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Computer simulation study of the phase behavior of a nematogenic lattice-gas model

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The phase behavior of a mesogenic lattice-gas model consisting of freely rotating spins located at the sites of a three-dimensional cubic lattice has been studied using grand canonical Monte Carlo simulations. When two neighboring sites are occupied, the spin vectors interact via the extensively studied anisotropic Lebwohl-Lasher potential, plus an isotropic term of variable strength. The interaction between occupied and empty sites and two empty sites is taken to be zero. If the parameter governing the strength of the isotropic term is zero, the model exhibits an isotropic fluid-nematic transition, which becomes increasingly stronger as the temperature is lowered. The additional isotropic term is found to be important if the model is to reproduce experimental phase behavior, that is, to exhibit both nematic-vapor coexistence at low temperature and isotropic-vapor coexistence at higher temperatures.

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I. INTRODUCTION

Computer simulation has become an important technique for understanding the physical properties and the phase transitions of liquid crystals at the microscopic level. For a model to be useful, it should be able to reproduce the phases of interest, and the transitions between them, and also provide properties of interest for comparison with experiment. In recent years, there have been a number of simulations based on atomistic models of liquid crystals [1] and these show encouraging signs, such as exhibiting nematic phases at temperatures where experimentally the nematic is known to be stable for the particular mesogen in question. However, a major drawback of such models is that the simulations are limited to both very small systems (∼100 molecules) and short time scales (∼10 ns). These models do not, therefore, lend themselves to either the study of phenomena that occur over large length scales nor to investigations over a range of temperatures, pressure, and densities. Single-site model potentials, such as that devised by Gay and Berne, have also been introduced [2]. These contain the essential molecular features, namely, the anisotropic shape and dispersion forces, and also retain the translational and rotational freedom of the atomistic models, although specific chemical detail is stripped away. While this class of potentials has been useful for studying the generic phase behavior of liquid crystals [3], there are typically two major problems when it comes to mapping out phase diagrams; these are the number of variable parameters in the potential (four for the Gay-Berne model) and the computational complexity of the interactions. Although it is possible to map out phase behavior for specific parametrizations of the potential [4], it is computationally expensive to do so; mapping out a global phase diagram in which all the parameters of the generic potential are varied is impossible. Moreover, it is not always obvious how to select the values for the small set of parametrizations to be investigated. For example, we would intuitively assume that, for a real liquid crystal, the interaction between a pair of molecules aligning side by side should be stronger than that of a pair aligning end to end. However, it turns out that to see even a common phenomenom such as nematic-vapor coexistence with a Gay-Berne model, a counter-intuitive parametrization in which the strength of these interactions are essentially equal must be chosen [4]. This clearly makes the task of identifying the regions of the global phase diagram that exhibit realistic behavior difficult.

An alternative view is to use very simplified, primitive models that contain the basic physics of the system of interest, but have the detailed short-range structure stripped away. This class of potentials is useful if we require an understanding of the truly generic or universal features of a system, that originate at longer length scales than the molecular size [5]. One of the most extensively studied models for liquid crystals, the Lebwohl-Lasher model [6,7], fits into this class. This model consists of a system of uniaxial particles placed at the sites of a cubic lattice, interacting via a potential of the form

$$U_{ij}=-\epsilon_{ij}P_2(\cos\beta_{ij}), \tag{1}$$

where ϵ_{ij} is a positive constant, ϵ, for particles i and j at neighboring lattice sites and zero otherwise. $P_2(x)=1/2(3x^2-1)$ is the second-rank Legendre polynomial and β_{ij} is the angle between the symmetry axes of i and j. Extensive simulations by Fabbri and Zannoni [8] in the region of the nematic-isotropic (NI) transition indicate that this simple model gives an extremely good description of the transition. Indeed, it accurately predicts the small difference in temperature between the observed first-order NI transition and the second-order limiting instability of the isotropic phase, where the second-rank Kirkwood coefficient diverges. The success of the Lebwohl-Lasher model can be traced back to the fact that the dominant orientational correlations of the nematic phase occur on a length scale considerably larger than the molecular interactions, and so the simplification of the molecular potential and the location of the molecules at fixed lattice sites have no adverse influence on the phase behavior.

One particular drawback of the Lebwohl-Lasher lattice model is that, by definition, the NI transition occurs at constant volume, whereas in real liquid crystals, we expect to observe a change in density, albeit small. Moreover, since the model is based on a fully occupied lattice, this also

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means that we cannot investigate phenomena such as isotropic-vapor (IV) or nematic-vapor (NV) coexistence, although we should point out that simulations have been performed using ''hard'' nematic-vapor interfaces, in which the density drops from its bulk value to zero within one lattice spacing [9].

We address these drawbacks in this paper, introducing a lattice-gas extension of the Lebwohl-Lasher model. The model and grand canonical Monte Carlo simulations are described in Secs. II and III, respectively. In Sec. IV, we show that, depending on the strength of the single-variable parameter in this model, it is found to exhibit NI, NV, and IV coexstence. Our conclusions are presented in Sec. V.

II. THE LATTICE-GAS LEBWOHL-LASHER MODEL

The lattice-gas model provides us with probably the simplest model with which to investigate liquid-vapor condensation phenomena [10]. In a lattice-gas model, each lattice site can host either zero or one particle, with the total occupation or density ρ of sites governed by an imposed chemical potential, μ [11]. The pair potential between two sites i and j is simply

$$U_{ij} = -s_i s_j \epsilon_{ij}, \tag{2}$$

where $s_i = 0,1$ is the occupation number of site i, and ϵ_{ij} is a positive constant ϵ for neighboring lattice sites i and j and zero otherwise. This model exhibits liquid-vapor coexistence (or a high-density–low-density transition) at low temperatures. As the temperature is increased, the density gap bewteen the phases decreases, and eventually the coexistence curve is terminated by a critical point, just as we expect for liquid-vapor coexistence.

This isotropic potential is readily extended to an anisotropic form reminiscent of the Lebwohl-Lasher model by multiplying the interaction in Eq. (2) by $P_2(\cos\beta_{ij})$,

$$U_{ij} = -s_i s_j \epsilon_{ij} P_2(\cos\beta_{ij}). \tag{3}$$

This model has recently been investigated using computer simulation and the phase diagram determined and compared to that of molecular-field theories [12–14]. The results of these simulations (see Fig. 1) were described in the context of mixtures of rod-shaped and spherical molecules in which the rods are modeled by the occupied sites and the spheres by the vacancies [15]. For a mixture with fixed-rod and sphere concentrations, the phase diagram is interpreted as follows. At high-rod concentrations, the phase sequence with decreasing temperature is observed to be isotropic, followed by a biphasic region of coexisting rod-rich nematic and rod-poor isotropic phases, followed by pure nematic and finally a re-entrant biphasic region. At lower-rod concentrations, the biphasic region observed on cooling from the isotropic phase is stable at all lower temperatures.

This phase diagram can also be (re)interpreted along the lines of constant temperature in the terms of a single-component system undergoing a nematic-isotropic phase transition. Starting at a low temperature, a high-density nematic coexists with a low-density isotropic fluid. On heating, the coexistence density of the isotropic phase increases and that of the nematic decreases. At $T^* \approx 0.87$, the coexistence density of the nematic starts to increase, but the strength of the transition continues to decrease, until at $T^* = T^*_{NI} \approx 1.127$, the nematic and isotropic phases coexist at full lattice occupancy, that is, the Lebwohl-Lasher limit is recovered [8].

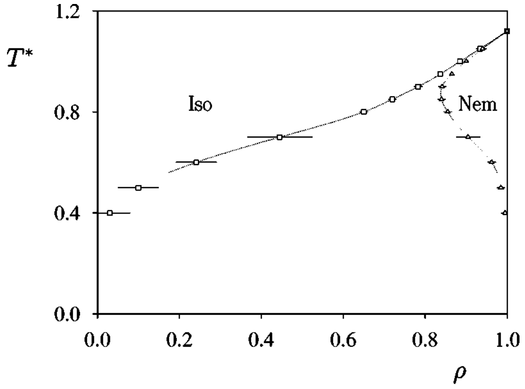

FIG. 1. Temperature-density phase diagram for the lattice-gas Lebwohl-Lasher model with $\lambda = 0$ [15], showing the regions of stability of the nematic- and isotropic-fluid phases. The unmarked region in the middle of the phase diagram is the biphasic region. Squares: isotropic coexistence density, triangles: nematic coexistence density. The dotted line is a guide to the eye. Units: temperature $T^* = T/\epsilon$, density $\rho = N_m/N_l$, where N_m is the number of occupied sites and N_l is the number of lattice sites.

While this model exhibits interesting behavior, there is a major difference between the phase behavior observed and that for real mesogens. Namely, for real systems, we expect to observe an isotropic phase in coexistence with its vapor at high temperature and a nematic phase in coexistence with its vapor at lower temperature. Thus, the model as it stands exhibits neither the IV or NV coexistence we intuitively expect, but just coexistence between a nematic phase and an isotropic fluid. As we have already discussed for the isotropic lattice-gas model, isotropic dispersion forces lead to liquid-vapor coexistence. It therefore seems reasonable that the liquid-crystal model described exhibits just an isotropic fluid, rather than distinct isotropic-liquid and vapor phases, because the isotropic term in Eq. (3) is too weak in comparison to the anisotropic term. Note that because it contains the second-rank Legendre polynomial, Eq. (3) is not purely anisotropic, but contains both isotropic and anisotropic contributions to the potential. Alternative versions of the potential sometimes used for Lebwohl-Lasher model simulations that are shifted by a scalar isotropic term, such as $U_{ij} = -\epsilon_{ij}\cos^2\beta_{ij}$, would lead to different phase behavior than that observed for the lattice-gas Lebwohl-Lasher model defined by Eq. (3), even though they exhibit the same behavior for the fully occupied lattice.

We have, therefore, used a model that allows the isotropic interactions between the occupied lattice sites to be varied. The interaction between a pair of sites i and j is then given by

$$U_{ij} = -s_i s_j \epsilon_{ij}[\lambda + P_2(\cos\beta_{ij})], \tag{4}$$

where the addition of the single-variable parameter λ increases the isotropic contribution to the potential between two neighboring occupied sites (for $\lambda > 0$). For $\lambda = 0$, we trivially recover the original anisotropic potential Eq. (3). In the limiting case of a completely saturated lattice, the addition of the isotropic term λ has no influence on the phase behavior because all lattice sites are occupied, and so this term serves only to shift the total potential energy of the system. This means that for all values of λ, we expect the system to behave exactly as the Lebwohl-Lasher model when the lattice is fully occupied, and so can actually guarantee the existence of an orientationally ordered nematic phase for this model, although this may be confined to the fully saturated line of the phase diagram ($\rho = 1$). However, we cannot *a priori* guarantee isotropic liquid-vapor coexistence, since, as we shall see, this depends on the strength of the isotropic interaction. Recall that the isotropic term should lead to IV coexistence, but this may be metastable with respect to nematic-isotropic fluid coexistence that arises due to the anisotropic potential. We should point out that while we may be able to reproduce the generic phase behavior of a nematogen and so study the properties of the nematic, isotropic, and vapor phases we cannot study, by definition, the translationally ordered smectic or solid phases with a lattice model.

III. SIMULATION DETAILS

The lattice-gas Lebwohl-Lasher models defined by Eq. (4) for various values of the variable parameter λ were studied using grand canonical Monte Carlo simulations at fixed chemical potential μ [16]. One cycle involved $N_t = \min(5N_m^\dagger, 2N_l)$ trials, where $N_m^\dagger$ is the number of molecules (occupied sites) at the start of the cycle and N_l is the number of lattice sites. The trials were conducted as follows: (a) A canonical trial, chosen with probability $N_m^\dagger/N_t$, in which a molecule i was chosen randomly and given a random rotation. Twenty percent of these trials also employed a translational move, in which the molecule is moved to either one of the six neighboring sites or to a completely random position; these were rejected if the trial position was already occupied. These trials are accepted or rejected with the usual Metropolis rules [16]. (b) A grand canonical trial, chosen with probability $(N_t - N_m^\dagger)/N_t$, in which a particle is either removed at random (and no record of its position or orientation is kept) or inserted at a random position with a random orientation. These removal/insertion trials are chosen with equal probabilities and accepted or rejected with the usual grand canonical rules [16]. Rejection is immediate if the chosen site for an insertion is already occupied. Note that $N_m^\dagger$, the number of molecules in the system at the start of the cycle, is used rather than N_m, the instantaneous number of molecules. This is to ensure that the probability of choosing the different types of trials does not change during the cycle, that is, after the insertion or removal of a molecule, and so strict detailed balance is maintained within each cycle.

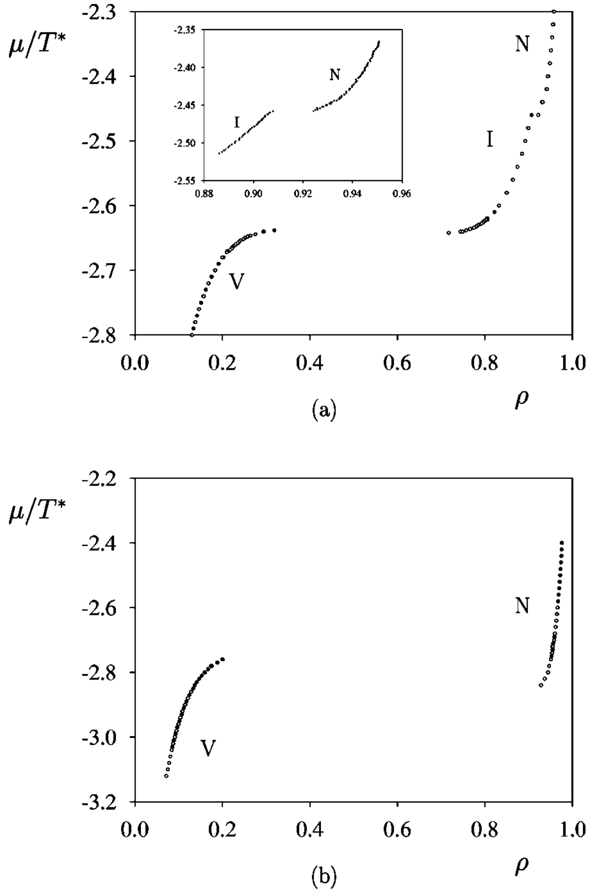

FIG. 2. Equation of state for the lattice-gas Lebwohl-Lasher model with $\lambda = 0.80$. (a) Nematic, isotropic liquid, and vapor branches of the equation of state at $T^* = 1.04$, (b) nematic and vapor branches at $T^* = 1.00$. The inset in (a) shows the nematic-isotropic transition in more detail. Open points: simulations started in the nematic phase. Closed points: simulations started in the vapor phase.

Initial simulations were performed on lattices of size $l^3 = 15^3$ to find values for the potential parameters and temperatures for which interesting phase behavior could be observed. These were followed by simulations of larger systems of size $l^3 = 40^3$, which were used to accurately determine the equation of state in the (ρ, μ) plane along various isotherms. A series of simulations for each temperature were performed in cascade, for both increasing chemical potential starting with an empty lattice and decreasing chemical potential starting with a saturated lattice of completely aligned particles. For the $l^3 = 40^3$ system, equilibration runs of 10 000–20 000 cycles were found to be adequate, and were followed by production runs of at least 25 000 cycles. Near any transitions, longer equilibration and production runs of 100 000's of cycles were used. Two typical equations of state are shown in Fig. 2 for $\lambda = 0.80$, one below the NIV triple point (ie., where NV coexistence is observed) and one between the triple point and the IV critical point (i.e., where both IV and NI coexistence can be observed, depending on the chemical potential).

The equations of state (see Fig. 2) were used to estimate the coexistence densities of the observed phases. In practice, for the higher temperatures, it is straightforward to extract the coexistence densities from the small but finite hysteresis in the equation of state. At lower temperatures, the hysteresis is somewhat larger, but this region of the phase diagram typically corresponds to a high-density nematic (almost fully saturated lattice) coexisting with a low-density gas (virtually empty lattice), and so is not as interesting as the higher-temperature region of the phase diagram. Indeed, these temperatures for the model system would most probably correspond to the regions of smectic or crystal stablility for real systems, which cannot, by definition, be investigated with the lattice model.

IV. PHASE BEHAVIOR AND DISCUSSION

The phase behavior was determined as outlined in the previous section for the lattice-gas Lebwohl-Lasher model with $\lambda = 0.50$, 0.75, 0.80, 0.85, and 1.00. The phase diagram for $\lambda = 0$ [15] has already been discussed in Sec. II and is shown in Fig. 1. The phase behavior for $\lambda = 0.50$ is similar to that exhibited by the model with $\lambda = 0$ in that only nematic- and isotropic-fluid phases are observed, although the nematic-isotropic fluid coexistence curve is shifted to higher temperatures. This temperature shift reduces the region of stability of the nematic phase. The phase diagram for the larger value of $\lambda = 0.75$ highlights this effect [see Fig. 3(a)]. The nematic is not stable at any temperatures below $\rho \approx 0.92$, compared to $\rho = 0.84$ for the original model with $\lambda = 0$. At this strength parameter, the first evidence of an IV critical point may be found. The equation of state (not shown) obtained for increasing chemical potential indicates that a density jump occurs between an isotropic-vapor and liquid phase, although the liquid phase exists only over a very narrow chemical potential range, as a second jump in density to nematic phase occurs on increasing the chemical potential further. On lowering the chemical potential starting in the nematic phase, the isotropic phase is not observed, rather the nematic transforms directly to a low-density vapor phase, with no further transitions observed. It seems likely that, for $\lambda = 0.75$, the isotropic liquid-vapor coexistence expected for a purely isotropic potential is just metastable with respect to the phase separation into a nematic- and isotropic-fluid phase. Thus, the liquid-vapor critical point is very close to the nematic-isotropic-vapor triple point for $\lambda = 0.75$.

On increasing λ to 0.80, the isotropic branch of the equation of state is clearly stable with respect to both the vapor and nematic phases over a range of temperatures [see Fig. 2(a) for the equation of state at $T^* = 1.04$] and so we do observe isotropic liquid-vapor coexistence. If the chemical potential is increased at fixed temperature, the system undergoes a further transition to the nematic phase, at which a much smaller change in density is observed. This, of course, is nothing strange since increasing the chemical potential in the simulation is similar to increasing the pressure in a real system [17]. It turns out to be much easier (for a lattice system) to specify the chemical potential rather than the pressure.

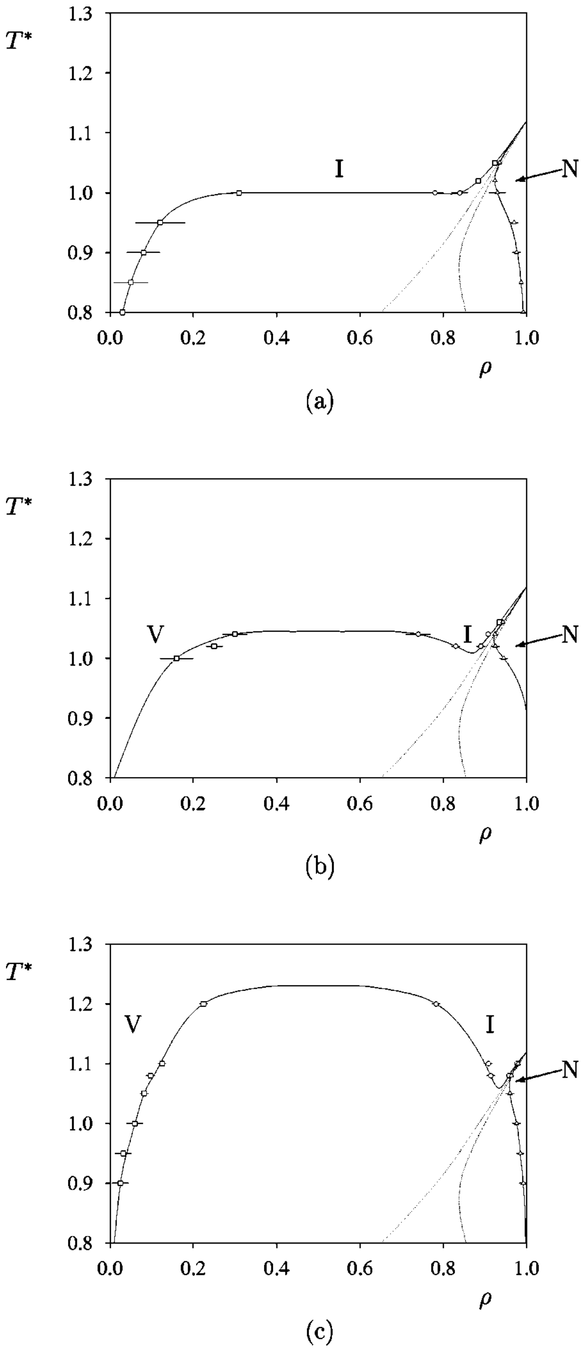

FIG. 3. Phase diagrams for the lattice-gas Lebwohl-Lasher model with (a) $\lambda = 0.75$, (b) $\lambda = 0.80$, and (c) $\lambda = 1.00$. The solid lines are guides to the eye, and the dotted lines indicate the nematic-isotropic fluid coexistence curves for the model with $\lambda = 0$ (see Fig. 1). N: nematic, I: isotropic liquid or fluid, V: vapor. Units are as Fig. 1.

Note that for $\lambda = 0.80$ [see Fig. 3(b)], the critical point for the isotropic-vapor transition is below the upper bound for the nematic-isotropic transition for the fully saturated Lebwohl-Lasher model. This means that for all temperatures where a distinct isotropic liquid is observed, a transition to a nematic phase will be observed at higher-chemical potential (or pressure). Since the energy parameter for the isotropic lattice-gas model [Eq. (2)] simply scales the temerature dependence of the coexistence curve for liquid-vapor separation, we expect that increasing the strength of the isotropic parameter λ in the mesogenic model should raise the liquid-vapor transition to higher temperatures. This is indeed what is observed, as shown in Fig. 3(c). The IV critical point occurs at a temperature higher than the NI transition temperature for the Lebwohl-Lasher model. This may be seen as an artifact of the model. Although we may expect the NI transition to occur at higher densities at higher temperatures, the model cannot access densities greater than $\rho=1$. Clearly, increasing λ would raise the critical point to even higher temperatures and further reduce the region of stability of the nematic phase. Indeed, if λ is increased so that the coexisting liquid and vapor phases have densities $\rho=1$ and 0, respectively, above the NI transition temperature of the Lebwohl-Lasher model, then the nematic phase would only be observed along the $\rho=1$ isochore, that is, for the fully occupied lattice model.

V. CONCLUSIONS

We have performed grand canonical Monte Carlo simulations on a lattice-gas extension of the well-known Lebwohl-Lasher model. We find that depending on the strength of the single-variable parameter λ, the model may exhibit either a two-phase phase diagram involving isotropic fluid and nematic phases or a three-phase phase diagram, containing distinct isotropic-vapor and liquid phases in addition to the orientationally ordered nematic. This, therefore, provides a useful model with which to study condensed mesogens in coexistence with their vapor phase, for example, at nematic-vapor and isotropic-vapor interfaces.

ACKNOWLEDGMENT

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