PHYSICAL REVIEW E VOLUME 55, NUMBER 3 MARCH 1997

Computer simulation study of the free surfaces of a liquid crystal model

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(Received 23 September 1996)

We present a computer simulation study of the liquid-vapor interface of the Gay-Berne fluid model for a range of temperatures above and below the vapor-isotropic liquid-nematic triple point. The molecular elongation is $\kappa=3$, and two values of the energy anisotropy parameter ($\kappa'=1$ and 1.25) are considered. Our results show that an excess of orientational order is developed at the isotropic liquid-vapor interface. The degree of orientational order grows as the temperature is lowered to its value at the triple point. Molecules in the nematic phase orient themselves parallel to the interface. Combining our results with those obtained previously for $\kappa=3$ and $\kappa'=5$, we conclude that a change in the preferred orientation at the isotropic free surface takes place when κ' is decreased (for a fixed value of κ), as the alignment changes from perpendicular to parallel. The behavior of the surface tension and the adsorption of the order parameter at the isotropic free surface close to the triple point are compatible with the existence of wetting at the isotropic liquid-vapor interface by the nematic phase. [S1063-651X(97)14902-9]

PACS number(s): 61.30.Gd, 61.30.Cz, 68.10.Cr

I. INTRODUCTION

Fluids of strongly anisotropic molecules, such as liquid crystals (LC's), exhibit a rich interfacial behavior, including wetting, layering, and orientational transitions. Some of these surface effects have been observed experimentally at interfaces involving simple fluids. On the other hand, LC's may exhibit characteristic interfacial effects as a result of the orientational degrees of freedom. For example, it is well established that in the absence of external fields, the orientation in the bulk nematic phase is determined by the orientation of the molecules close to the interface [1].

In the particular case of the nematic free surface (interface between nematic and vapor phases below the triple point), the molecular orientation at the interface is not universal, and depends strongly on the details of the intermolecular potential [1]. Experimentally, this preferred orientation is found to be parallel, perpendicular, or tilted with respect to the interface. Moreover, this orientation may change as the temperature is varied.

A number of theories have been proposed to explain the wealth of experiments on interfacial effects at the nematic free surface [2–5]. These theories have undoubtly contributed to a better understanding of the microscopic mechanisms which control the interfacial properties of LC's. However, a full theoretical description is still lacking. Moreover, some of these approaches arrive at contradictory conclusions [3]. Considering the success of computer simulation in other areas of liquid state theory, it is hoped that this approach may shed some light on an understanding of the interfacial behavior of LC's. It is important to recall that computer simulation yields information on physical magnitudes that are difficult to measure in the laboratory, and may constitute a strong test of the validity of different theoretical approaches.

Although computer simulations of interfacial properties of simple and complex fluids have been reported, there is a striking scarcity of simulations for systems involving LC phases. The first simulation studies of inhomogeneous systems including liquid and vapor phases in coexistence were based on the Lennard-Jones fluid model (see Ref. [6] for a critical review of these works). These studies were mainly devoted to the calculation of the surface tension and its long-tail correction, as it is possible to compare the simulation data with those obtained experimentally for noble gases. Subsequent works extended these studies to deal with the interfacial properties of mixtures of simple fluids (see, for example, Refs. [6–8]).

The first attempt to simulate the interfacial properties of molecular fluids was made by Thompson and Gubbins [9–11]. These studies considered fluids of moderate anisotropic (diatomic) molecules interacting through a two-site Lennard-Jones potential. As expected, no liquid crystal phases were found due to the low degree of molecular anisotropy, although a preferred molecular orientation at the (isotropic) liquid-vapor interface was reported. Additionally, orientational changes at the interface were predicted on theoretical grounds by an explicit consideration of a (sufficiently strong) quadrupolar term in the intermolecular potential model [12,13].

A large number of simulation studies of the interfacial properties of different fluid models has emerged since the pioneering work of Thompson and Gubbins. Due to its practical applications and biological interest, most of these works have focused on the free surface properties of water or mixtures containing water [14].

To the best of our knowledge, there has been only one set of works in which the study of the free surface of nematic liquid crystal models has been addressed from the perspective of computer simulation. These works were based on the

Lebwhol-Lasher model [15–17]. Within this lattice model, the study of the nematic free surface was performed by considering a nematic film confined between two hard walls. It is important to note that this model *does not* induce any preferential orientation at the interface, as it does not couple the translational and rotational degrees of freedom [18]. Moreover, the (trivial) distance dependence in this model does not allow the virial route to be applied for evaluating the surface tension, which has to be calculated using indirect methods. The simulation results indicated that the liquid at the interface was less ordered than the bulk nematic, i.e., that the free surface induced orientational disorder. Wetting of the nematic free surface by the isotropic phase was found.

More recently, we reported a simulation study of the liquid-vapor interface of the Gay-Berne (GB) fluid model [19] for certain values of the anisotropic potential parameters. Considering the general features of the corresponding phase diagram [20], no direct coexistence between nematic and vapor phases is expected for this choice of parameters. Consequently, the simulation study reported in Ref. [19] was restricted to the interfacial properties of *orientationally disordered* phases. However, it has been recently shown [21] that, upon a suitable choice of anisotropic parameters, the GB fluid model presents a triple point at which vapor (V), isotropic (I) liquid, and nematic (N) liquid phases coexist simultaneously. For temperatures below this triple point, the liquid phase in coexistence with the V phase is orientationally ordered (nematic). The work in Ref. [21] was limited to the study of bulk phases in the neighborhood of the V-I-N triple point, and no interfacial properties were reported. The study of the inhomogeneous system is addressed here. As far as we are aware, this is the first simulation study of the nematic-vapor interface based on a continuous microscopic model.

The remaining of this paper is organized as follows. In Sec. II we describe briefly the intermolecular model used in this work. In Sec. III we give details on the simulation technique used for studying the liquid-vapor (L-V) interface. The results concerning the interfacial properties of the system are presented in Sec. IV. The final section contains a discussion about the main results obtained in this work.

II. GAY-BERNE MODEL

Within the context of the GB model [22], molecules are viewed as rigid units with axial symmetry. Each individual molecule is represented by a vector $\mathbf{r}$, which defines the position of its center of mass with respect to an (arbitrary) fixed reference frame, and a unit vector $\mathbf{u}$, which defines the direction of the main symmetry axis of the molecule. The interaction energy between a pair of molecules i-j is given by

$$U_{ij}=4\epsilon(\hat{\mathbf{r}}_{ij},\mathbf{u}_i,\mathbf{u}_j)\left[\left(\frac{\sigma_0}{r_{ij}-\sigma(\hat{\mathbf{r}}_{ij},\mathbf{u}_i,\mathbf{u}_j)+\sigma_0}\right)^{12}-\left(\frac{\sigma_0}{r_{ij}-\sigma(\hat{\mathbf{r}}_{ij},\mathbf{u}_i,\mathbf{u}_j)+\sigma_0}\right)^{6}\right], \tag{1}$$

where r_{ij} is the distance between the centers of mass of molecules i and j, and $\hat{\mathbf{r}}_{ij}=\mathbf{r}_{ij}/r_{ij}$ is a unit vector along the intermolecular vector $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$. According to these definitions, σ is the distance (for given molecular orientations) at which the intermolecular potential vanishes, and is given by

$$\sigma(\hat{\mathbf{r}}_{ij},\mathbf{u}_i,\mathbf{u}_j)=\sigma_0\left\{1-\frac{\chi}{2}\left[\frac{(\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_i+\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_j)^2}{1+\chi(\mathbf{u}_i\cdot\mathbf{u}_j)}+\frac{(\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_i-\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_j)^2}{1-\chi(\mathbf{u}_i\cdot\mathbf{u}_j)}\right]\right\}^{-1/2}, \tag{2}$$

where $\chi=(\kappa^2-1)/(\kappa^2+1)$ and $\kappa=a/b$, with a being the molecular length along the main symmetry axis, and b the cross-section diameter of the molecule. Accordingly, the parameter κ is a measure of the length-to-breadth ratio of the molecule. Values of $\kappa>1$ are appropriate for rodlike (prolate) molecules and values $\kappa<1$ correspond to disclike (oblate) molecules.

The strength of the interactions, ϵ, also depends on the relative orientations of the molecules, and takes the form

$$\epsilon(\hat{\mathbf{r}}_{ij},\mathbf{u}_i,\mathbf{u}_j)=\epsilon_0[\epsilon_1(\mathbf{u}_i,\mathbf{u}_j)][\epsilon_2(\hat{\mathbf{r}}_{ij},\mathbf{u}_i,\mathbf{u}_j)]^2, \tag{3}$$

with

$$\epsilon_1(\mathbf{u}_i,\mathbf{u}_j)=[1-\chi^2(\mathbf{u}_i\cdot\mathbf{u}_j)^2]^{-1/2}, \tag{4a}$$

$$\epsilon_2(\hat{\mathbf{r}}_{ij},\mathbf{u}_i,\mathbf{u}_j)=1-\frac{\chi'}{2}\left[\frac{(\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_i+\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_j)^2}{1+\chi'(\mathbf{u}_i\cdot\mathbf{u}_j)}+\frac{(\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_i-\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_j)^2}{1-\chi'(\mathbf{u}_i\cdot\mathbf{u}_j)}\right], \tag{4b}$$

where $\chi'=(\kappa'^{1/2}-1)/(\kappa'^{1/2}+1)$ and $\kappa'=\epsilon_1/\epsilon_2$. ϵ_1 is the minimum of the potential for a pair of parallel molecules placed side by side ($\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_i=\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_j=0$), and ϵ_2 is the minimum for a pair of parallel molecules placed end to end ($\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_i=\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_j=1$).

It can be checked that if the anisotropy parameters κ and κ' are set equal to 1, Eq. (1) reduces to the well-known Lennard-Jones (LJ) model potential with $\sigma=\sigma_0$ and $\epsilon=\epsilon_0$. Bearing this in mind, the GB potential can be considered as a generalization of the LJ model to fluids of nonspherical molecules with range and energy parameters which are orientation dependent. On the other hand, molecules interacting through the GB potential have a quasiellipsoidal shape. This is assessed by the fact that the range parameter $\sigma(\hat{\mathbf{r}}_{ij},\mathbf{u}_i,\mathbf{u}_j)$ is, to a first approximation, the contact distance between two hard ellipsoids of elongation κ with orientations $\mathbf{u}_i$ and $\mathbf{u}_j$.

In a recent study by de Miguel *et al.* [21], it was shown that the GB fluid with $\kappa=3$ and $\kappa'=1$ and 1.25 exhibits a triple point where the V, I, and N phases coexist simultaneously. The triple point temperature (in units of ϵ_0/k_B) is $T_{\mathrm{tr}}\approx0.63$ for $\kappa'=1$ and $T_{\mathrm{tr}}\approx0.54$ for $\kappa'=1.25$. As pointed out previously, these findings have motivated the present work, as they indicate that GB seems to be an appropriate potential model to study the nematic free surface

In the present study, the molecular elongation was fixed to $\kappa=3$. Two different values of the parameter κ' were considered, namely, $\kappa'=1$ and 1.25. It should be noted that for $\kappa'=1$ all configurations (for parallel molecules) are equally stable [21]. Nevertheless, the attractive interactions are still anisotropic for this value of κ', as the shape of the well depth is very nonspherical [21].

III. SIMULATION DETAILS

We have investigated the L-V interfacial properties of the GB fluid model with $\kappa=3$ and $\kappa'=1$ for temperatures in the range $0.59 \leqslant T \leqslant 0.68$ (in units of ϵ_0/k_B, where k_B is Boltzmann's constant), around the V-I-N triple point by using computer simulation. The simulations were performed using molecular dynamics at constant volume and temperature. The temperature was kept constant by rescaling the velocities each time step [23].

The simulation box was a rectangular prism of dimensions $L_x=L_y$ and L_z containing a liquid film between two vapor slices. According to this setup, the inhomogeneous system included two L-V interfaces. The initial configuration was built up at $T=0.65$ by placing a liquid slab between two empty cells. The liquid film was previously equilibrated at the coexistence density corresponding to this temperature as obtained from Gibbs ensemble simulations [21]. The system was then allowed to evolve. If the temperature of the system is below the critical temperature, as is the case for $T=0.65$ [21], the densities of both phases (liquid and vapor) will eventually reach their corresponding coexistence values. A different initial configuration was generated at a slightly lower temperature ($T=0.64$) following the same procedure. The final configuration for $T=0.65$ ($T=0.64$) was then used to study the inhomogeneous system at higher (lower) temperatures by increasing (decreasing) the value of T in steps of 0.01, in units of ϵ_0/k_B. At each temperature, the system was typically equilibrated for 150 000 time steps. Quantities of interest were calculated and averaged over 150 000 additional time steps. Simulations two or three times longer were performed for certain values of the temperature.

The total (fixed) number of particles used was $N=1728$. The dimensions of the simulation box were $L_x=L_y=15\sigma_0$ and $L_z=50\sigma_0$. Full periodic boundary conditions were considered [23]. The moment of inertia perpendicular to the main symmetry axis was set to $I=1$ in units of $(m\sigma_0^2)$, where m is the molecular mass. The intermolecular potential was truncated and shifted at a distance $r_c=4\sigma_0$. The time step used for the numerical solution of the equations of motion was $\delta t=0.0015\,(m\sigma_0^2/\epsilon_0)^{1/2}$. The system was globally displaced in the z direction (taken as the normal direction to the interface) every ten time steps in order to keep the center of mass of the system in the plane $z=L_z/2$.

In the following, all quantities are assumed to be expressed in conventional reduced units, with m, σ_0, and ϵ_0 as units of mass, distance, and energy, respectively. According to this convention, the pressure is given in units of ϵ_0/σ_0^3, the temperature in units of ϵ_0/k_B, the density in units of σ_0^{-3}, and the surface tension in units of ϵ_0/σ_0^2.

The orientational order in the system was quantified by diagonalizing the order tensor, defined as

$$Q_{\alpha\beta}=\frac{1}{N}\sum_{i=1}^{N}\tfrac{1}{2}(3u_{i\alpha}u_{i\beta}-\delta_{\alpha\beta}) \tag{5}$$

where $u_{i\alpha}$ is the α component ($\alpha=x,y,z$) of the axial unit vector of molecule i. The nematic order parameter S is defined as the ensemble average of the largest eigenvalue of the order tensor, and the director $\hat{\mathbf{n}}$ (average direction of alignment) is its corresponding eigenvector.

In order to analyze the interfacial structure, we have calculated the density, order parameters and pressure profiles by dividing the simulation box in $N_c=100$ bins (of thickness $\Delta z \approx 0.5$) along the z direction. The density profile $\rho(z_i)$ is the number density of molecules in the plane $z=z_i$. It is possible to obtain the densities of both coexisting phases and the interfacial thickness by fitting the simulation results for $\rho(z)$ to a hyperbolic tangent of the form

$$\rho(z)=\tfrac{1}{2}(\rho_l+\rho_v)+\tfrac{1}{2}(\rho_l-\rho_v)\tanh[(z-z_G)/2\delta], \tag{6}$$

where the adjustable parameters are ρ_l (ρ_v), the density of the bulk liquid (vapor) phase; z_G, the position of the Gibbs dividing surface; and δ, the interfacial thickness.

The definition of the interfacial order parameters is somewhat arbitrary. In principle, one could define an infinite set of order parameters as angular averages of appropriate linear combinations of spherical harmonics. In line with related works [3,4,18], we shall only consider the order parameters of second order which, in terms of the components of the molecular axial vectors, are explicitly given by

$$\eta(z)=\langle \tfrac{1}{2}(3u_z^2(z)-1)\rangle, \tag{7a}$$

$$\epsilon(z)=\langle 2u_y(z)u_z(z)\rangle, \tag{7b}$$

$$\nu(z)=\langle 2u_x(z)u_z(z)\rangle, \tag{7c}$$

$$\sigma(z)=\langle u_x^2(z)-u_y^2(z)\rangle, \tag{7d}$$

$$\tau(z)=\langle 2u_x(z)u_y(z)\rangle, \tag{7e}$$

where the brackets imply an angular average. In the limiting case of perfect alignment perpendicular to the interface, $\eta(z)=1$ while the other order parameters are zero. On the other hand, if all the molecules are aligned parallel to the interface, $\eta(z)=-\frac{1}{2}$, $\epsilon(z)=\nu(z)=0$, and the other two order parameters give information on the orientation of the director in the xy plane with respect to a fixed (arbitrary) reference frame.

The pressure tensor was calculated following Harashima's definition [24]

$$p_N(z)=\rho(z)T-\frac{1}{2V_c}\left\langle \sum_{i,j}{}^{(k)} z_{ij}\frac{\partial U_{ij}}{\partial z_{ij}}\right\rangle, \tag{8a}$$

$$p_T(z)=\rho(z)T-\frac{1}{4V_c}\left\langle \sum_{i,j}{}^{(k)} x_{ij}\frac{\partial U_{ij}}{\partial x_{ij}}+y_{ij}\frac{\partial U_{ij}}{\partial y_{ij}}\right\rangle, \tag{8b}$$

where p_N and p_T are the normal and transverse components of the pressure tensor, respectively. In the above expressions, V_c is the volume of each bin ($V_c=L_xL_y\Delta z$), and the symbol (k) means that the summation is restricted to those pairs of molecules (i,j) of which at least one is in the corresponding bin.

TABLE I. Results for the liquid (ρ_l) and vapor (ρ_v) densities, surface tension (γ), interfacial thickness (δ), and nematic order parameter (S) obtained from molecular dynamics simulations of a GB inhomogeneous system with $\kappa=3$ and two different values of κ'. Values for γ and S were obtained as averages over the simulation and the corresponding errors are indicated in parentheses; values for ρ_l, ρ_v, and δ were obtained by fitting the simulation density profiles to Eq. (6).

T	ρ_v	ρ_l	γ	δ	S
$\kappa'=1$					
0.68	0.238	0.0056	0.176 (52)	0.80	0.041 (11)
0.67	0.242	0.0043	0.184 (53)	0.76	0.063 (27)
0.66	0.245	0.0029	0.213 (66)	0.74	0.076 (26)
0.65	0.248	0.0027	0.242 (36)	0.72	0.086 (31)
0.64	0.252	0.0028	0.230 (50)	0.70	0.079 (26)
0.63	0.258	0.0021	0.217 (69)	0.69	0.138 (44)
0.62	0.287	0.0014	0.259 (72)	0.72	0.604 (34)
0.61	0.293	0.0006	0.299 (58)	0.67	0.656 (22)
0.60	0.298	0.0008	0.349 (76)	0.64	0.704 (13)
0.59	0.303	0.0004	0.368 (75)	0.58	0.732 (9)
$\kappa'=1.25$					
0.55	0.262	0.0010	0.254 (48)	0.61	0.062 (22)
0.51	0.300	0.0006	0.267 (76)	0.55	0.660 (16)

The surface tension γ was obtained by numerical integration according to the expression [25]

$$\gamma=\int_{z_v}^{z_l}[p_N(z)-p_T(z)]dz, \tag{9}$$

where the limits of integration refer to values in the bulk liquid and vapor phases far away from the interface. In practice, averages for the surface tension were calculated over blocks of 10 000 time steps.

IV. RESULTS

A. $\kappa=3$, $\kappa'=1$

In Table I we present the results for the coexistence densities of the two fluid phases and the interfacial thickness obtained by fitting the simulation profiles to Eq. (6). The values for the nematic order parameter S at each temperature are also included in the table. We note that all the molecules in the system were used in obtaining S from Eq. (5). Considering that in our simulations the number of molecules in the vapor phase is always much less than the number of molecules in the liquid phase, the values of S so obtained may be considered as a good estimate of the orientational order occurring in the liquid film. The results obtained for S indicate that the liquid phase undergoes an orientational transition at the vapor pressure as the temperature is decreased. For $T\leqslant 0.62$ the liquid phase that coexists with the vapor phase is nematic. This is consistent with previous results obtained by using different simulation methods [21]. The orientational order developed in the liquid film for the lower temperatures becomes noticeable in the order-parameter profiles. This point will be addressed below.

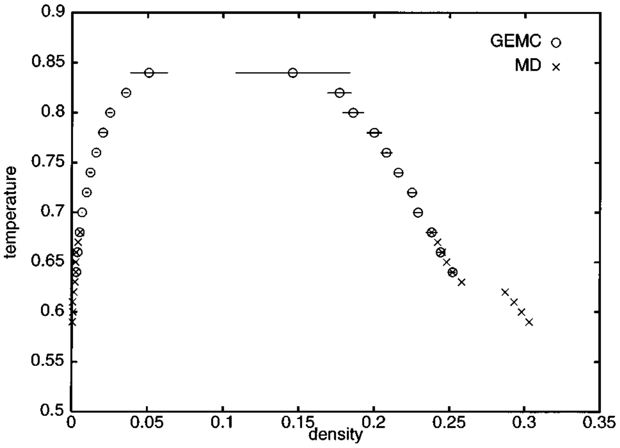

FIG. 1. Liquid-vapor coexistence curve of the GB fluid with $\kappa=3$ and $\kappa'=1$. Dots represent the vapor and liquid densities as obtained by using the Gibbs ensemble Monte Carlo (GEMC) technique (from Ref. [21]). Crosses correspond to the coexistence densities obtained from molecular dynamics (MD) simulations of an inhomogeneous system as explained in the text. The isotropic-nematic transition at the vapor pressure implies a jump on the liquid density which is clearly visible on the scale of the figure. The density is in units of σ_0^{-3} and the temperature in units of ϵ_0/k_B.

The coexistence curve in the ρ-T plane for $\kappa'=1$ is shown in Fig. 1. For completeness, the results obtained in Ref. [21] using Monte Carlo simulation in the Gibbs ensemble have also been included in this figure. It can be seen that, when data from both methods are available, they are compatible. The jump in density due to the first-order transition from I to N phases is clearly visible on the scale of this figure.

The density profile [and its corresponding fit to Eq. (6)] as well as the order parameter $\eta(z)$ of the system at $T=0.67$ are shown in Fig. 2. For this value of the temperature, the liquid phase is isotropic, as indicated by the vanishing value of η in the center of the simulation box (all the other order-parameter profiles did show no significant structure and are

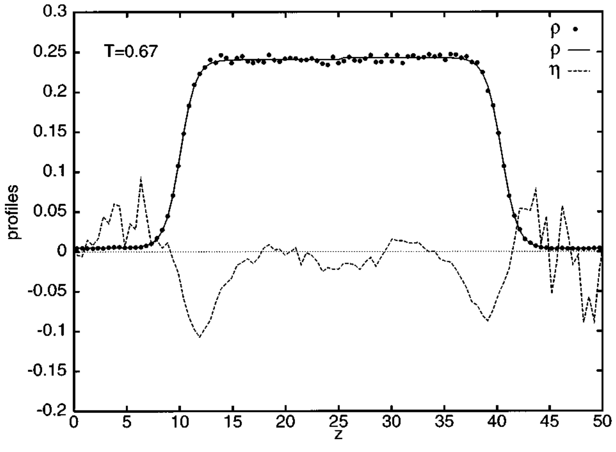

FIG. 2. Density $\rho(z)$ (dots) and order parameter $\eta(z)$ (dashed line) profiles obtained from MD simulation of an inhomogeneous GB system with $\kappa=3$ and $\kappa'=1$ at $T=0.67$. The continuous line represents the fit of the simulation density profile to Eq. (6). The z coordinate is in units of σ_0 and the density in units of σ_0^{-3}.

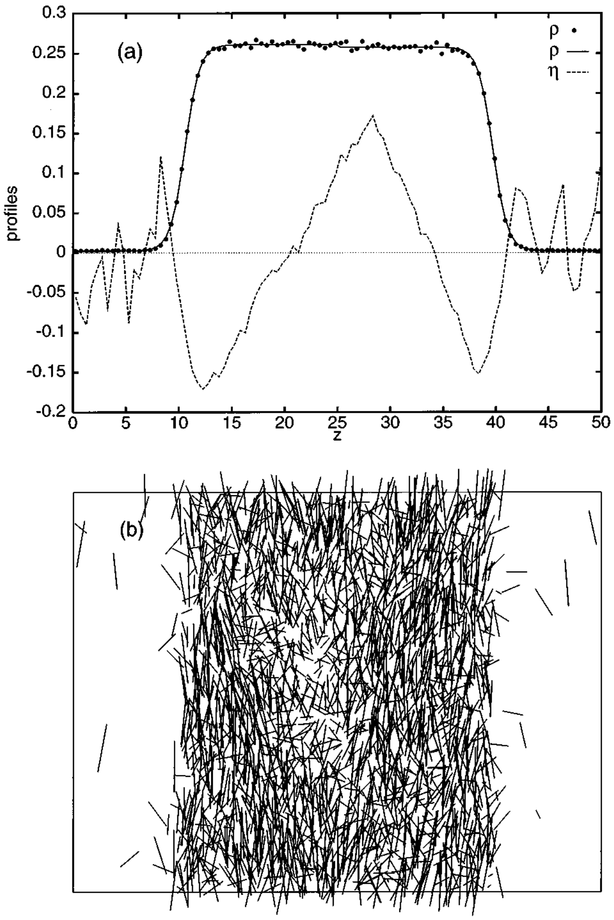

FIG. 3. (a) Density $\rho(z)$ (dots) and order parameter $\eta(z)$ (dashed line) profiles obtained from MD simulation of an inhomogeneous GB system with $\kappa=3$ and $\kappa'=1$ at $T=0.63$ (just above the triple point). The continuous line represents the fit of the simulation density profile to Eq. (6). The z coordinate is in units of σ_0 and the density in units of σ_0^{-3}. (b) Corresponding snapshot of the final configuration in the xz plane. Molecules are represented by a segment of length $1\sigma_0$ along the main symmetry axis.

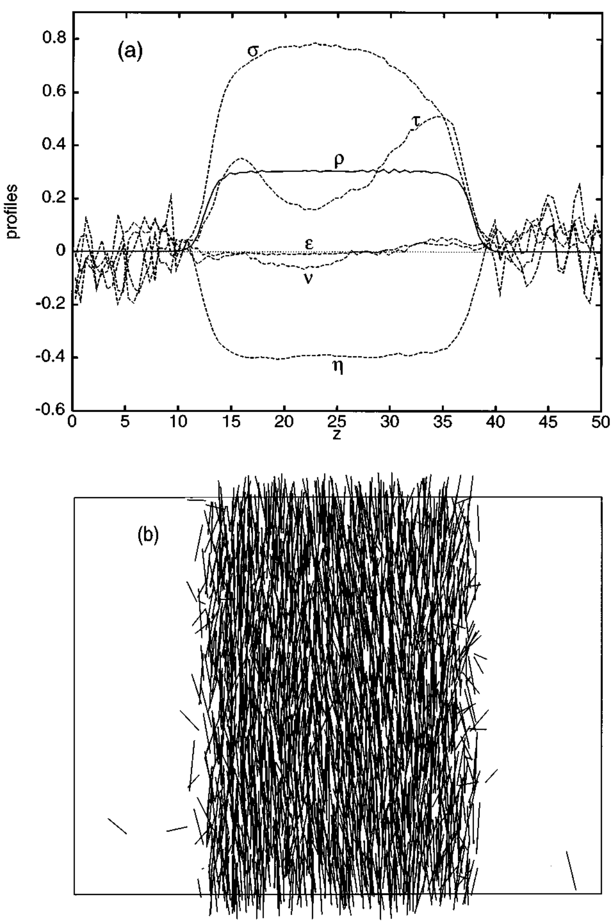

FIG. 4. (a) Density (full line) and order parameter (dashed lines) profiles obtained from MD simulation of an inhomogeneous GB system with $\kappa=3$ and $\kappa'=1$ at $T=0.59$ (below the triple point). The z coordinate is in units of σ_0 and the density in units of σ_0^{-3}. (b) Corresponding snapshot of the final configuration in the xz plane. Molecules are represented by a segment of length $1\sigma_0$ along the main symmetry axis.

not shown in the figure). The corresponding profiles for $0.65 \leqslant T \leqslant 0.68$ are qualitatively similar to those included in Fig. 2. The order parameter η shows a negative peak on the liquid side of the interface, indicating that the molecules are oriented parallel to the interface. This surface excess order is noticeable even at the highest temperature ($T=0.68$) considered in this study.

We recall that in a previous study of the GB fluid model with the same molecular elongation ($\kappa=3$) but a larger value of κ' ($\kappa'=5$), a *perpendicular* alignment was found at the I-V interface [19], although the interfacial orientational order for $\kappa'=5$ was less pronounced than that found in the present case for $\kappa'=1$. Thus we conclude that the orientation at the isotropic free surface of the GB fluid with $\kappa=3$ changes as the parameter κ' is decreased from $\kappa'=5$ to $\kappa'=1$.

As the temperature is further lowered toward the triple point ($T=0.64$ and 0.63), nematic fluctuations start to develop in the bulk liquid. This is illustrated in Fig. 3(a), where the density and order parameter η profiles at $T=0.63$ are shown. The orientational fluctuations originate, approximately, in the center of the liquid film far from the interface (as indicated by the maximum in η) and, therefore, the orientation induced by these fluctuations is not to be coupled with the orientation imposed by the interface. As for higher temperatures, the molecules tend to orient themselves parallel to the interface on the liquid side. This effect is further illustrated in Fig. 3(b), where a snapshot of the final configuration at $T=0.63$ is shown. This figure shows an apparent deficiency of molecules in the center of the liquid film. This is merely an optical effect due to local orientational fluctuations, with molecules pointing in the direction perpendicular to the plane of the figure.

For $T \leqslant 0.62$ the situation is completely different. This is illustrated in Fig. 4(a), where the simulation profiles are shown for $T=0.59$. The order parameter η has a nonzero constant value inside the liquid phase, which indicates that this phase has spontaneously developed nematic order. Moreover, the negative value of η ($\eta \approx -0.4$) constitutes a signature of the director being (approximately) contained in the xy plane. This is further corroborated by the almost vanishing values of the order parameters ϵ and ν. A similar behavior was found for all temperatures $T\leqslant 0.62$. According to the behavior of the order parameter σ in Fig. 4(a), the nematic director of the liquid phase lies almost parallel to the x axis of the simulation box at $T=0.59$ [see also Fig. 4(b)]. The orientation of the director within the xy plane was rather constant with varying temperature (for $T\leqslant 0.62$). This is just incidental, as any orientation within this plane is expected, on symmetry grounds, to be equally stable in the absence of external fields.

The order-parameter profile $\eta(z)$ changes from being negative to positive at the interface [see Fig. 4(a)], thus indicating that molecules in the vapor side of the interface are oriented perpendicular to molecules in the liquid side. This effect (that is also observed at the I-V interface of the GB model) is quite general [9–11,19], and has a simple explanation in qualitative terms [26].

B. $\kappa=3$, $\kappa'=1.25$

We have pointed out previously that the orientation at the free surface of the GB fluid with $\kappa=3$ changes from perpendicular to parallel as κ' is decreased. In a recent study [21] it was shown that there exists direct nematic-vapor coexistence for $\kappa'=1.25$ for $T\leqslant 0.54$. This prompted us to investigate the properties of the free surfaces for this value of κ'. We have simulated the L-V interface of the GB model with $\kappa=3$ and $\kappa'=1.25$ for two different values of temperature, namely, $T=0.55$ (at which the liquid is isotropic) and $T=0.51$ (at which the liquid is nematic). An initial configuration was generated for both temperatures following the same procedure as before. The total number of molecules was $N=1728$, and the simulation box dimensions were $L_x=L_y=14.91$ and $L_z=49.82$ for $T=0.55$, and $L_x=L_y=14.22$ and $L_z=48.44$ for $T=0.51$. The results obtained for the coexistence densities, interfacial thickness, and surface tension have been included in Table I. The orientation found at both I-V and N-V interfaces is similar to that found for $\kappa'=1$, i.e., the molecules are oriented parallel to the interface. According to this result, we can assess that the orientational change occurring at the isotropic free surface of the GB model with $\kappa=3$ must take place for a value of $\kappa'>1.25$.

C. Surface tension

Before discussing the results obtained for γ, we would like to comment on the behavior of the components of the pressure tensor. In Fig. 5 we illustrate the behavior of the normal and tangential components of the pressure tensor, the function $p_N(z)-p_T(z)$, and the function $\gamma(z)=\int_0^z[p_N(z')-p_T(z')]dz'$. All these curves were obtained for the GB fluid with $\kappa=3$ and $\kappa'=1$ at $T=0.62$. Plots of the different quantities shown in Fig. 5 were found to be qualitatively similar for all the temperatures considered in the present work, independently of the particular nature (nematic or isotropic) of the liquid phase.

One of the criteria used in this work to ensure that the system was well equilibrated was that $p_N(z)$ be constant (fluctuating around the bulk pressure) along the simulation box [25]. According to Fig. 5(a), this function is, indeed, constant in the vapor and liquid phases, although it exhibits larger fluctuations inside the liquid film. On the other hand, the normal component of the pressure tensor presents a well defined structure at the interface, namely, a minimum on the vapor side followed by a maximum on the liquid side. It should be noted that this structure does not make any contribution to the value of γ. This follows from the fact that the area around the maximum is approximately equal to the area around the minimum and, consequently, the contributions (opposite in sign) cancel out after integrating Eq. (9). A similar pattern was observed for all temperatures considered here, although the peak amplitudes were smaller with decreasing temperature. This observed structure should not be confused with statistical noise, as the amplitude of the peaks were significantly larger that the typical fluctuations of the pressure in the liquid phase. Moreover, this behavior in $p_N(z)$ was not ascribed to an insufficient equilibration of the system.

We attribute this effect to the criterion used for evaluating the pressure tensor [Eq. (8)]. It should be noted that there is

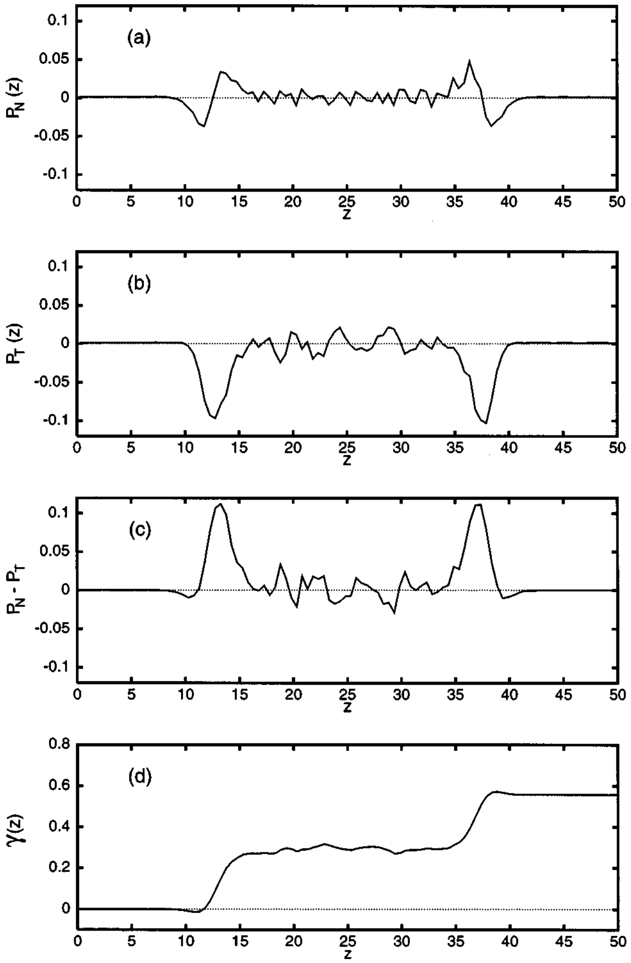

FIG. 5. Behavior of the components of the pressure tensor $p_N(z)$ (a) and $p_T(z)$ (b), the function $p_N(z)-p_T(z)$ (c), and $\gamma(z)=\int_0^z[p_N(z')-p_T(z')]dz'$ (d) along the z direction. All these curves were obtained from the simulation of an inhomogeneous GB system with $\kappa=3$ and $\kappa'=1$ at $T=0.62$ using Harashima's definition for the pressure tensor [24]. The z coordinate is in units of σ_0, the pressure in units of ϵ_0/σ_0^3, and the surface tension in units of ϵ_0/σ_0^2.

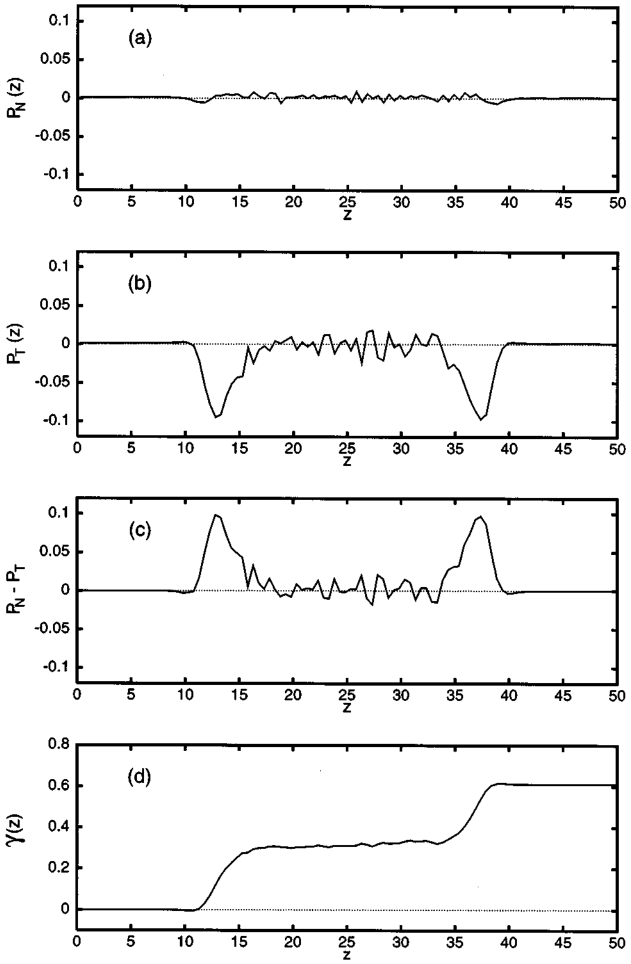

FIG. 6. Behavior of the components of the pressure tensor $p_N(z)$ (a) and $p_T(z)$ (b), the function $p_N(z)-p_T(z)$ (c), and $\gamma(z)=\int_0^z[p_N(z')-p_T(z')]dz'$ (d) along the z direction. All these curves were obtained from the simulation of an inhomogeneous GB system with $\kappa=3$ and $\kappa'=1$ at $T=0.62$ using Irving-Kirkwood's definition for the pressure tensor [27,28]. The z coordinate is in units of σ_0, the pressure in units of ϵ_0/σ_0^3, and the surface tension in units of ϵ_0/σ_0^2.

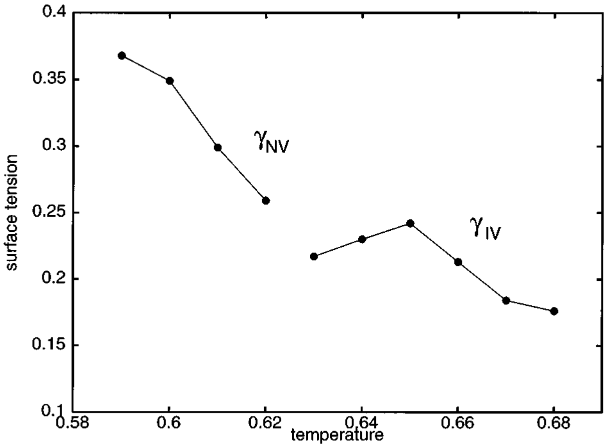

FIG. 7. Surface tension of the free surfaces of an inhomogeneous GB system with $\kappa=3$ and $\kappa'=1$ as a function of temperature. The lines have been drawn as a guide for the eye. The surface tension is in units of ϵ_0/σ_0^2 and the temperature in units of ϵ_0/k_B.

no unique way of microscopically defining the pressure tensor of an inhomogeneous system (although the surface tension is independent of the definition). According to Harashima's definition, the contribution resulting from the interaction between a pair of molecules is divided in two halves which are assigned to the bins containing each particle. On the other hand, within Irving-Kirkwood's (IK) definition [27,28] this contribution is equally distributed among all the intermediate bins connecting the bins where both molecules are located. It seems very likely that the IK criterion will tend to wash out the structure observed at the interface. To clarify this point further, a simulation was performed at $T=0.62$, starting from the final configuration of the simulation used to obtain the results presented in Fig. 5, but now considering the IK definition for evaluating the pressure tensor. As shown in Fig. 6, the function $p_N(z)$ obtained by using IK's criterion does not show any significant structure at the interface. This result allows us to conclude that the (apparent) anomalous behavior of $p_N(z)$ shown in Fig. 5(a) does not correspond to any physical phenomena, nor to a poor equilibration of the system, but to the particular criterion considered for its calculation. According to Figs. 5 and 6, the behavior of $p_T(z)$ does not depend on the definition used for the pressure tensor.

From the condition of hydrostatic equilibrium, it follows [25] that the tangential component of the pressure tensor must be $p_T(z)=p_N(z)$ (and both equal to the bulk pressure) in the bulk liquid and vapor phases. It should differ from this value at the interface. This is the behavior illustrated in Figs. 5(b) and 6(b), where the deep minimum exhibited by $p_T(z)$ in the interfacial region is noticeable. In Figs. 5(c) and 6(c), it is clearly shown that both components of the pressure tensor are equal in the bulk phases, and that the main contribution to γ arises from the depression of $p_T(z)$.

The surface tension is calculated as an integration of the difference between the pressure tensor components [Eq. (9)]. From Figs. 5(d) and 6(d), it follows that the contributions to γ arise only from the interface. Moreover, it can be checked that the function $\gamma(z)$ is constant throughout the liquid phase. This fact is commonly used in simulations as an indication that the inhomogeneous system has relaxed to equilibrium [6].

The dependence of the surface tension on temperature is shown in Fig. 7. γ_{IV} increases as the temperature decreases in the range $0.65 \leq T \leq 0.68$; however, close enough to the triple point, γ_{IV} exhibits an anomalous behavior, with γ_{IV} decreasing as T is decreased. The behavior of γ_{IV} as a function of T indicates that the interface is more ordered than the bulk isotropic liquid. γ_{NV} exhibits the usual linear dependence with T. Complete wetting at the *I*-*V* interface by the *N* phase implies a positive value of $d\gamma_{IV}/dT$ [2], although a positive value of $d\gamma_{IV}/dT$ does not necessarily imply complete wetting by the *N* phase. A suitable magnitude to investigate the possibility of wetting by *N* is the adsorption Γ_η of the order parameter η, which is defined as $\Gamma_\eta=-\int \eta(z)dz$. We have evaluated Γ_η in the *I*-*V* interface, considering as integration limits the values of z at which η vanishes. Accordingly, the lower integration limit (for the

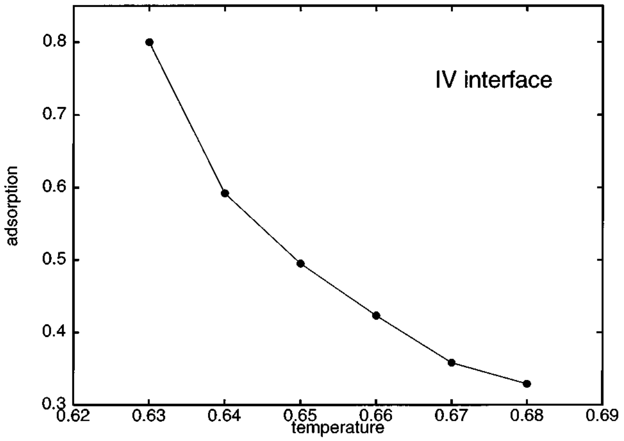

FIG. 8. Adsorption of the order paramenter η at the I-V interface of an inhomogeneous GB system with $\kappa=3$ and $\kappa'=1$ as a function of temperature. The line has been drawn as a guide for the eye. The adsorption of the order paramenter is in units of σ_0 and the temperature in units of ϵ_0/k_B.

interface at the left) was taken as the value of z at which η changes from positive to negative values [this point is approximately equivalent to the position of the Gibbs dividing surface; see Eq. (6)], and the upper integration limit was taken as the value of z at which η changes its sign again. Following this (arbitrary) criterion, we expect to isolate the (relevant) interfacial contribution from the (nonrelevant) contribution arising from orientational fluctuations in the isotropic phase close to the triple point.

The results for Γ_η as a function of temperature are represented in Fig. 8. According to this figure, Γ_η grows rapidly as the temperature is decreased toward the triple point. This is the kind of behavior expected if there is wetting by the nematic phase. From our data, it was not possible to determine if Γ_η diverges as $T \rightarrow T_{\mathrm{tr}}$, although this seems to be the case. Incidentally, we note that this information is required in order to discriminate complete from partial wetting.

In Fig. 9, we have represented the interfacial thickness δ, as obtained by fitting the simulation density profiles to Eq. (6), in terms of the temperature. It is observed that δ increases with increasing temperature, as expected. This figure indicates that there seems to be a negative jump for temperatures just above the triple point.

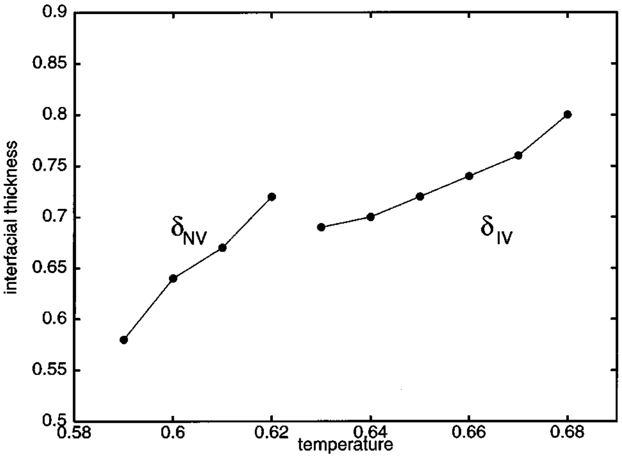

FIG. 9. Surface thickness of an inhomogeneous GB system with $\kappa=3$ and $\kappa'=1$ as a function of temperature. The lines have been drawn as a guide for the eye. The interfacial thickness is in units of σ_0 and the temperature in units of ϵ_0/k_B.

V. CONCLUDING REMARKS

Considering that the orientational and translational degrees of freedom are coupled in the GB model, a nontrivial surface behavior is expected. We remark that this ingredient is crucial, and it is absent in the Lebwhol-Lasher model.

We have performed a detailed simulation study of the free surfaces of the GB with $\kappa=3$ and $\kappa'=1$ in a range of temperatures $(0.59 \leqslant T \leqslant 0.68)$ around the V-I-N triple point. In this region, the liquid phase that coexists with the vapor undergoes an orientational transition as the temperature is decreased. For $T \leqslant 0.62$, the liquid phase is nematic. To the best of our knowledge, these results constitute the first computer simulation study of the nematic free surface based on a continuous model.

It has been shown that the I-V interface induces orientational order, and that the molecules orient themselves parallel to the interface at the liquid side. This effect is noticeable even for the highest temperature considered in this study. In a previous work, perpendicular alignment at the I-V interface was reported for the GB fluid with the same value of the molecular elongation $(\kappa=3)$ but larger anisotropy parameter $(\kappa'=5)$. This indicates that the orientation at the isotropic free surface of the GB model (with $\kappa=3$) changes from perpendicular to parallel as κ' is decreased. We have not attempted to find the exact value of κ' at which this change takes place. The simulations performed for $\kappa'=1.25$, however, suggest that it must occur for some value in the range $1.25<\kappa'<5$. This orientational change at the I-V interface is not necessarily related to a thermodynamic transition. The order parameters σ and τ, which give information on the in-plane order, were found to be approximately zero at the I-V interface, thus indicating that this interface is uniaxial (as it is in the case of perpendicular alignment). As there is no symmetry change and the magnitude of the order parameter η is small, a surface transition does not seem very likely to occur.

We note that the situation would be completely different if this orientational change occurred at the N-V interface. In this case, a thermodynamic transition would be expected on symmetry grounds as the system changed from uniaxial (perpendicular alignment) to biaxial (parallel alignment) [29].

It is worth mentioning that our conclusions are in qualitative agreement with theoretical predictions. Tjipto-Margo and Sullivan [30] developed a mean-field theory for the study of the interfacial properties of the GB model. Their results indicate that short-range attractive and repulsive contributions of the intermolecular potential induce perpendicular alignment while the long-range attractive contributions induce parallel alignment. As a result of the competition between these contributions, a change in the preferred orientation is predicted as the long-range attractive contributions are increased. This prediction agrees with our simulation results if one bears in mind that decreasing the value of κ' (for a fixed value of κ) implies an increase of the relative contributions of the attractive interactions in the GB model.

We have shown that the surface tension of the I-V interface decreases with temperature in the range $0.65 \leqslant T \leqslant 0.68$. However, sufficiently close to the triple point this behavior is switched over, and the surface tension increases as the temperature decreases toward the triple point. On the other hand, the surface tension of the N-V interface exhibits the usual linear dependence with temperature. The anomalous behavior of the surface tension above the triple point has been related to the excess of orientational order at the interface. The adsorption of the order parameter η at the I-V interface grows rapidly as the temperature decreases. These results are consistent with the existence of wetting by the nematic phase. The theory developed by Tjipto-Margo and Sullivan [30] predicts total wetting by N for $\kappa=2$ and 3, and a partial wetting for $\kappa \geqslant 4$. Further simulations close to the triple point are needed to clarify the nature of the wetting regime.

ACKNOWLEDGMENTS

We wish to thank M. M. Telo da Gama for helpful discussions and for her critical reading of the manuscript. We would also like to thank M. P. Allen for useful comments.

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