \int d(i) \exp\{-\beta \varphi_i(i)\}, \int_i d(i) \equiv \int_v dq_i \int_\alpha de_i, \Phi(ij)$ is the interaction potential of two molecules, $\varphi_i(i)$ and $\varphi_{ij}(ij)$ are the mean force potentials (MFPs) an are sums of the forms

$$\varphi_i(i) = \sum_{j \neq i}^{N} \varphi_{i,j}(i), \qquad \varphi_{ij,l}(ij) = \sum_{l \neq ij}^{N} \varphi_{ij,l}(ij). \tag{3}$$

Of course, the $\varphi_{i,j}(i)$ will also depend on the distance of the i cell from the solid wall. The term in the sums (3) are given by

$$\nabla_i \varphi_{i,j}(i) = \int_j d(j) \nabla_i \Phi(ij) F_{ij}(ij)/F_i(i), \tag{4}$$

$$\nabla_i \varphi_{ij,l}(ij) = \int_l d(l) \nabla_i \Phi(il) F_{ijl}(ijl)/F_{ij}(ij). \tag{5}$$

The subscripts before the comma correspond to the MFP dependence on the positions of the molecules; those after the comma correspond to the average states. Using now the relations between the single and binary functions which follow from their definition, we have

$$\int_i d(i) F_i = 1, \quad F_i(i) = \int_j d(j) F_{ij}(ij), \tag{6}$$

The two particle function is related to the three particle function by an integral relation, etc. Below we take into account the first two functions of the infinite hierarchy; these corresponds to taking into account only pair correlations between molecules. In order to close this system of equations, we decompose the mean force potentials into irreducible parts.[11-13] In the case considered here we have

$$\varphi_{ij,l}(ij) = \varphi_{i,l}(i) + \varphi_{j,l}(j) + \xi_{ij,l}(ij), \tag{7}$$

If the irreducible part of the potential is set equal to zero:

$$\xi_{ij,l}(ij) = 0, \tag{8}$$

which corresponds to neglecting three-particle and higher-order correlations, the expression for the binary function takes the form

$$F_{ij}(ij) = \exp(\beta(\varphi_{i,j}(i) + \varphi_{j,i}(j))) K(ij) F_i(i) F_j(j), \tag{9}$$

where $\beta^{-1} \equiv \theta = kT$ is temperature and $K(ij) \equiv \exp(-\beta \Phi(ij))$. The exponential factor in this expression reflects the correlation between molecules and distinguishes the approach used here from the mean field approximation. Substitution of (9) into (6) leads to a closed system of nonlinear integral equations (NIE) for the MEPs.

$$\exp(-\beta\varphi_{i,j}(i)) = \int_j d(j)\exp(\beta\varphi_{j,i}(j))K(ij)F_j(j). \tag{10}$$

Knowing the solution of this system one can compute the microscopic characteristics of the LC (expressed in terms of the one-particle and two-particle functions) and also the macroscopic characteristics, which can be expressed in terms of the free energy of the system. The free energy per molecule is given by

$$f = -\beta^{-1}\ln\int_i d(i)\exp\{-\beta\varphi_i(i)\}. \tag{11}$$

It should be mentioned that in the nematic phase the MEPs $\varphi_{i,j}(i)$ are equal for cells in the same layer, parallel to the planar wall and differ for cells in the adjacent layers, perpendicular to the wall and, theoretically, one should take into account an infinite the number of adjacent layers. But in practice, it should be taken into account a finite the number of adjacent layers and as will be shown, that MFPs decays back to its bulk values. The decay length or the number of layers in which MFPs are different from ones in the bulk depends strongly on an external field due to the solid wall, pairwise interaction potential and intermolecular correlations.

3 METHOD OF SOLVING NON-LINEAR INTEGRAL EQUATION

For a system which is non-uniform only in the x-direction the solution of Eq. (10) can be written in the form

$$\varphi_{i,j}(i) = \varphi_{i,j}^{(o)}(i) + h_{i,j}(x), \tag{12}$$

where $\varphi_{i,j}^{(o)}(i)$ is the nematic equilibrium MFP and $|h_{i,j}(x_i)| \ll |\varphi_{i,j}^{(o)}(i)|$. Now our purpose is to find the $\varphi_{i,j}^{(o)}(i)$ which satisfies Eq. (10) and the $h_{i,j}(x_i)$, equation for which will be derived in the next section. The solution of Eq. (10) for the nematic phase is based upon the fact that the one-particle function $F_i(i)$ is a function of $\cos\theta_i$, where θ_i is the angle between the z_i axis and long molecular axis of the ith molecule. The most general form of $F_i(i)$ is

$$F_i(i) = \psi_i(\cos\theta_i)/\int_i d(i)\psi_i(\cos\theta_i), \quad \psi \equiv \exp\{-\beta\psi^{(o)}\}. \tag{13}$$

The method of solution of the five-dimensional problem (10) is most complicated. It is convenient to rewrite (10) in the form

$$\psi_{i,j}(Q_i) = \left(\int_{W_j} dQ_j K(Q_i,Q_j)\psi_j(Q_j)\psi_{j,i}^{-1}(Q_j)\right)\bigg/\int_{W_j} dQ_j\psi_j(Q_j), \tag{14}$$

where Q_j is a vector in the five-dimensional space $W_j = v_j \times \Omega_j$. The solution can be found using successive approximations calculated from the formula

$$\psi_{i,j}^{[N+1]}(Q_i) = (\psi_{i,j}^{[N]}(Q_i)\biggl(\int_{W_j} dQ_j\, K(Q_i, Q_j)\psi_j^{[N]}(Q_j)/\psi_{j,i}^{[N]}(Q_j)\biggr)\bigg/\int_{W_j} dQ_j \psi_{\mathrm{j}}^{[N]}(Q_j)\biggr)^{1/2} \quad (15)$$

and the solution does not depend on the intial approximation. The basic difficulty in solving the equation is that the algorithm (15) requires the successive evaluation of five-dimensional integrals.

We apply the method of I. M. Sobol[14] based on the functions of Haar, calculating the multi-dimensional integrals

$$\int_0^1 dx_1 \cdots \int_0^1 dx_n f(x_1 \cdots x_n) \approx (1/N) \sum_{\alpha=0}^{N-1} f(Q_\alpha), \quad (16)$$

where q_α are points uniformly (mod 1) distributed in n-dimensional unit cube. These points belong to an LP_τ-sequence, N is the number of points. This sequence is fixed and the error in the calculation of a multidimensional integral with this approach is about $R = O(N^{-1}\ln^n N)$. Our calculations were executed using $N = 100$. For case with $N = 200$, the difference between the potentials $\psi_{i,j}^{[100]}$ and $\psi_{i,j}^{[200]}$ in the nematic phase $\delta = |\psi_{i,j}^{[100]} - \psi_{i,j}^{[200]}|/|\psi_{i,j}^{[200]}|$ for $Q_i \in W_i$ is about 0.1%. The cells form a simple cubic structure with six nearest neighbours, which were also taken into account in the calculations. This restriction was dictated by the computer available for the study. The implementation of the algorithm (15) for Eq. (14) was done as follows. The initial approximation was chosen to be $\psi_{i,j}^{[0]}(Q_i) = \psi_i^{[0]}(Q_i) = 1$. Then the integral on the right-hand side of (15) was calculated according to (16) with help of a LP_τ sequence. This procedure was repeated for all six neighbours of the particle in cell i. The coordinate Q_i in the (15) was chosen such that $\psi_{i,j}^{[1]}(Q_i)$ would be calculated at the points forming the same stationary LP_τ sequences as that used in the evaluation of the integrals with the initial approximation $\psi_{i,j}^{[0]}(Q_i)$. Then $\psi^{[1]}(Q_i)$ was calculated by simple multiplication of $\psi_{i,j}^{[0]}(Q_i)$. The procedure was then iterated until a given accuracy was achieved, were the translational invariance of the total potential was taken into account.

4 DERIVATION OF THE LINEARIZED INTEGRAL EQUATION FOR SMALL H-EXPANSION

The natural way to study the "small" solution of $h_{i,j}(x_i)$ is connected with linearization of the nonlinear functional

$$\exp(-\beta h_{i,j}(x_i)) \approx 1 - \beta h_{i,j}(x_i). \quad (17)$$

Using now the notation $\psi_{i,j}(i) \equiv \exp(-\beta \varphi_{i,j}^{(0)}(i))$, we come to the linearized integral equation for "small" perturbation $h_{i,j}(x_i)$

$$\begin{aligned} 1 - \beta h_{i,j}(x_i) = \biggl(\int_j d(j)\,\psi_j(j)\cdot(1 - \beta\,\psi_{i,j}(i)\cdot K(ij)\cdot(h_j(x_j) \\ - h_{j,i}(x_j))\biggr)\bigg/\psi_{j,i}(j))\bigg/\biggl(\int_j d(j)\,\psi_j(j)\cdot(1 - \beta\, h_j(x_j))\biggr), \quad (18) \end{aligned}$$

where $h_j(x_j)=\sum_{j\neq i}h_{i,j}(x_j)$. The function $\psi_{i,j}(i)$ is the MFP for uniform nematic phase and jsatisfy the Equation (10). We split up the volume V into molecular layers parallel to the solid plane, and ascribe a number n to each layer. In each of these layers there are N_n molecules which occupied single cells. The all MFPs belong to each layer are equal and changing with a variable x_i and a number n. In principle, of course, this system of linear integral equations is infinite, but in the bulk fluid $h_{i,j}(x_i)=0$, and in any application this system must be truncated after a finite number of disturbed layers. If we suppose further that $h_{i,j}(x_i)=\alpha_{i,j}x_i$, we can simplify Eq. (18) and to extend the "analytical theory". We have

$$\alpha_{i,j}x_i=\beta^{-1}-(\beta^{-1}A-(\alpha_j-\alpha_{j,i})\,C(i))/(A-\beta\,\alpha_j\,B), \tag{19}$$

where $A=\int_i d(i)\psi_i(i)$; $B=\int_i d(i)x_i\psi_i(i)$; $C(i)=\psi_{i,j}^{-1}(i)\int_i d(j)K(ij)\psi_j(j)x_j\psi_{ji}^{-1}(j)$, $\alpha_j=\sum_{j\neq i}\alpha_{j,i}$. We get an infinite set nonlinear algebraic of equations. The general solution of this system cannot be given. However, an important special solution can be obtained. Let n is number of disturbed layers. In this case the last Equation in (19) may be rewritten as

$$\alpha_{n-1,n}=\beta^{-1}(x_i^{-1}+A/B), \tag{20}$$

so long as $\alpha_n=\alpha_{n-1,n}$. Now, it is clear that the next equation in (19) can be expressed in terms of $\alpha_{n-1,n}$ as

$$\alpha_{n-2,n-1}=(Z(i)\,\beta^{-1}\,\alpha_{n-1,n})^{1/2}, \tag{21}$$

where $Z(i)=(B-C(i))/(\beta\,x_iB)$. Using (21) and (20), one obtains after some manipulation recursion relation for $\alpha_{j,j+1}$;

$$\alpha_{j,j+1}=Y_{j+1,j+2}+(Y_{j+1,j+2}^2+4Z(i)\,\alpha_{j+1,j+2})^{1/2}, \tag{22}$$

where $Y_{j+1,j+2}=(x_i(A-\beta\,B\,\alpha_{j+1,j+2})+B)/(2x_i\beta\,B)$, and $0\leqslant j\leqslant n-2$, and

$$C(i)=\begin{cases}C_0(i), & j=0,\\ C(i), & j\neq 0.\end{cases} \tag{23}$$

Here we have defined the new parameter $C_0(i)$ as in (19), but use the solid-LC potential $\Phi(x_i)$ instead of the liquid-liquid potential $\varphi(ij)$. Knowing the $\alpha_{i,i}$ one can compute the full solution $\exp(-\beta\psi_{i,j}(i))=\psi_{i,j}(i)\prod_{j\neq i}\exp(-\beta\alpha_{i,j}x_i)$, and surface free energy

$$f_s=f-f_v=\theta\left(\ln\int_i d(i)\exp(-\beta\,\varphi_i(i))-\ln\int_i d(i)\exp(-\beta\,\varphi_i^{(0)}(i))\right) \tag{24}$$

5 MODELS OF THE MOLECULAR INTERACTIONS

The kernel of the integral Equation (10) is determined by the molecular interaction potential. We chose the interaction potential of two molecules in the form[15]

$$\Phi(e_i,e_j,e_{ij})=\frac{4\,\varepsilon_0\varepsilon(e_i,e_j)}{\sigma^2(e_i,e_j,e_{ij})}\left\{\left\{\frac{\sigma_0\sigma(e_i,e_j,e_{ij})}{q_{ij}}\right\}^{12}-\left\{\frac{\sigma_0\sigma(e_i,e_j,e_{ij}}{q_{ij}}\right\}^{6}\right\} \tag{25}$$

which is constructed from the Lifshits-Mac Langhlin theory. The parameters in the potential are orientation dependent; $\varepsilon(e_i, e_j)$ is the well depth and $\sigma(e_i, e_j, e_{ij})$ is the intermolecular separation at which the attractive and repulsive terms cancel. The functional dependence of this distance is

$$\sigma(e_i, e_j, e_{ij}) = \left\{ 1 - \frac{\chi}{2}\left(\frac{(e_i\cdot e_{ij} + e_j\cdot e_{ij})^2}{(1+\chi e_i\cdot e_j)} + \frac{(e_i\cdot e_{ij} - e_j\cdot e_{ij})^2}{(1-\chi e_i\cdot e_j)} \right) \right\}^{-1/2}, \tag{26}$$

and the depth of the well as

$$\varepsilon(e_i, e_j) = \left(1 - \chi^2 (e_i\cdot e_j)^2 \right)^{-1/2}, \tag{27}$$

here $q_{ij} = q_i - q_j$, is the distance between the molecular centers, e_i, e_j are unit vectors giving the orientation of the two molecules i and j, $e_{ij} = q_{ij} / |q_{ij}|$, ε_0 and σ_0 are the energy and size parameters of the potential. The shape parameter, χ, is

$$\chi = (\sigma_{\parallel}^2 - \sigma_{\perp}^2)/(\sigma_{\parallel}^2 + \sigma_{\perp}^2), \tag{28}$$

where $\sigma_{\parallel}$ is separation when the molecules are end-to-end and $\sigma_{\perp}$ that when they are side-by-side. The molecule-wall interaction is denoted by[16]

$$\Phi(e_i, x_i) = \frac{2\pi}{3}\frac{\varepsilon_w}{\sigma_w^2}\left(\frac{2}{15}\left(\frac{\sigma_0\sigma_w}{x_i}\right)^9 - \left(\frac{\sigma_0\sigma_w}{x_i}\right)^3 \right). \tag{29}$$

The parameters in the potential are also orientation dependent:

$$\begin{aligned} \varepsilon_w(e_i) &= \varepsilon_{0w}(1 - \chi^2 e_{i,z}^2)^{-1/2}, \\ \sigma_w(e_i) &= \{ 1 - \chi e_{i,x}^2/(1 - \chi^2 e_{i,z}^2) \}^{-1/2}, \end{aligned} \tag{30}$$

where ε_{0w} is a constant which we shall identify shortly, and x_i designates the distance from the wall to the molecule i, $e_i = (e_{i,x}, e_{i,y}, e_{i,z})$.

6 RESULTS AND DISCUSSION

If there is any interaction between the solid and the molecules of the fluid each solid surface has an effect not only on the structure of the fluid near it but also on the thermodynamic properties. The question how long this effect propagate for some distance into the fluid has been of strong research interest. To test the practical utility of ideas described in this paper, it is necessary to have detailed computer simulation data on the structure of orientationally ordered systems. Such data are lacking at present. Our calculations were carried out with the values of the potential parameters of the corresponding values for PAA: $\sigma_0 = 5.01$ Å, $\varepsilon_0/k = 520$ K, and surface parameter $\varepsilon_{0w} = 5.0\ \varepsilon_0$; $0.5\varepsilon_0$. This system is characterized by reduced parameters: the reduced density $\rho^* = \rho\sigma_0^3$, the reduced temperature $\beta^{-1} \equiv \theta = (kT/\varepsilon_0)$ and the anisotropy parameter χ. A nematic liquid's orientational order is characterized by the value of a nematic order parameter (OP) $\eta = \langle P_2(\cos\theta_i)\rangle$, where $P_2(\cos\theta_i)$ is the Legendre polynomial of order 2, and angular brackets mean $\langle\cdots\rangle = \int d(i)\, F_i(i)\,(\cdots)$. The calculation of the OP η shows (Figure 1) that it decreases with increasing temperature and the

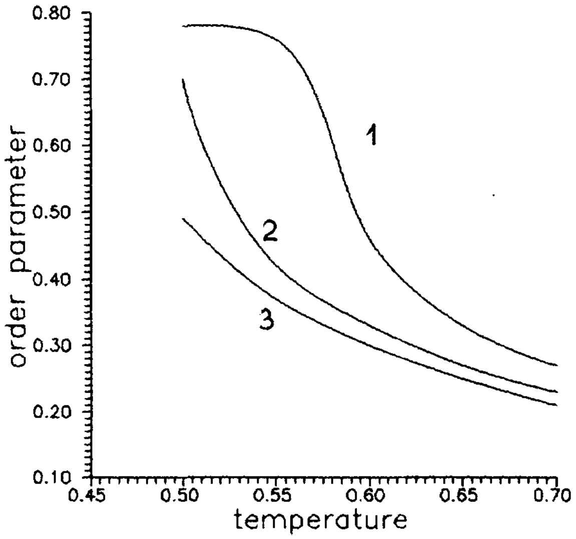

FIGURE 1 Temperature dependence of the order parameter η in the bulk for different values of the ellipticity parameter $\gamma = \sigma_{\parallel}/\sigma_{\perp} = 3.0$ (curve 1), 2.5 (curve 2), 2.0 (curve 3) and for reduced density $\rho^* = \sigma_0^3/v = 0.2$.

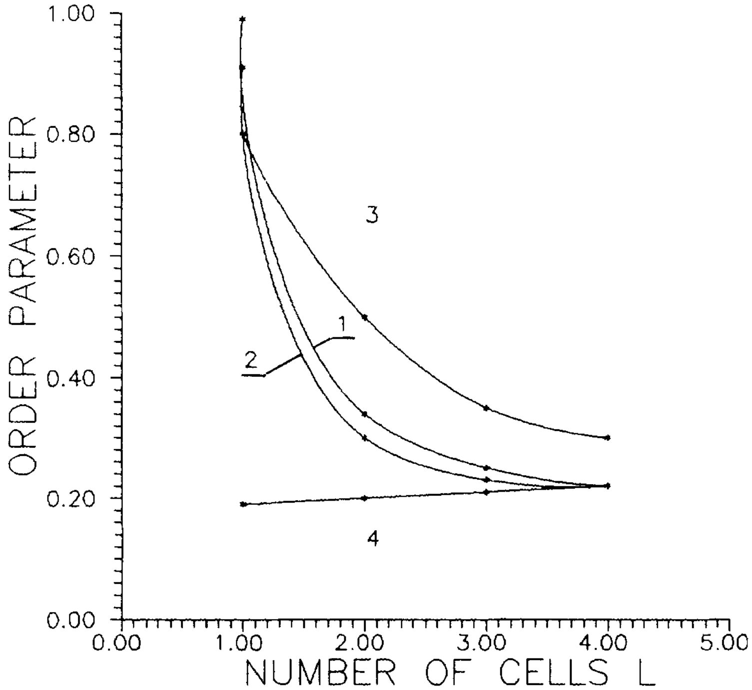

FIGURE 2 Dependence of the order parameter $\eta(L)$ on the number of cells L from the wall for $\gamma = 3.0$ and the reduced density $\rho^* = 0.2$ and the reduced temperatures $\theta = (kT/\varepsilon_0) = 0.75$ (curve 1); 0.827 (curve 2) for $\varepsilon_{0_w} = 5.0\ \varepsilon_0$ and the reduced temperature $\theta = 0.75$ and $\varepsilon_{0_w} = 0.5\ \varepsilon_0$ (curve 4). MD simulations data at the $\theta = 0.75$ are plotted as curve 3 (Ref. 14).

rate of decreasing strongly depend on the ellipticity parameter $\gamma = \sigma_{\parallel}/\sigma_{\perp}$. The orientational structure the nematic phase at the interacting surface also can be characterized by the order parameter $\eta(L) = \langle P_2^{(L)}(\cos\theta_i)\rangle$ as a function of the number of cells L or the distance from the wall. These calculations are plotted in Figure 2 for various temperatures θ (in units of kT), parameters $\varepsilon_{0_w} = 5.0\varepsilon_0; 0.5\varepsilon_0$, anisotropy parameter $\chi = 0.8$ and the reduced density $\rho^* = 0.2$. It found that the order parameter $\eta(L)$ decrease with the growth of the value L. $\eta(L)$ is expected to vary rapidly (typically over two or three cells) between the *OP* $\eta(1)$ and η_b (η_b is the bulk order parameter). The values of the *OP* $\eta(1)$ decrease with increasing temperature and the order profile become less "sharp". The most rigorous test of the theory would be a comparison to the molecular dynamics OP $\eta(L)$ for the same pair potential. Such computer experiment data are reported in.[16] Generally, the agreement between the calculated values and the computer experimental data is reasonable. The surface free energy f_s/ε_0 can be calculated using the expression (24). The dependence of the scaled f_s/ε_0 on the reduced temperature θ at a fixed density is plotted in Figure 3. One can readily see from the figure that the surface free energy decreases with increasing temperature for the case of the strong interaction between the solid wall and nematic phase ($\varepsilon_{0_w} = 5.0\varepsilon_0$) and increases with increasing temperature for the case of the weak interaction ($t_{0_w} = 0.5\varepsilon_0$). The ellipticity parameter γ was varied between 2 and 3 in the calculations.

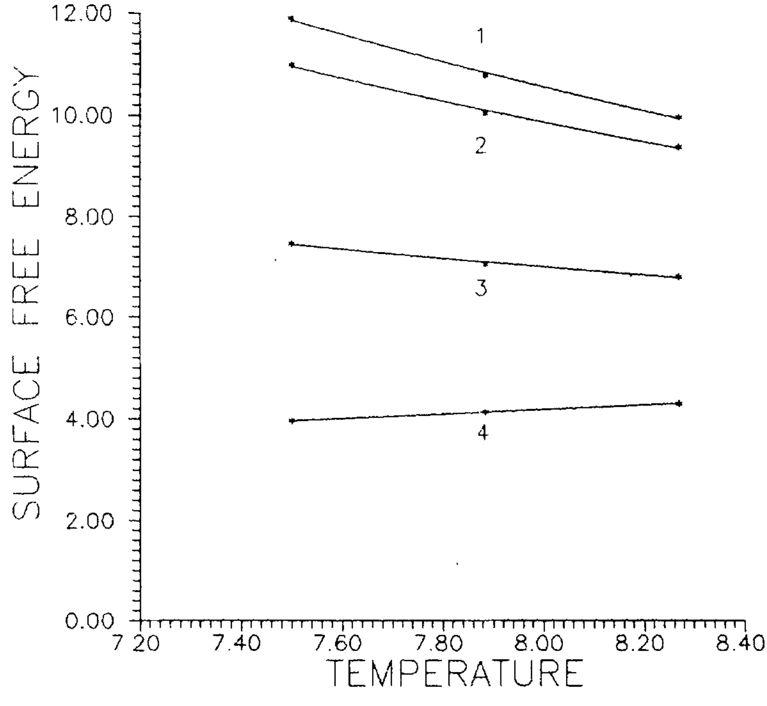

FIGURE 3 Dependence surface free energy f_s/ε_0 on the reduced temperature $\theta = (kT/\varepsilon_0) \times 10$, for reduced density $\rho^* = 0.2$ and for a number of parameters $\gamma = \sigma_{\parallel}/\sigma_{\perp} = 3.0$(curve 1); 2.5 (curve 2); 2.0 (curve 3) for $\varepsilon_{0_w} = 5.0\varepsilon_0$ and $\gamma = 3.0$ (curve 4) for $\varepsilon_{0_w} = 0.5\varepsilon_0$.

References

1. B. Jerome, *Rep. Prog. Phys.*, **54**, 391 (1990).
2. R. G. Horn, J. N. Israelachvili and E. Perez, *J. de Phys.*, **42**, 39 (1981).
3. R. G. Horn and J. N. Israelachvili, *Chem. Phys. Lett.*, **71**, 192 (1980).
4. P. G. de Gennes, The Physics of Liquid Crystals, (Oxford; Clarendon, 1974).
5. M. M. Telo da Gama, *Mol. Phys.*, **52**, 611 (1984).
6. T. Sluckin and A. Poniewierski, In Fluid Interfacial Phenomena, Ed. C. A. Croxton (Wiley, Chichester, 1986).
7. H. Kimura and H. Nakano, *J. Phys. Soc. Japan*, **54**, 1730 (1985).
8. R. Holyst and A. Poniewierski, *Phys. Rev.*, **A38**, 5227 (1988).
9. B. Tjipto-Margo and D. Sullivan, *J. Chem. Phys.*, **88**, 6620 (1988).
10. M. A. Osipov and S. Hess, *J. Chem. Phys.*, **99**, 4181 (1993).
11. A. V. Zakharov, *Physica* **A175**, 327 (1991); E. T. Brook-Levinson, A. V. Zakharov and V. B. Nemtsov, *J. de. Phys.* (France) 2,2075 (1992).
12. L. A. Rott, Statistical Theory of Molecular Systems. (Nauka, Moscow, 1979); L. A. Rott and V. S. Vikhrenko, *Fortschr. Phys.*, **23**, 133 (1975).
13. A. V. Zakharov, *Physica* **A166**, 540 (1990).
14. I. M. Sobol, SIAM *J. Number. Anal.*, **16**, 4213 (1979).
15. J. Berne and P. J. Pechukas, *J. Chem. Phys.*, **56**, 4213 (1972).
16. A. L. Tsykalo and A. D. Bagment, *Acta Phys. Polonica.*, **A55**, 111 (1975).