

Conditional distribution function approach to the theory of the solid–nematic–fluid interface

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A statistical-mechanical theory which takes into account translational-translational, orientational-orientational, and mixed correlations, based upon the method of conditional distribution functions, is applied to calculations of the order parameters and surface free energy of a system composed of interacting ellipsoidal molecules near an interacting wall. The calculations have been carried out for cubic close packing with the nearest-neighbor Gay-Berne intermolecular potential and with a (9-3)-like orientation-dependent molecule-wall interaction. The theory shows that the number of surface layers which must be taken into account depends more on the character of intercell correlations in the system than on the direct wall-nematic interaction. The equilibrium order parameter and surface free energy profiles at the solid–nematic–fluid interface have been calculated. It is found that the number of surface layers for the case of a strong interaction between the solid wall and nematic phase and for the case of a weak one is the same and equal approximately four.

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I. INTRODUCTION

The surface properties of liquid crystals (LCs) have been a subject of intense interest for many years [1]. Anchoring phenomena are especially interesting due to their technological importance in the fabrication of various electro-optic devices. Recent theoretical studies have shed significant light on interfacial phenomena in nematic-liquid crystals (NLCs) [2–8]. The first molecular model for the nematic-wall interface was developed by Telo da Gama [2], who used a Maier-Saupe type of anisotropic pairwise potential while the solid was modeled by an impenetrable wall which exerts an anisotropic external potential on the fluid molecules. Another kind of microscopic theory which takes into account anchoring transitions at LC surfaces in the framework of the Fowler approximation has been used by Teixeira and Sluckin [5]. The more realistic Gay-Berne intermolecular potential has been used by Sullivan and co-workers [3,4], who have studied orientational alignment and nematic wetting at the free liquid-vapor interface in the framework of a generalized mean-field theory. A similar approach has also been used by Osipov and Hess [6], who have developed a general density functional theory for the interfacial properties of NLCs and expressed the coefficients of the Landau–de Gennes expansion for the free energy of the nematic surface in terms of the direct correlation function. The existing molecular theories [2–7] of inhomogeneous systems are based mainly on the so-called generalized mean-field approximation, in which all intermolecular correlations are neglected.

Recently a kind of Bethe theory, which takes account of intercell pair correlations for describing NLC systems composed of interacting ellipsoidal molecules near an interacting wall, has been proposed [8]. In the framework of that theory, which is based on the concept of average force potentials [9,10], the influence of the interacting

wall on the order parameter and surface free energy has been calculated. However, in Ref. [8] the influence of the wall was considered as a small perturbation on the bulk values of the average force potentials, which is not likely to be valid in the case of a strong wall-molecule interaction.

In the present paper, I make an attempt to combine the previous [8] advantages of integral equation theory and of the cell model approach to construct a statistical-mechanical theory for calculating equilibrium properties of NLCs near an interacting wall, which will be applicable to the case of a strong wall-molecule interaction.

The plan of this paper is as follows. A description of the model is given in Sec. II, the method of solving the resulting system of nonlinear integral equations is presented in Sec. III, the intermolecular potential is described in Sec. IV, results of the numerical calculations are given in Sec. V, and finally I summarize my main results and conclusions in Sec. VI.

II. MODEL

I consider a one-component fluid consisting of molecules with coordinates $i \equiv (\mathbf{q}_i, \mathbf{e}_i)$ describing molecular positions \mathbf{q}_i and orientations \mathbf{e}_i ($|\mathbf{e}_i| = 1$) of prolate ellipsoids of revolution, of major semiaxis σ_{\parallel} and minor semiaxis σ_{\perp} , respectively, in contact with a solid planar wall. The x axis of the coordinate frame is chosen to be normal to the wall, and the nematic molecules occupy the half-space $x \geq 0$. The space-fixed z axis is chosen so that the nematic director lies in the xz plane. Of course, in the general case the orientation of the director for each layer should be calculated from the condition of minimizing the Helmholtz free energy. However, here I will assume homogeneous anchoring.

One uses a statistical scheme in which the total volume V of the system of N molecules is divided into n molecular layers parallel to the solid wall. In layer L there are N_L cells, so that $N = \sum N_L$, and the volume of each cell is $v = V/N$. The model which is used here assumes that every cell is occupied by a molecule and thus the number of cells equals that of molecules, which seems reasonable for a condensed system. The potential energy associated with the N particles is a sum of potentials $U = \sum_{i \neq j} \Phi(ij) + \sum_i \Phi(i)$, where $\Phi(ij)$ is the intermolecular pair potential and $\Phi(i)$ is the molecule-wall potential. By integration of the Gibbs canonical distribution, a set of functions $F_L(i), F_{LL}(ij), F_{LK}(ij)$, etc., is introduced in order to define the probability densities for the molecules to be found at the coordinates i, i and j , etc. [8–10]. Below I take into account only the first two kinds of functions of the infinite hierarchy, the singlet function $F_L(i)$ which defines the probability density for a molecule to be found at the coordinates i inside a cell of volume v , which belongs to the layer L , and the binary functions $F_{LL}(ij)$ and $F_{LK}(ij)$ which define the joint probability densities for two molecules to be found at the coordinates i and j inside two different cells, belonging to the same layer L , or to different layers L and K , respectively. Using mean force potentials (MFPs), I can present the above-mentioned functions in the form

$$F_L(i) = Q_L^{-1} \exp\{-\beta\varphi_L(i)\}, \quad (1)$$

$$F_{LL}(ij) = Q_L^{-2} \exp\{-\beta[\Phi(ij) + \varphi_{LL}(ij)]\}, \quad (2)$$

$$F_{LK}(ij) = \{Q_L Q_K\}^{-1} \exp\{-\beta[\Phi(ij) + \varphi_{LK}(ij)]\}, \quad (3)$$

where L, K are the layer numbers, respectively, and

$$Q_L = \int_L d(i) \exp\{-\beta\varphi_L(i)\}, \quad \int_L d(i) \equiv \int_w d\mathbf{q}_i d\mathbf{e}_i.$$

Here $\beta \equiv (kT)^{-1}$ is the inverse temperature and $w = v \otimes \alpha$, where α is the volume associated with orientations. The integration is over the volume of a representative cell in layer L . The functions $\varphi_L(i)$, $\varphi_{LK}(ij)$, and $\varphi_{LL}(ij)$ are the singlet and binary mean force potentials belonging to the indicated layers. These are given by sums of the form

$$\varphi_L(i) = \sum_{j \neq i} \varphi_{i,j}(i), \quad i \in L, \quad (4)$$

$$\varphi_{LL}(ij) = \sum_{l \neq ij} \varphi_{ij,l}(ij), \quad i \in L, \quad j \in L, \quad (5)$$

$$\varphi_{LK}(ij) = \sum_{l \neq ij} \varphi_{ij,l}(ij), \quad j \in K, \quad i \in L. \quad (6)$$

Here $\varphi_{i,j}(i)$ and $\varphi_{ij,l}(ij)$ are the mean force potentials: $\varphi_{i,j}(i)$ is the singlet mean force potential energy of a molecule in the i th cell due to a molecule in the j th cell, averaged over the state of the latter. Similarly, $\varphi_{ij,l}(ij)$

is the binary mean force potential energy of molecules i and j in the i th and j th cells due to a molecule in the l th cell, averaged over the state of the latter. The subscripts before the comma correspond to the MFP dependence on the coordinates of the molecules; those after the comma correspond to the average states. Using now the relations between the singlet and binary functions which follow from their definition, one has

$$\int_L d(i) F_L(i) = 1, \quad \int_K d(j) F_{LK}(ij) = F_L(i), \quad j \in K. \quad (7)$$

The two-particle function is similarly related to a three-particle function by an integral relation, etc. Below I take into account only the first two functions of the infinite hierarchy; this corresponds to considering only pair correlations between cells. In order to make this a closed system of equations, I separate the mean force potentials into irreducible parts [11]. In the approximation considered here, which corresponds to neglecting three-cell and higher-order correlations, I have

$$\varphi_{ij,l}(ij) = \varphi_{i,l}(i) + \varphi_{j,l}(j), \quad (8)$$

and then the expressions for the binary functions take the forms

$$F_{LK}(ij) = F_L(i) F_K(j) \exp\{\beta[\varphi_{i,j}(i) + \varphi_{j,i}(j)]\} V(ij), \quad \text{for } i \in L, j \in K \quad (9)$$

$$F_{LL}(ij) = F_L(i) F_L(j) \exp\{\beta[\varphi_{i,j}(i) + \varphi_{j,i}(j)]\} V(ij), \quad \text{for } i \in L, j \in L \quad (10)$$

where $V(ij) = \exp\{-\beta\Phi(ij)\}$. The exponential factors in Eqs. (9) and (10) reflect the correlations between cells and distinguishes the approach used here from the mean field approximation. Substitution of Eqs. (1)–(10) into Eq. (7) leads to a closed system of nonlinear integral equations (NIEs) for the MFPs [8,11],

$$\exp\{-\beta\varphi_{i,j}(i)\} = \int_M d(j) \exp\{\beta\varphi_{j,i}(j)\} V(ij) F_M(j), \quad M = L, K. \quad (11)$$

Since $\varphi_{i,j}(i)$, $\varphi_{j,i}(j)$, and $F_M(j)$ are related through Eqs. (1), (4)–(6), and (8), Eq. (11) provides a system of nonlinear integral equations for the mean force potentials. Knowing the solution of these equations, one can compute the microscopic characteristics of the LC system (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 Helmholtz free energy per molecule is given by [8,9,14],

$$f = \sum_L f_L, \quad f_L = -\beta^{-1} \ln \int_L d(i) \exp\{-\beta\varphi_L(i)\}. \quad (12)$$

It should be noted that in the case of a homogeneous system, the MFPs $\varphi_{i,j}(i)$ and $\varphi_{j,i}(j)$ do not depend on the positions of the cells i and j . This means that one reduces the system of NIEs (11) to a single equation. Note that the same system of equations appear in the Bethe approximation for a lattice model of surfactant mixtures in [12] [see Eq. (12)].

Theoretically, of course, the system of Eq. (11) is infinite, but in practice only a finite number of adjacent layers can be taken into account. It will be shown that the MFPs decay to their bulk values. The decay length, or the number of layers in which the MFPs are different from the ones in the bulk, depends strongly on the pairwise interaction and correlations between the cells. In this case, the system of Eq. (11) must be truncated after a finite number n of perturbed layers. Accordingly, one arrives at the finite system of NIEs

$$\begin{aligned} \psi_{1,k}(i) &= \int_{L_1} d(j) \tilde{V}(ij) \psi_{k,1}^{-1}(j) F_1(j), \quad k = 0, 1 \\ \psi_{1,2}(i) &= \int_{L_2} d(j) V(ij) \psi_{2,1}^{-1}(j) F_1(j), \\ &\vdots \\ \psi_{n,m}(i) &= \int_{L_m} d(j) V(ij) \psi_{m,n}^{-1}(j) F_n(j), \quad m = n - 1, \\ \psi_{n,n}(i) &= \int_{L_n} d(j) V(ij) \psi_{n,n}^{-1}(j) F_n(j), \end{aligned} \quad (13)$$

where $\psi_{L,M}(i) \equiv \exp\{-\beta\varphi_{i,j}(i)\}$ for $i \in L, j \in M$, and

$$\tilde{V} = \begin{cases} V_w(j) & \text{for } k = 0 \\ V(ij) & \text{for } k = 1. \end{cases}$$

Here $V_w(i) = \exp[-\beta\Phi(i)]$ is the kernel of the integral equation determined by the wall-molecule interaction potential which I shall identify shortly, and

$$F_L(i) = Q_L^{-1} \prod_{j \neq i} \psi_{i,j}(i), \quad i \in L, \quad (14)$$

$$F_n(i) = Q_n^{-1} \left\{ \prod_{j \neq i} \psi_{i,j}(i) \right\} \psi_{i,j}^b(i), \quad i \in n, \quad (15)$$

where $\psi_{i,j}^b(i)$ is the bulk MFP. It should be noted that in the present paper I have considered only a simple cubic structure where every cell has six neighbors. The layer $L = 0$ corresponds to the top layer of the substrate. The products over j in Eqs. (14) and (15) are over all nearest-neighbor cells of cell i .

III. METHOD OF SOLVING THE SYSTEM OF NONLINEAR INTEGRAL EQUATIONS

The method of solution of the five-dimensional problem (13) is very complicated and there are no good general

methods for solving systems of more than one nonlinear equation. Except in linear problems, obtaining solutions invariably proceeds by numerical iteration using the method

$$\psi^{(k+1)}(P_i) = \{\psi^{(k)}(P_i) \widehat{L}\psi^{(k)}(P_i)\}^{1/2}, \quad (16)$$

where $\|\widehat{L}\| \leq 1$ is the five-dimensional nonlinear integral operator defined by Eq. (13) in the space $W_i = v \otimes \alpha$, and P_i is a five-dimensional vector in that space. Cronrade (in Ref. [13]) investigated the existence and uniqueness of such solutions in one dimension. His findings can, however, be generalized to multidimensional domain as well [14]. For smoothly varying functions, good algorithms will always converge, provided that the initial guess is accurate enough. Success strongly depends on having a good initial guess for the solution $\psi(i)$, and from that point of view it is convenient to choose $\psi^{(0)}(i) = \psi^b(i)$. The procedure of construction of the bulk MFPs $\psi^b(i)$ for the nematic phase was described in Refs. [8,11]. The algorithm (16) was implemented as follows: the initial approximation was set to be $\psi_{1,k}^{(0)}(P_i) = \psi_{1,2}^{(0)}(P_i) = \dots = \psi_{n,n}^{(0)}(P_i) = \psi^b(P_i)$. Then the integrals of the right-hand side of (16) were calculated with the help of the Sobol's method [15], using the Haar functions for calculating multidimensional integrals as

$$\int_0^1 dx_1, \dots, \int_0^1 dx_n f(x_1, \dots, x_n) \approx \frac{1}{M} \sum_{\alpha=0}^{M-1} f(P_\alpha). \quad (17)$$

Here P_α 's are the points uniformly (mod 1) distributed in the n -dimensional unit cube. These points belong to a LP_τ sequence [16] and were generated by means of an LP_τ generator [15], and M is the number of points. The precision of the calculations is about $R = O(M^{-1} \ln^5 M)$, whereas for Monte-Carlo integration the analogous estimate is $\sim O(1/\sqrt{M})$.

The procedure of the calculations was repeated for all neighbors of the cells in the first n layers. The coordinates P_i in Eq. (16) were chosen such that $\psi^{(1)}(P_i)$ could be calculated at the points forming the same stationary LP_τ sequence as used in the evaluation of the integrals with the initial approximation $\psi^{(0)}(P_i)$. Then $F_L^{(1)}(P_i)$ was calculated by a simple multiplication of $\psi^{(1)}(P_i)$. The procedure was then iterated until a given accuracy was achieved. The calculations were executed using $M = 200$, which corresponds to 200^2 points of a Monte Carlo method for the same estimates of the integrals. This has been achieved owing to the fact that the LP_τ sequences possess a more uniformly distributed set of M points in the five-dimensional unit cube than independent random sequences.

IV. MODEL OF MOLECULAR INTERACTIONS

The kernel of the integral equations (13) is determined by the molecular interaction potential. This was chosen to be the Gay-Berne [17] intermolecular potential

$$\Phi(\mathbf{q}_{ij}, \mathbf{e}_i, \mathbf{e}_j) = 4\epsilon_0 \epsilon(\mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij}) \left\{ \left[\frac{\sigma_0}{|\mathbf{q}_{ij} - \sigma(\mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij}) + \sigma_0|} \right]^{12} - \left[\frac{\sigma_0}{|\mathbf{q}_{ij} - \sigma(\mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij}) + \sigma_0|} \right]^6 \right\}, \quad (18)$$

where $\mathbf{e}_i, \mathbf{e}_j$ are, respectively, unit vectors along the molecular symmetry axes, \mathbf{q}_{ij} the vector between the molecular centers, and $\mathbf{e}_{ij} = \mathbf{q}_{ij}/|\mathbf{q}_{ij}|$. The potential energy parameter $\epsilon(\mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij})$ and size parameter $\sigma(\mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij})$ are angle-dependent functions defined in Eqs. (3), (4), and (8)–(10), respectively, of Ref. [17]. The former depends on the molecular elongation or length-to-breadth ratio γ (denoted $\sigma_{\parallel}/\sigma_{\perp}$ in Ref. [17]), while $\epsilon(\mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij})$ depends on both γ and another parameter which can be used to adjust the ratio between the end-to-end and side-by-side well depth, denoted ϵ_l/ϵ_s . In our calculations the parameters μ and ν of Ref. [17] have been fixed at the values 1 and 2, respectively. The molecule-wall interaction is given by [18]

$$\Phi(\mathbf{e}_i, x_i) = \frac{2\pi}{3} \frac{\epsilon_w}{\sigma_w^2} \left[\frac{2}{15} \left(\frac{\sigma_0}{\sigma_w x_i} \right)^9 - \left(\frac{\sigma_0}{\sigma_w x_i} \right)^3 \right]. \quad (19)$$

The parameters in this potential are also orientation dependent, and are given by

$$\epsilon_w = \epsilon_{ow} (1 - \chi^2 e_{i,z}^2)^{-\frac{1}{2}}, \quad (20)$$

$$\sigma_w = \left(1 - \frac{\chi e_{i,x}^2}{1 - \chi^2 e_{i,z}^2} \right)^{-\frac{1}{2}}, \quad (21)$$

where $\chi^2 = (\gamma^2 - 1)/(\gamma^2 + 1)$, $\epsilon_{ow} = \epsilon \epsilon_o$, ϵ is a strength parameter, x_i denotes the distance from the wall to the molecule i , and $\mathbf{e}_i = (e_{i,x}, e_{i,y}, e_{i,z})$.

V. RESULTS OF THE NUMERICAL CALCULATIONS

The equilibrium order parameter (OP) and surface free energy (SFE) profiles at the solid–nematic–fluid interface corresponding to the layers can be expressed by means of the functions $\psi_L(i) = \prod_{j \neq i} \psi_{i,j}(i)$, for $i \in L$ as

$$\eta(L) = \langle P_2^{(L)}(\cos \theta_i) \rangle = \int_L d(i) P_2(\cos \theta_i) F_L(i), \quad (22)$$

$$f_s(L) = -\beta^{-1} \ln \frac{\int_L d(i) \psi_L(i)}{\int_b d(i) \psi_i^b(i)}, \quad f_s = \sum_L f_s(L), \quad (23)$$

respectively, where $P_2(\cos \theta_i)$ is the Legendre polynomial of order 2, θ_i is the polar angle or the angle between the

long axis of the molecule and the director, $F_L(i)$ is the singlet function corresponding to the L th layer, satisfying the system of NIE (13), and $\psi_i^b(i)$ is the full bulk MFP. In the case considered here, only one orientation of the director for each layer, parallel to the surface (homogeneous anchoring) has been investigated. It is reasonable to assume homogeneous anchoring due to the fact that this orientation minimizes the wall potential $\Phi(\mathbf{e}_i, x_i)$. In the general case, of course, one should investigate the question of which orientation of the director $\gamma_{\text{tilt}} = \cos^{-1}(\mathbf{n} \cdot \mathbf{k})$, where \mathbf{n} is the director and \mathbf{k} is the normal vector to the surface, minimizes the Helmholtz free energy.

In the present theory I have not investigated the question of the separate influence of biaxiality on the behavior of the surface free energy and assumed that the surface structure is uniaxial. Our system is characterized by reduced parameters: the reduced volume $v^* = v/\sigma_o^3$, the reduced temperature $\beta^{-1} = kT/\epsilon_o$, and anisotropy parameter γ . The latter was chosen to be $\gamma = 3$. One can readily see from Fig. 1 that the number of perturbed layers for the case of a strong interaction between the solid wall and nematic phase ($\epsilon_{ow} = 5\epsilon_o$) (Fig. 1, curves 1, 2, and 3) and in the case of weak interaction ($\epsilon_{ow} = 0.5\epsilon_o$) (Fig. 1, curve 4) is the same and equal approximately four. The

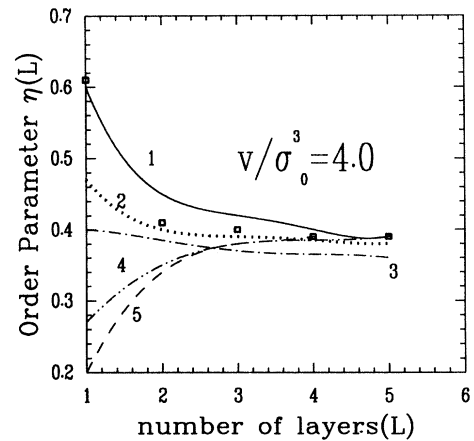


FIG. 1. Dependence of the order parameter $\eta(L)$ on the number of cells L from the wall, for $\gamma = 3.0$, reduced volume $v/\sigma_0^3 = 4.0$, in the case of a strong interaction $\epsilon_{ow} = 5.0\epsilon_o$, for different values of the reduced temperature $\beta^{-1} \equiv kT/\epsilon_o = 0.5$ (curve 1), 0.6 (curve 2), 0.7 (curve 3), and in the case of a weak interaction $\epsilon_{ow} = 0.5\epsilon_o$ for $\beta^{-1} = 0.5$ in the framework of the present theory (curve 4) and by linearization of the nonlinear MFPs [8] (curve 5). Open squares indicate points calculated by means of molecular dynamics [18] at the reduced temperature $\beta^{-1} = 0.5$ and the same volume.

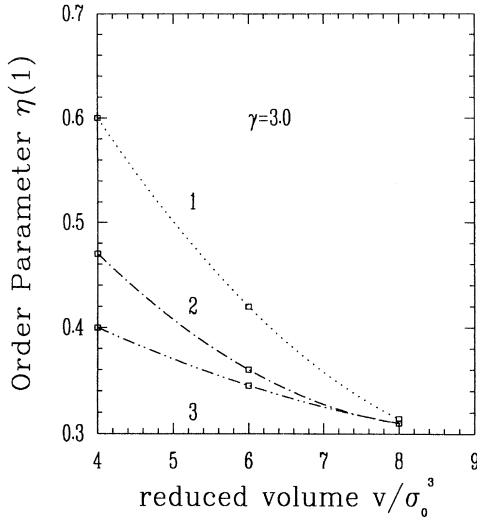


FIG. 2. Volume dependence of the order parameter $\eta(1)$ for the first layer in the case of a strong interaction $\epsilon_{ow} = 5.0 \epsilon_0$ and $\gamma = 3.0$, for different values of the reduced temperature: $\beta^{-1} = 0.5$ (curve 1), 0.6 (curve 2), and 0.7 (curve 3).

direct interaction has a strong influence on the behavior of the molecules only in the layer nearest to the wall. It is seen that the OP $\eta(L)$ varies rapidly with growth of the value L (typically over two or three cells) to the value of the bulk order parameter. In the previous calculation of the OP $\eta(L)$ by linearization of the MFP's [8], the number of distinct layers which must be taken into account equals approximately three, whereas in the present

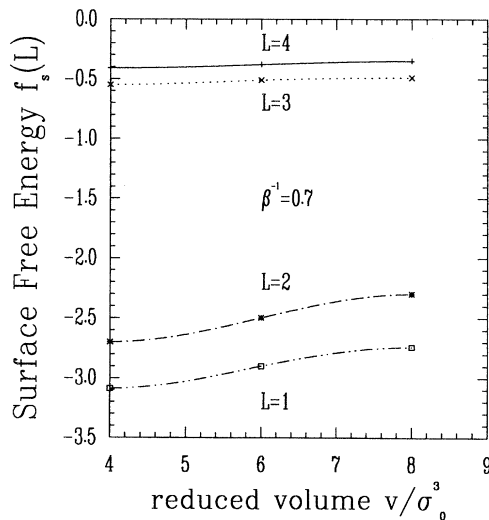


FIG. 3. Volume dependence of the surface free energy $f_s(L)/\epsilon_0$ for the case of a strong interaction $\epsilon_{ow} = 5.0\epsilon_0$, $\gamma = 3.0$ and reduced temperature $\beta^{-1} = 0.7$ for the first (curve 1), second (curve 2), third (curve 3), and fourth layers (curve 4).

theory four distinct layers are needed, and the degree of ordering near the solid surface is greater. The value of the OP $\eta(1)$ decreases with increasing temperature, as shown in Fig. 2. The most rigorous test of the theory would be a comparison to the molecular dynamics OP $\eta(L)$ for the same pair potential and wall potential. Such computer simulation data have been reported [18]. Generally, agreement between the calculated values and the computer data are reasonable, see Fig. 1 (open squares indicate points calculated by MD at the reduced temperature $\beta^{-1} = 0.5$ and reduced volume $v/\sigma_0^3 = 4.0$). The dependence of the scaled SFE $f_s(L)/\epsilon_0$ for layer L on the reduced volume v/σ_0^3 is plotted in Fig. 3 for the case of a strong interaction ($\epsilon_{ow} = 5\epsilon_0$) and for scaled temperature $\beta^{-1} = 0.7$. The SFE decreases with increasing volume and temperature in both cases.

VI. CONCLUSION

In this paper a statistical-mechanical theory has been developed which takes into account the translational-translational, orientational-orientational, and mixed correlations for describing the equilibrium order parameter and surface free energy profiles at the solid-nematic-fluid interface. The calculations have been carried out for a cubic close packed system composed of molecules interacting by means of the Gay-Berne potential and with a (9-3)-like orientation-dependent molecule-wall interaction. The calculations show that the number of distinct layers which must be taken into account depend mainly on the character of cell correlations. It should be mentioned that a similar problem for the same nonuniform system has been solved in the framework of linearization of the nonlinear functional [8] $\varphi_{i,j}(i) = \varphi_{i,j}^b(i) + h_{i,j}(i)$, where $|h_{i,j}(i)| \ll |\varphi_{i,j}^b(i)|$. In that case, one has a system of linear integral equations in addition to the bulk MFPs, but, in the case of the strong interaction ($\epsilon_{ow} = 5.0\epsilon_0$), it is questionable whether can one use a such decomposition. Here I have extended the conditional distribution function approach to the case of a strong wall-molecule interaction. A similar picture appears in a solid crystal system composed of spherical molecules interacting by mean of a Lennard-Jones potential at a solid-vacuum interface. In that case, the bulk values of the concentration of vacancies is reached at the fourth or third layer from the interface [19,20].

In future work, I will investigate the possibility of different preferred orientations of the director, based on minimizing the Helmholtz free energy.

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