Surface-induced ordering in thin uniaxial liquid crystal films

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The interface localization transition in thin uniaxial liquid crystal films with competing surface fields has been studied using Metropolis Monte Carlo simulations. The model is constructed from a lattice of continuously orientable interacting spins, and the Hamiltonian contains both bilinear and biquadratic contributions. The biquadratic contribution to the Hamiltonian is familiar from the Lebwohl-Lasher model, and accounts for the particle anisotropy in a liquid crystal. The head-tail asymmetry of the molecules in a uniaxial liquid crystal is taken into account through a bilinear contribution familiar from the classical ferromagnetic Heisenberg model with exchange anisotropy Λ. The critical temperature T_c, characterizing the interface localization transition within the uniaxial liquid crystal film, depends strongly on the relative magnitudes of the bilinear and biquadratic interactions between the spins. For systems dominated by the biquadratic interaction, T_c is found to be close to the bulk critical temperature of the system. But as the biquadratic interaction strength is reduced, T_c departs markedly from the bulk critical temperature of the system.

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I. INTRODUCTION

The interface localization transition in thin ferromagnetic films with competing surfaces has been the subject of many recent investigations. Extensive studies of the Ising ferromagnet by Binder and co-workers [1–4] distinguished the nature of this transition from the bulk phase transition and the wetting transition observed in thin films with cooperative surface fields. Both the Ising and Heisenberg models have been widely used to model the magnetic properties of materials. In the classical Heisenberg model, the magnetic spins can rotate through all possible orientations, and this distinguishes it from the Ising model, in which the spins are restricted to orientations along a particular axis, conventionally denoted as the z axis. For thin ferromagnetic films, the phase behavior of the Heisenberg spin system has been studied under the action of competing surface fields with different types of model anisotropy [5,6]. For sufficiently large values of the anisotropies, the characteristic interface localization transition of thin ferromagnetic Ising films with competing surface fields is recovered. But for small anisotropies the phase behavior of the thin ferromagnetic Heisenberg film has a markedly different character.

The role of surface effects in the physics of nematic liquid crystals is of great significance because of their application in the thin visual display cells. The presence of bounding surfaces promotes competing types of molecular alignment between surface and bulk that provide a capacity to modify the orientation of the nematic axis. Conventionally one distinguishes between parallel (or random planar or homogeneous) and perpendicular (or homeotopic) forms of surface alignment, and most theoretical studies of thin nematic films with surface alignment centered on the use of Landau–de Gennes theory [7]. Simulation studies have primarily focused on films with free surfaces and no surface fields [8]. However, Chiccoli *et al.* [9] recently performed a Monte Carlo simulation study of the topological defects in thin nematic films with hybrid boundary conditions. These studies used a lattice spin model, the Lebwohl-Lasher model, confined between two surfaces, one of which favored a normal spin alignment while the other preferred a tangential orientation of the spins.

The Lebwohl-Lasher model [10] is a lattice spin version of the famous Maier-Saupe model of an anisotropic liquid. The molecules are represented by headless spins that can be viewed as rodlike anisotropic particles, and the coupling between translational and orientational degrees of freedom present in a real nematogen are neglected. Thus it is an appropriate model for orientational ordering in a solid. However, it is believed that the model still reveals the essential transitional properties of liquid crystals near the nematic-isotropic phase transition, and it has been extensively used in computer simulation studies of liquid crystals [11–18]. At high temperatures, the spins rotate through all possible orientations, and the system is an isotropic state. But at sufficiently low temperatures the spins display a spontaneous orientational ordering. The order parameter for the nematic-isotropic phase transition is the orientational order parameter $\langle P_2 \rangle$. This measures the degree of orientation of the molecular axes along the director, which is the preferred direction of orientation. As a result of the continuous degeneracy of the nematic ordering in the absence of an external field, the orientation of the director varies during the simulation. The orientation of the director can however be pinned by the application of a one-body external field that aligns the director parallel to the field [12,13].

The molecules of a uniaxial liquid crystal possess a head-tail asymmetry in addition to their rodlike anisotropy. A simple model to investigate the physics of uniaxial liquid crystals, based on the Lebwohl-Lasher model, was introduced by Biscarini *et al.* [15,16], in which the biquadratic interaction of the Lebwohl-Lasher model was supplemented by a bilinear exchange interaction between the spins familiar from the classical Heisenberg model of ferromagnetism. Such a model was first introduced to study orientational phase transitions in molecular crystals [19], and has also previously been applied to magnetic systems in which the exchange interaction between the magnetic spins possesses

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''quadropolar'' as well as ''dipolar'' characteristics [20]. In the Lebwohl-Lasher model, the biquadratic interaction favors a parallel alignment of the spins in a preferable direction below a critical temperature T_c^N. At high temperatures the spin orientation is isotropic. In the absence of an external field the classical Heisenberg model only displays a spontaneous nonzero magnetization at zero temperature. However, if a sufficiently large bilinear exchange anisotropy is included in the Hamiltonian for the Heisenberg model, Ising-like behavior is recovered in which the spins order spontaneously below a critical temperature T_c^F even in the absence of an external field.

This paper investigates the phase behavior of thin uniaxial liquid crystal films with competing surface fields. In Sec. II a full description of the model is given and the details of the Monte Carlo simulation method are presented. The dependence of the equilibrium phase behavior of the film on the strength of the biquadratic interaction is studied in Sec. III, while the corresponding order parameter structures in the film are discussed in Sec. IV. The temperature dependence of the interface localization transition is investigated in Sec. V and the paper concludes with a summary of the key findings in Sec. VI.

II. MODEL

Krieger and James [19] introduced a lattice spin model defined by the Hamiltonian

$$\mathcal{H}_{KJ}=-\sum_{\langle i,j\rangle}\left[J(\mathbf{S}_i\cdot\mathbf{S}_j)-\varepsilon(\mathbf{S}_i\cdot\mathbf{S}_j)^2\right] \tag{1}$$

to describe the successive orientational transitions in molecular crystals. In the Hamiltonian (1), $\mathbf{S}_i=(S_i^x,S_i^y,S_i^z)$ is a unit vector representing the ith spin, and the notation $\langle i,j\rangle$ means that the sum is restricted to nearest-neighbor pairs of spins. The coupling constants J and ε characterize the magnitudes of the bilinear and biquadratic exchange interactions between the spins respectively. When $J=0$ and $\varepsilon\neq 0$, the model reduces to the Lebwohl-Lasher model [10], and the system displays nematic order below a critical temperature T_c/ε in which the spins spontaneously orient in a preferred direction termed the director. However, in the absence of any external field, the orientation of the director is not fixed in space due to the fluctuation in the spin orientations. When $\varepsilon=0$ and $J\neq 0$, the model reduces to the familiar classical Heisenberg model of magnetism, and for ferromagnetism $J>0$. When both $J\neq 0$ and $\varepsilon\neq 0$, the model has been used to describe uniaxial liquid crystals in which ferroelectric and antiferroelectric ordering are both possible [15,16]. The molecules of a uniaxial liquid crystal are characterized by a head-tail asymmetry, and hence a short ranged bilinear interaction supplements the biquadratic spin-spin interaction of the Lebwohl-Lasher model.

This paper focusses on a lattice spin model with a generalization of the Krieger-James Hamiltonian (1) that allows for anisotropy of the bilinear exchange interaction with

$$\boldsymbol{\mathcal{H}}_0=-\sum_{\langle i,j\rangle}\left\{J[(1-\Lambda)(S_i^xS_j^x+S_i^yS_j^y)+S_i^zS_j^z]-\varepsilon(\mathbf{S}_i\cdot\mathbf{S}_j)^2\right\}, \tag{2}$$

where Λ is the exchange anisotropy which determines the strength of the bilinear exchange interaction of the x and y components of the spin. When $\varepsilon=0$ and $\Lambda=0$, the model reduces to the familiar classical Heisenberg model of magnetism.

The system under consideration here is a three-dimensional thin uniaxial liquid crystal film of finite thickness D under the action of competing surface fields with Hamiltonian

$$\boldsymbol{\mathcal{H}}=\boldsymbol{\mathcal{H}}_0-\sum_{i\in\text{surface }1}\mathbf{H}_1\cdot\mathbf{S}_i-\sum_{i\in\text{surface }D}\mathbf{H}_D\cdot\mathbf{S}_i, \tag{3}$$

where $\mathbf{H}_1$ and $\mathbf{H}_D$ are the applied surface fields. We consider a simple cubic lattice of size $L\times L\times D$, in units of the lattice spacing, and apply periodic boundary condition in the x and y directions. Free boundary conditions are applied in the z direction which is of finite thickness D. The system is subject to competing surface fields applied a layer $n=1$ and $n=D$ of the film with

$$\mathbf{H}_1=h\hat{\mathbf{z}}\delta_{i1}, \tag{4}$$

$$\mathbf{H}_D=-h\hat{\mathbf{z}}\delta_{iD}, \tag{5}$$

giving a Hamiltonian

$$\boldsymbol{\mathcal{H}}=\boldsymbol{\mathcal{H}}_0-h\left(\sum_{i\in\text{surface }1}S_i^z-\sum_{i\in\text{surface }D}S_i^z\right). \tag{6}$$

A film thickness $D=12$ and surface field strength $h=-0.55$ were used throughout to aid comparison with the corresponding Ising and Heisenberg films investigated elsewhere [1,2,5,6]. The results do not depend significantly on the value of h, and $D=12$ corresponds to the crossover regime between wall and bulk dominated behavior for thin Ising films [2]. In thinner films it is difficult to distinguish between ''interface'' and ''bulk'' phases in the film, since all layers of the film feel the effect of the competing surface fields rather strongly. For thicker films the surfaces of the film only interact close to the bulk critical point.

Results are reported for lattices of size $L=32$. A number of additional simulations were performed for $L=64$ and 128, but no significant differences were found from the results presented here for non-critical values of the parameters. The Metropolis algorithm [21] was used in the Monte Carlo simulations with trial configurations generated from Barker-Watts [22] spin rotations. The magnitude of the maximum spin rotation was adjusted to ensure approximately 50% of trial configurations were rejected in the bulk equilibrium state.

The ''magnetic'' order of the film is characterized by z component of the magnetization for the film,

$$M_z=\frac{1}{D}\sum_{n=1}^{D}M_n^z, \tag{7}$$

where the z component of the magnetization for the nth layer of the film:

$$M_n^z=\frac{1}{L^2}\sum S_i^z. \tag{8}$$

In addition to the ''magnetic'' order M_z, in studying this model, it is also necessary to consider the ''nematic'' order resulting from the biquadratic exchange term in the Hamiltonian. In common with studies of the nematic-isotropic phase transition in liquid crystals, the orientational order parameter for the film is

$$P_2=\frac{1}{D}\sum_{n=1}^{D} P_{2n}, \tag{9}$$

where the orientational order parameter for the nth layer of the film is

$$P_{2n}=\frac{1}{L^2}\sum P_2(\mathbf{S}_i\cdot\hat{\mathbf{z}}), \tag{10}$$

and $P_2(\mathbf{S}_i\cdot\hat{\mathbf{z}})$ is the second Legendre polynomial. The presence of the unit vector $\hat{\mathbf{z}}$ in Eq. (10) indicates that the director is assumed to be in a time-independent alignment along the z axis. One effect of the applied surface fields is to suppress fluctuations in the orientation of the director, which is then fixed in the z direction perpendicular to the plane of the film. Equilibrium averages of the order parameters were typically taken over 2×10^5 Monte Carlo steps per spin (MCS/spin) with initial transients ignored.

III. INTERFACE LOCALIZATION AND THE BIQUADRATIC EXCHANGE INTERACTION

For thin ferromagnetic Ising films with competing surface fields, an interface localization transition is observed that is absent in the corresponding isotropic Heisenberg model. If the bilinear exchange interaction in the Heisenberg model is made anisotropic, then the interface localization transition is recovered for sufficiently strong anisotropies. Here the changes in the phase behavior of the thin film resulting from the introduction of a biquadratic exchange interaction are investigated.

First we focus on a system with a bilinear exchange anisotropy of $\Lambda=0.1$. For $\varepsilon=0$, this system corresponds to a thin ferromagnetic Heisenberg film with weak exchange anisotropy whose phase behavior is like that observed for the isotropic Heisenberg system. The orientational order parameter, $\langle P_2\rangle$, and the z component of the mean magnetization per spin, $\langle M_z\rangle$, for the film are shown in Fig. 1 as a function of the strength of the biquadratic exchange interaction for $0.1<\varepsilon<1$ at reduced temperatures of $T^*=k_BT/J=1.0$ and 1.5. In all cases the initial spin configuration was a ferromagnetically ordered state with $S_i^z=+1$ for all i. At the lower temperature of $T^*=1.0$, both $\langle P_2\rangle$ and $\langle M_z\rangle$ are smooth monotonic increasing functions of ε, and nonzero for all ε. This is as expected, since even at $\varepsilon=0$ the film displays a well-developed ferromagnetic order in the z direction at $T^*=1.0$. The degree of order of the spins is enhanced as ε increases. However, at the higher temperature $T^*=1.5$, for small ε the film is in a paramagnetic state with no spontaneous directional ordering of the spins and $\langle M_z\rangle=0$. But there is a sharp increase in $\langle M_z\rangle$ for $\varepsilon>0.3$, indicating the onset of ferromagnetic order. The paramagnetic-ferromagnetic phase transition in the film is characterized by a critical value of the biquadratic coupling constant $\varepsilon_c=0.32\pm0.01$ for $T^*=1.5$.

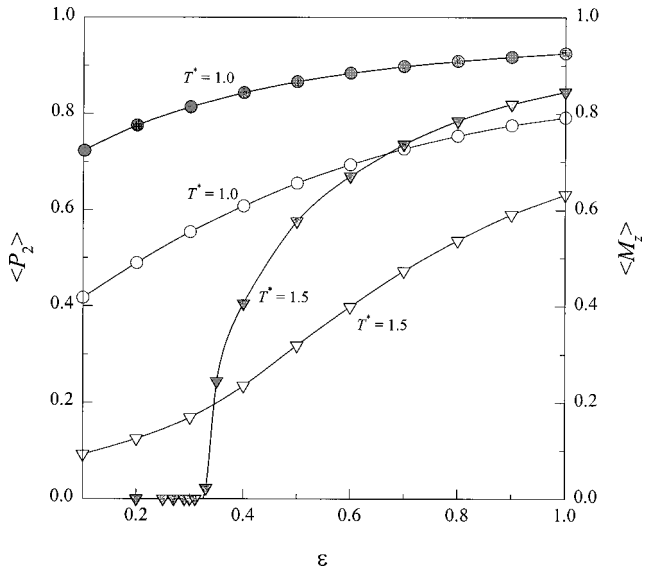


FIG. 1. The orientational order parameter $\langle P_2\rangle$ (open symbols) and z component of the magnetization per spin $\langle M_z\rangle$ (solid symbols) for different values ε with $\Lambda=0.1$ at temperatures of $T^*=1.0$ and 1.5.

However at $T^*=1.5$, in marked contrast to the ε dependence of $\langle M_z\rangle$, $\langle P_2\rangle$ is seen to be a smoothly increasing function of ε with $\langle P_2\rangle>0$ for all ε. Thus while the qualitative form of the ε dependence of $\langle P_2\rangle$ is the same at both temperatures, the ε dependence of $\langle M_z\rangle$ is qualitatively different. Note that a temperature of $T^*=1.5$ is above a critical temperature T_c, characterizing the interface localization transition in a thin ferromagnetic Heisenberg film with an exchange anisotropy $\Lambda=0.1$ [6]. No spontaneous magnetization of the film is observed for $T>T_c$. However, a small nonzero value of ε is sufficient to give rise to spontaneous ferromagnetic ordering with $\langle M_z\rangle>0$ even though $T>T_c$ for the Heisenberg film in which $\varepsilon=0$. Thus the addition of a biquadratic exchange interaction clearly plays an important role in controlling the order-disorder characteristics of the system.

Next the dependence of the phase behavior on the bilinear exchange anisotropy Λ is investigated for $0\leqslant\Lambda\leqslant1$. Over this range of Λ, in the thin film geometry under investigation here with $D=12$ and $h=-0.55$, the characteristic phase behavior of the anisotropic Heisenberg ferromagnetic film with $\varepsilon=0$ has been shown [6] to change from Heisenberg-like to Ising-like. Figure 2 shows results for the film order parameters $\langle P_2\rangle$ and $\langle M_z\rangle$ as a function of the ferromagnetic exchange anisotropy Λ for two cases: (i) $T^*=1.0$ and $\varepsilon=0.1$ and (ii) $T^*=1.5$ and $\varepsilon=0.3$. It can immediately be seen that the qualitative dependence of $\langle P_2\rangle$ and $\langle M_z\rangle$ on the control variable is similar to that seen in Fig. 1. However, the figure shows that $\langle M_z\rangle=0$ when the model has an isotropic exchange interaction $\Lambda=0$. In this case the bilinear component of the model Hamiltonian reduces that of a classical isotropic Heisenberg model, and ordered spin states are quickly destroyed at finite temperature. Increasing the value of Λ leads to spontaneous spin alignment along the z axis and ferromagnetic order. In contrast, the orientational order parameter, $\langle P_2\rangle$, is a smoothly increasing function of Λ with $\langle P_2\rangle>0$ for all Λ. It is notable that for $T^*=1.0$, there is a sharp decrease in $\langle M_z\rangle$ toward zero for $\Lambda<0.1$. While at the

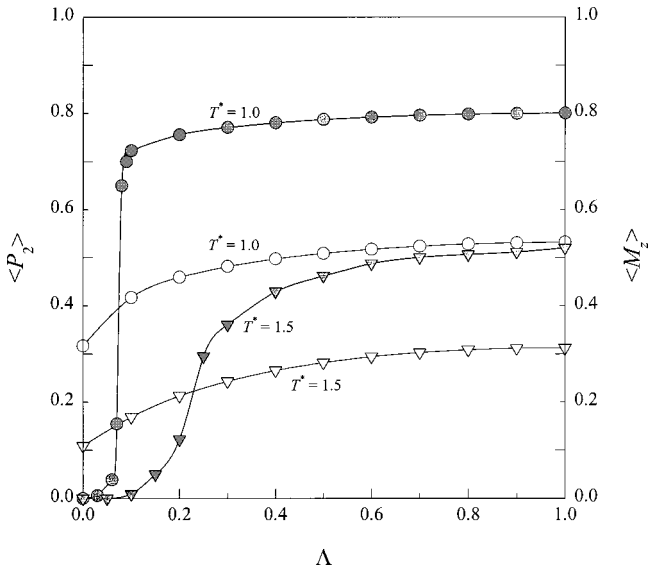


FIG. 2. The orientational order parameter $\langle P_2 \rangle$ (open symbols) and z component of the magnetization per spin $\langle M_z \rangle$ (solid symbols) for different values Λ at a temperature of $T^*=1.0$ with $\varepsilon=0.1$ and at a temperature $T^*=1.5$ with $\varepsilon=0.3$.

higher temperature of $T^*=1.5$, the decrease in $\langle M_z \rangle$ toward zero with decreasing Λ occurs at much higher values of Λ, and is spread over a much larger range of Λ values than for $T^*=1.0$.

IV. STRUCTURE WITHIN THE FILM

A greater insight into the phase behavior of the film seen above is obtained from the information contained in the layer order parameters across the film. The layer orientational order parameter $\langle P_{2n} \rangle$ across the film for temperature $T^*=1.5$ and biquadratic exchange anisotropy $\Lambda=0.1$ is shown in Fig. 3(a) for a set of values of the biquadratic interaction strength ε in the range $0.2<\varepsilon<1$. The corresponding results for the film orientational order parameter $\langle P_2 \rangle$ are contained in Fig. 1. For $\varepsilon=0.2$ and 0.3, the profiles of $\langle P_{2n} \rangle$ across the film are symmetric about the center of the film, and the minimum value of $\langle P_{2n} \rangle$ is located at the center of the film. This indicates that there is an enhanced ordering of the spins near the surface due to the applied surface fields. An isotropic state is observed in the bulk of the film. However, for $\varepsilon=0.4$, the location of the minimum value in $\langle P_{2n} \rangle$ is displaced from the center of the film toward the surface, and is located in the surface layer for $\varepsilon>0.4$. Moreover, in the bulk of the film the spins order spontaneously and as a consequence $\langle P_{2n} \rangle$ within the bulk increases with increasing ε. For $\varepsilon>0.4$, $\langle P_{2n} \rangle$ in the surface layers is less than the bulk value. This is a result of the competition between ordering tendencies of the applied surface fields and the disorder in the surface layers introduced by the free boundary conditions on the film. For $\varepsilon>0.4$ the surface field strength is insufficient to suppress the enhanced fluctuations in the spin orientation in the surface layers where the number of nearest neighbors are smaller. Thus, for larger ε, $\varepsilon>0.4$, the spin ordering within the film occurs principally within the bulk of the film. However, for $\varepsilon<0.4$, the isotropic phase is observed in the bulk of the film, and this produces a low value

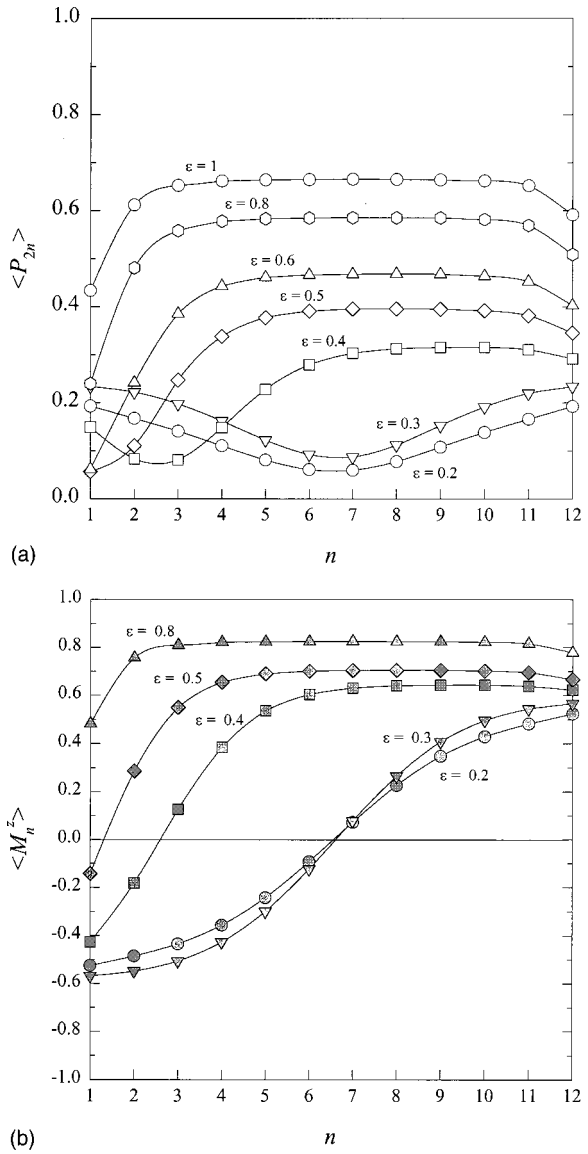


FIG. 3. (a) The layer orientational order parameter across the film $\langle P_{2n} \rangle$, and (b) the layer magnetization across the film $\langle M_n^z \rangle$ for different values of ε with $\Lambda=0.1$ at a temperature $T^*=1.5$. All results were obtained from an initial spin state of $S_i^z=+1$ for all i, competing surface fields with $h=-0.55$ and a film thickness of $D=12$.

of $\langle P_{2n} \rangle$ in middle of the film. Ordering of the film is then principally found at the surfaces.

The qualitative difference in film behavior between the results for $\varepsilon<0.4$ and $\varepsilon>0.4$ can be observed immediately in the magnetization profiles across the film, $\langle M_n^z \rangle$, presented in Fig. 3(b). The figure shows the surface fields locally constrain the spins to align in a negative direction near one surface and in a positive direction near the other surface. In the bulk of the film, the mean spin orientation of the layers varies smoothly from one surface to the other. For $\varepsilon=0.2$ and 0.3, the interface between regions of negative and positive magnetization is not localized, and the point of zero magnetization is located at the center of the film. However, for $\varepsilon=0.4$, the interface is shifted toward the surface and disappears into the film surface with increasing ε. Note that the minimum values of $\langle P_{2n} \rangle$ for each ε are located in the

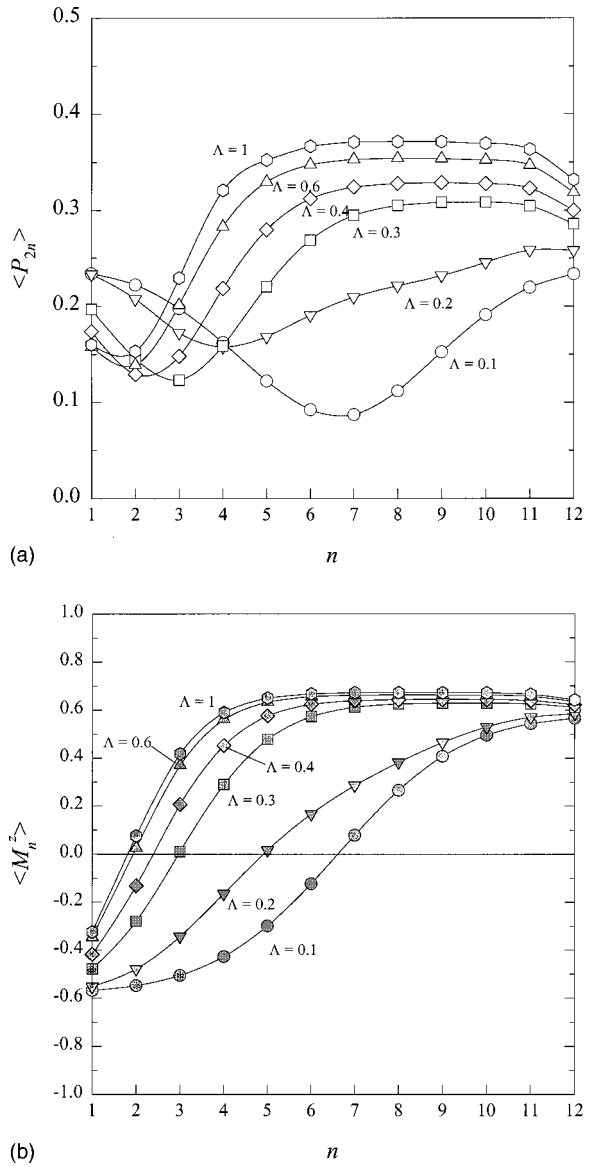


FIG. 4. (a) The layer orientational order parameter across the film $\langle P_{2n} \rangle$, and (b) the layer magnetization across the film $\langle M_n^z \rangle$ for different values of Λ with $\varepsilon = 0.3$ at a temperature $T^* = 1.5$. All results were obtained from an initial spin state of $S_i^z = +1$ for all i, competing surface fields with $h = -0.55$ and a film thickness of $D = 12$.

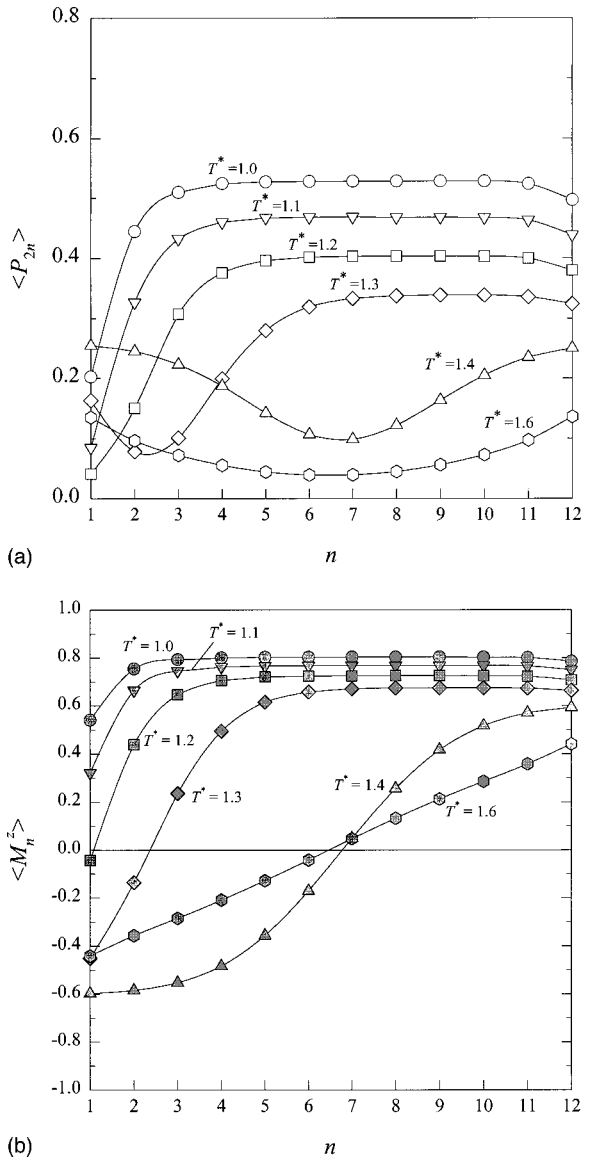


FIG. 5. (a) The layer orientational order parameter across the film $\langle P_{2n} \rangle$, and (b) the layer magnetization profiles across the film $\langle M_n^z \rangle$ for different temperatures with $\varepsilon = 0.2$ and $\Lambda = 0.1$. All results were obtained from an initial spin state of $S_i^z = +1$ for all i, competing surface fields with $h = -0.55$ and a film thickness of $D = 12$.

same layer as the point of zero magnetization in the $\langle M_n^z \rangle$ profiles. For smaller ε the spins in the center of the film are in an isotropic state, and the interface between regions of negative and positive magnetization is not localized. However, for larger ε nematic ordering occurs in the bulk of the film and promotes ferromagnetic order there, leading to a localization of the interface between regions of negative and positive magnetization at or near the surface of the film.

The bilinear exchange anisotropy Λ can play a similar role in controlling the existence and location of an interface localization transition in the film. The layer orientational order parameter profile $\langle P_{2n} \rangle$ and layer magnetization profile $\langle M_n^z \rangle$ across the film at a temperature $T^* = 1.5$ with $\varepsilon = 0.3$ is shown in Fig. 4 for different values of Λ in the range $0.1 < \Lambda < 1$. For $\Lambda = 0.1$ neither nematic nor ferromagnetic order is observed in the system. Both the minimum value of $\langle P_{2n} \rangle$ and the interface between regions of negative and positive magnetization are located at the center of the film. However for $\Lambda > 0.1$, the interface between regions of negative and positive magnetization becomes localized, and is shifted toward the surface together with the minimum in $\langle P_{2n} \rangle$.

V. TEMPERATURE DEPENDENCE

The temperature dependence of the order parameter profiles $\langle P_{2n} \rangle$ and $\langle M_n^z \rangle$ across the film is shown in Fig. 5 for a biquadratic coupling constant $\varepsilon = 0.2$ and a bilinear exchange anisotropy $\Lambda = 0.1$. At high temperatures $T^* = 1.4$ and 1.6, an isotropic paramagnetic phase is observed in the film, and the system shows no spontaneous orientational ordering. The minimum value of $\langle P_{2n} \rangle$ and the interface between regions of negative and positive magnetization are both located at the

center of the film. However, as the temperature is reduced from $T^*=1.3$ to 1.0, the interface between regions of negative and positive magnetization becomes increasingly localized and is shifted toward the surface, disappearing into the surface at low temperatures. This interface motion across the film is also seen in the location of the minimum in $\langle P_{2n}\rangle$. Large shifts in the location of the interface between regions of negative and positive magnetization are seen for temperatures between $T^*=1.3$ and 1.4. Mirroring this, a qualitative change in the profiles of $\langle P_{2n}\rangle$ across the film also occurs between these temperatures. For $T^*>1.3$ the layer orientational order parameter in the bulk of the film is small, and the minimum is located at the center of the film. Thus the paramagnetic phase of the film is associated with a delocalized interface between regions of positive and negative magnetization and an absence of orientational order away from the film surfaces. The ferromagnetic behavior of the film is associated with interface localization within the film and the onset of nematic order in the center of the film.

In a uniaxial liquid crystal film with competing surface fields, a sufficiently strong biquadratic interaction between the spins promotes orientational ordering within the film. This can give rise to interface localization in the film at temperatures above the critical temperature for the interface localization transition in the corresponding anisotropic Heisenberg film in which $\varepsilon=0$. Thus the critical temperature characterizing the interface localization transition in a uniaxial liquid crystal film is a function of ε, Λ and D, i.e., $T_c=T_c(\varepsilon,\Lambda,D)$. Simulations have been performed to determine $\langle P_2\rangle$ and $\langle M_z\rangle$ as functions of temperature for different values of the biquadratic coupling constant ε to study the ε dependence of $T_c(\varepsilon,\Lambda,D)$. Figures 6(a) and 6(b) show the results for one value of the bilinear exchange anisotropy, $\Lambda=0.1$. The dependence of the critical temperature on Λ in similar models has been studied elsewhere [6]. As expected, the critical temperature $T_c(\varepsilon,\Lambda,D)$ is a monotonic increasing function of ε for fixed Λ and D. There is no spontaneous magnetic ordering for $T>T_c$, with $\langle M_z\rangle=0$. For $T<T_c$, spontaneous ordering of the film is observed with $\langle M_z\rangle>0$. However, although $\langle M_z\rangle$ decreases sharply to zero as $T^*\rightarrow T_c^*$, $\langle P_2\rangle$ is a much more smoothly decreasing function of increasing T^*, and $\langle P_2\rangle>0$ even in the high temperature phase. This is a direct result of the symmetry of the layer orientational order parameter profile about the center of the film, which ensures a residual nonzero contribution to $\langle P_2\rangle$ even in the isotropic phase due to field induced order at the surfaces. In contrast, the antisymmetric magnetization profile of the film in the high temperature phase ensures $\langle M_z\rangle=0$.

Further information on the nature of the phase transition in the film can be obtained from the temperature dependence of the fourth-order cumulant of magnetization [2,3,23]:

$$U_L=1-\frac{\langle M^4\rangle}{3\langle M^2\rangle^2}. \tag{11}$$

For $\varepsilon=0.5$, Fig. 7 shows U_L as a function of temperature for three different lattice sizes of $L=8$, 16, and 32. The characteristic shape of the curves in the figure is consistent with a second-order phase transition [23]. The critical temperature T_c for the paramagnetic-ferromagnetic phase transition can be estimated from the point of intersection of U_L for different values of L. Unfortunately, a precise estimation of T_c for the interface localization transition of the film is difficult. Since the points of intersection of U_L are spread over a small, but significant, temperature range. Similar observations for U_L have been reported for interface localization transition in thin Isisng films by Binder and co-workers [2,4]. From the results of Fig. 7, the critical temperature for $\varepsilon=0.5$ and $\Lambda=0.1$ is $T_c^*=1.660\pm0.005$, this estimate being obtained from an average of the intersection points of results for different L. The value of T_c obtained from U_L is in good agreement with the temperature for which $\langle M_z\rangle\rightarrow0$ in Fig. 6(a). This indicates that the critical temperatures for the other values of ε can be directly estimated from the temperatures for which $\langle M_z\rangle\rightarrow0$ in a plot of $\langle M_z\rangle$ vs T^*. The determination of a more precise estimate for T_c is beyond the scope of this paper.

One interesting feature of Fig. 6(a) is that for $\varepsilon=5.0$, where the system is dominated by the biquadratic exchange

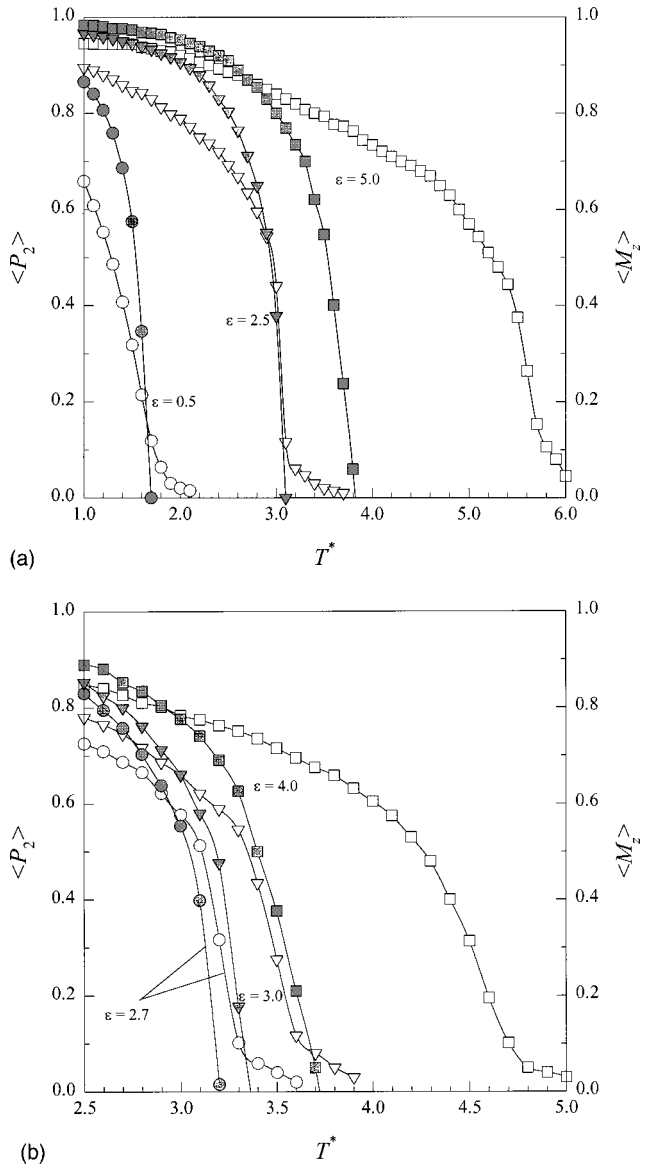


FIG. 6. Temperature dependence of the film orientational order parameter $\langle P_2\rangle$ (open symbols) and the z component of the magnetization per spin $\langle M_z\rangle$ (solid symbols) for $\Lambda=0.1$ with (a) $\varepsilon=0.5$, 2.5, and 5.0 and (b) $\varepsilon=2.7$, 3.0, and 4.0.

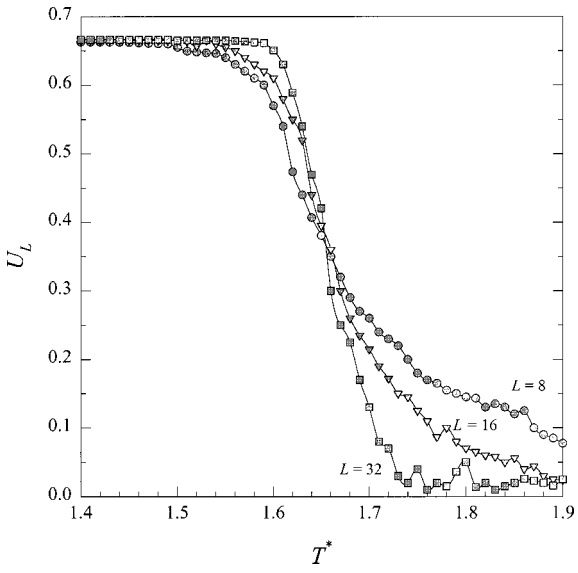
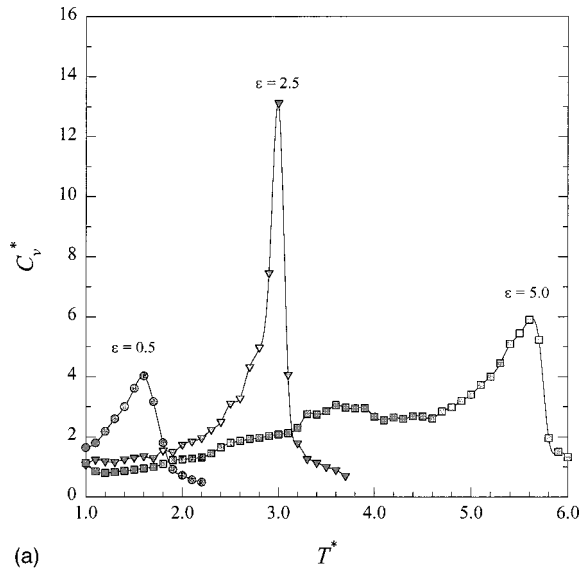


FIG. 7. Fourth-order cumulant of magnetization U_L vs temperature for three different lattice sizes of $L=8$, 16, and 32, with $\varepsilon=0.5$ and $\Lambda=0.1$.



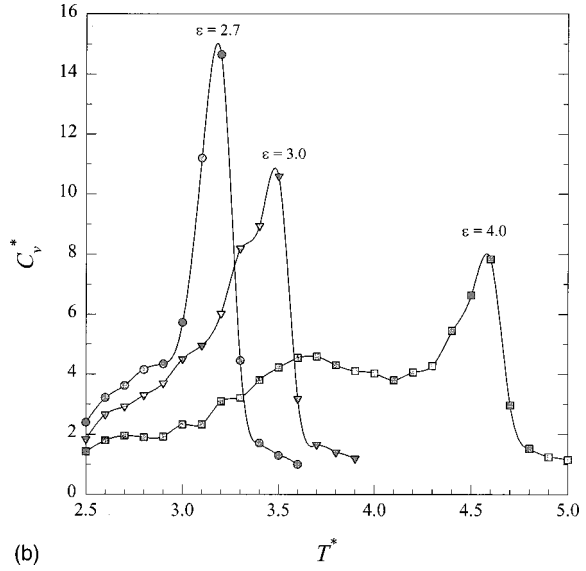


FIG. 8. Temperature dependence of the reduced heat capacity C_v^* for $\Lambda=0.1$ with (a) $\varepsilon=0.5$, 2.5, and 5.0 and (b) $\varepsilon=2.7$, 3.0, and 4.0.

interaction, there is no longer a single phase transition in the film. The temperature at which magnetic order disappears differs markedly from the temperature at which orientational order disappears. This would suggest that for $T^*<3.9$ the film displays a ferromagnetic order, while for $T^*>5.9$ the system is in a paramagnetic isotropic state. But for $3.9<T^*<5.9$ the system displays nematic order without any magnetic order. Such a polar phase was previously observed in studies of bulk uniaxial liquid crystals by Biscarini *et al.* [15,16]. However, for $\varepsilon\leqslant 2.5$ there is only a single phase transition. Systems with a pair of phase transitions and intermediate polar phase only appear for $\varepsilon>2.5$. Further results of $\langle P_2\rangle$ and $\langle M_z\rangle$ as a function of temperature are shown in Fig. 6(b) for three different values of ε in the range $2.5<\varepsilon<5.0$. For $\varepsilon=2.7$, the two separate magnetization and nematic ordering transitions are distinct, but only with a small difference in the critical temperatures associated with the two transitions of $\Delta T_c\approx 0.1$. As ε increases further, ΔT_c increases smoothly with $\Delta T_c\approx 0.3$ for $\varepsilon=3.0$, $\Delta T_c\approx 1.0$ for $\varepsilon=4.0$, and $\Delta T_c\approx 2.0$ for $\varepsilon=5.0$.

The parameter values used in Fig. 6(a) were chosen to provide a direct comparison with the cluster Monte Carlo simulations by Biscarini *et al.* [15,16] of a bulk uniaxial liquid crystal with the Krieger-James Hamiltonian (1). Most remarkably the interface localization temperatures of the film found in this work are essentially the same as the bulk critical temperatures obtained by Biscarini *et al.* In thick ferromagnetic films, the interface localization transition is coincident with the bulk critical temperature of the film. But for the film sizes used in this work, the anisotropic Heisenberg film with $\varepsilon=0$ show marked differences between the interface localization temperatures and the bulk critical temperatures for all Λ. Similar observations have also been made for thin Ising films of this size [2]. Unfortunately, it is not possible to tell whether a reduction in film thickness for the uniaxial liquid crystal film would lead to a significant difference between the interface localization and bulk critical temperatures, since for thinner films the identification of surface and bulk regions of the film becomes problematic. Clearly as $\varepsilon\rightarrow 0$, one would expect the interface localization temperature in a uniaxial liquid crystal film to differ from the bulk critical temperature. However a full investigation of the ε dependence of the interface localization temperature film and bulk critical temperature in the $\varepsilon\rightarrow 0$ limit is beyond the scope of this work.

Further information on the phase transition in the film can be obtained from the temperature dependence of the specific heat $C_v=(\partial U/\partial T)_V$ where U is the energy of the system. The excess specific heat $C_v^*=(C_v-C_v^{\mathrm{id}})/k_B$, where C_v^{id} is the specific heat of an ideal gas, is obtained from the fluctuation of the energy throughout the course of the simulation [24]. Figures 8(a) and 8(b) show $C_v^*(T)$ for the same system parameters as in Figs. 6(a) and 6(b), respectively. The figure shows a single peak in C_v^* centered on $T^*=1.6$ for $\varepsilon=0.5$, on $T^*=3.0$ for $\varepsilon=2.5$, and on $T^*=3.1$ for $\varepsilon=2.7$. The peak is more pronounced for large values of ε. However, for ε

$=4.0$ and 5.0 the specific heat as a function of temperature shows two distinct peaks. The sharper peak is centered on the higher temperature polar-isotropic phase transition of the film. But a broad, less distinct peak is also found for temperatures around the nematic-polar transition. For $\varepsilon=3.0$ a shoulder on the low T^* side of the peak in $C_v^*(T^*)$ is the result of a superposition of peaks associated with separate magnetic and nematic ordering transitions with only a small difference in their transition temperatures.

Thus the temperature dependence of the specific heat mirrors the behavior observed in the temperature dependence of the order parameters. That is, the interface localization transition for the uniaxial liquid crystal film splits into separate magnetic and nematic ordering transitions for sufficiently large values of ε. For the system under investigation here, the separation of the magnetic and nematic transitions occurs for $\varepsilon>2.5$, with the temperature difference between the two transitions smoothly increasing with ε.

VI. CONCLUSION

We have studied the phase behavior of thin uniaxial liquid crystal films with competing surface fields. In the model Hamiltonian, the Lebwohl-Lasher model has been used to account for the biquadratic spin-spin interactions, and the anisotropic Heisenberg model has been used for the bilinear exchange interaction. The coupling constant ε and the ferromagnetic exchange anisotropy Λ in the Hamiltonian are clearly seen to be important factors in controlling the phase behavior of the film. This work shows that the role of these factors is to control the orientational fluctuations of the spins within the film. Larger values of both ε and Λ tend to suppress orientation fluctuations of the spins about the z direction picked out by the film geometry and competing surface fields. This then tends to increase the interface localization transition temperature of the film. Remarkably for films with non-negligible biquadratic exchange interactions, the critical temperatures for the phase transitions within the film are found to be consistent with the bulk critical temperatures. This is in marked contrast to the anisotropic Heisenberg ferromagnet $(\varepsilon=0)$, where for all Λ there is a significant difference between the bulk critical temperature and the critical temperature for the interface localization transition in films of the size studied here.

[1] K. Binder, D. P. Landau, and A. M. Ferrenberg, Phys. Rev. Lett. **74**, 298 (1995).
[2] K. Binder, D. P. Landau, and A. M. Ferrenberg, Phys. Rev. E **51**, 2823 (1995).
[3] K. Binder, R. Evans, D. P. Landau, and A. M. Ferrenberg, Phys. Rev. E **53**, 5023 (1996).
[4] A. M. Ferrenberg, D. P. Landau, and K. Binder, Phys. Rev. E **58**, 3353 (1998).
[5] H. Jang and M. J. Grimson, Phys. Rev. B **55**, 12 556 (1997).
[6] H. Jang and M. J. Grimson, J. Phys.: Condens. Matter **10**, 9641 (1998).
[7] J. Quintana and A. Robledo, Physica A **248**, 28 (1998).
[8] D. J. Cleaver and M. P. Allen, Mol. Phys. **80**, 253 (1993).
[9] C. Chiccoli, O. D. Lavrentovich, P. Pasini, and C. Zannoni, Phys. Rev. Lett. **79**, 4401 (1997).
[10] P. A. Lebwohl and G. Lasher, Phys. Rev. A **6**, 426 (1972).
[11] G. R. Luckhurst and P. Simpson, Mol. Phys. **47**, 251 (1982).
[12] G. R. Luckhurst, P. Simpson, and C. Zannoni, Chem. Phys. Lett. **78**, 429 (1981).
[13] G. R. Luckhurst and P. Simpson, Chem. Phys. Lett. **95**, 149 (1983).
[14] Z. Zhang, O. G. Mouritsen, and M. J. Zuckermann, Phys. Rev. Lett. **69**, 2803 (1992).
[15] F. Biscarini, C. Zannoni, C. Chiccoli, and P. Pasini, J. Non-Cryst. Solids **131–133**, 1190 (1991).
[16] F. Biscarini, C. Zannoni, C. Chiccoli, and P. Pasini, Mol. Phys. **73**, 439 (1991).
[17] U. Fabbri and C. Zannoni, Mol. Phys. **58**, 763 (1986).
[18] E. Berggren, C. Zannoni, C. Chiccoli, P. Pasini, and F. Semeria, Phys. Rev. E **50**, 2929 (1994).
[19] T. J. Krieger and H. M. James, J. Chem. Phys. **22**, 796 (1954).
[20] M. F. Thorpe and M. Blume, Phys. Rev. B **5**, 1961 (1972).
[21] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
[22] J. R. Barker and R. O. Watts, Chem. Phys. Lett. **3**, 144 (1969).
[23] S. H. Tsai and S. R. Salinas, Braz. J. Phys. **28**, 58 (1998).
[24] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).