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Monte Carlo study with reweighting of uniaxial nematic liquid crystals composed of biaxial molecules

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We present a high accuracy Monte Carlo simulation study of the uniaxial nematic (N_U) to isotropic (I) phase transition of a lattice dispersion model of uniaxial nematics composed of biaxial molecules. The N_U-I coexistence curve terminating at the Landau critical point has been determined using the multiple histogram reweighting technique. A close investigation reveals a sharp departure in the nature of the N_U-I coexistence curve in the temperature-biaxiality parameter phase diagram in comparison to the earlier theoretical (either mean-field or computer simulation) predictions. The coexistence curve shows a change in curvature with increasing value of the degree of molecular biaxiality.

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I. INTRODUCTION

In recent years, a great deal of attention has been devoted to investigations of the phase transformations in thermotropic liquid crystals composed of bent-core molecules [1,2]. Such molecules can be assumed to possess D_{2h} symmetry and are commonly referred to as biaxial molecules, in contrast to the conventional uniaxial molecules having $D_{\infty h}$ symmetry. It is well known from Landau–de Gennes (LDG) [3] and Maier-Saupe mean field (MF) theories that the isotropic to nematic phase transition in thermotropic liquid crystals (LCs) composed of cylindrically symmetric molecules is weakly first order. This has been confirmed by experiments [4,5] as well as by computer simulations [6,7]. In a more recent experimental study, Wiant *et al.* [8] observed that the isotropic (I) to the uniaxial nematic (N_U) transition for LCs composed of biaxial (bent-core) molecules is notably weaker than conventional thermotropic LCs formed from uniaxial molecules. These authors observed [8] that for nematics composed of bent-core molecules $T_{NI} - T^- \approx 0.4\,^\circ\mathrm{C}$, whereas for typical calamitic (rod-shaped) liquid crystals $T_{NI} - T^- \geqslant 1\,^\circ\mathrm{C}$. Here T_{NI} is the nematic-isotropic transition temperature and T^- is the supercooling limit of the nematic phase.

Bent-core molecules possess a high degree of molecular biaxiality. The possible effects of molecular biaxiality on nematic order have been studied theoretically using a number of techniques. These include molecular field treatments [9–16], computer simulation studies of lattice dispersion models [17–20] and the off-lattice biaxial Gay-Berne model [21,22]. All these studies predict sequences of phase transitions, from N_U to I at a higher temperature and from biaxial nematic (N_B) to uniaxial nematic (N_U) at a lower temperature. Also a direct N_B to I transition is predicted at a particular molecular geometry.

Apart from the above observations, molecular field studies [14,16] have shown that the increase in degree of molecular biaxiality influences the N_U-I transition in a number of ways. First, as the molecular biaxiality parameter λ (a measure of the molecular biaxiality and to be defined later) increases, the nematic order parameter S at the phase transition becomes smaller and thus the jump in S at the N_U-I transition decreases. Second, the transition temperature T_{NI} decreases monotonically with increase in λ. Third, the difference between the N_U-I transition temperature and the orientational spinodal temperature (T^-) decreases monotonically with increasing λ and finally these two temperatures merge as λ approaches its critical value $\lambda = \lambda_C = 1/\sqrt{6} = 0.40825$.

More recently, a Monte Carlo (MC) simulation study [23] based on a lattice dispersion model investigated the influences of molecular biaxiality on the N_U-I transition using the multiple histogram reweighting technique [24], and the relevant part of the free energy was generated for two different systems: one composed of uniaxial molecules and the other of biaxial molecules. Although the work reported in Ref. [23] emphasized the effect of an external field on uniaxial and biaxial molecules, from free energy analysis it was pointed out that molecular biaxiality weakens further the weak first-order N_U-I transition. The investigations presented in Ref. [23] were limited to only two values of molecular biaxiality parameter (0 and 0.20) and also the aim of the study was different, namely the effects of an external magnetic field on nematic order.

The fact that the increase in λ leads to weakening of N_U-I transition was also observed in a previous MC study [18] from the plots of order parameter and heat capacity, where the same dispersion model with three different values of λ (0.2, 0.3, and 0.40825) was used. However, to explore the effects of molecular biaxiality on the N_U-I transition and the associated pretransitional behavior, more accurate simulation technique is necessary.

In this paper we present an MC study using the reweighting technique [24] on a lattice dispersion model to investigate

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the influences of molecular biaxiality on the N_U-I transition. We have found that after a certain value of the molecular biaxiality parameter λ, the nematic-isotropic phase transition temperature behaves anomalously. We report a biaxiality-induced change of curvature of the isotropic-nematic coexistence curve in the temperature–biaxiality parameter phase diagram for a widely studied dispersion model of biaxial molecules [17,18].

The plan of this paper is as follows: in Sec. II we discuss the dispersion model; in Sec. III we provide the technical details of the simulations; in Sec. IV we present the results. Conclusions are presented in Sec. V.

II. THE MODEL

We consider a lattice model of biaxial prolate molecules possessing D_{2h} symmetry (board-like), whose centers of mass are associated with a simple-cubic lattice. We use the dispersion potential [17,18] between two identical neighboring molecules, say the ith and jth molecules,

$$U_{ij}^{\rm disp} = -\epsilon_{ij}\big\{R^2_{00}(\Omega_{ij}) + 2\lambda\big[R^2_{02}(\Omega_{ij}) + R^2_{20}(\Omega_{ij})\big] + 4\lambda^2 R^2_{22}(\Omega_{ij})\big\}. \tag{1}$$

Here $\Omega_{ij} = \{\phi_{ij}, \theta_{ij}, \psi_{ij}\}$ denotes Euler angle triplets defining the relative orientation of ith and jth molecules. To define the Euler angles, we have followed the convention used by Rose [25]. The strength parameter, ϵ_{ij}, is assumed to be a positive constant (ϵ) when the particles i and j are nearest neighbors and zero otherwise. R^L_{mn} denote combinations of symmetry-adapted (D_{2h}) Wigner functions

$$R^2_{00} = \frac{3}{2}\cos^2\theta - \frac{1}{2}, \tag{2}$$

$$R^2_{02} = \frac{\sqrt{6}}{4}\sin^2\theta\cos 2\psi, \tag{3}$$

$$R^2_{20} = \frac{\sqrt{6}}{4}\sin^2\theta\cos 2\phi, \tag{4}$$

$$R^2_{22} = \frac{1}{4}(1+\cos^2\theta)\cos 2\phi\cos 2\psi - \frac{1}{2}\cos\theta\sin 2\phi\sin 2\psi. \tag{5}$$

The parameter λ is a measure of the degree of molecular biaxiality. For dispersion interactions λ can be expressed in terms of the eigenvalues (ρ_1, ρ_2, ρ_3) of the polarizability tensor ρ of the biaxial molecule as $\lambda = \sqrt{3/2}(\rho_2 - \rho_1)/(2\rho_3 - \rho_2 - \rho_1)$. The condition for the maximum biaxiality is $\lambda = \lambda_C = 1/\sqrt{6}$. $\lambda < \lambda_C$ corresponds to the case of prolate molecules, whereas $\lambda > \lambda_C$ corresponds to oblate molecules. The above dispersion model reproduces both the uniaxial and the biaxial orientational orders and various order-disorder transitions as a function of temperature and molecular biaxiality [17,18].

We consider a range of values of the biaxiality parameter in our simulations. For $\lambda = 0$ the pair potential takes the usual Lebwohl-Lasher (LL) form [26] for nematic liquid crystals of perfectly uniaxial molecules and has been extensively studied by Zhang *et al.* [6]. The LL model exhibits a single weak first-order N_U-I transition at a dimensionless temperature ($T = kT_K/\epsilon$, T_K being the temperature measured in Kelvin and k the Boltzmann constant) $T = 1.1232 \pm 0.0001$ [6,23] ($T = 1.1232 \pm 0.0006$ [7]). On the other hand, the biaxial model ($0 < \lambda < 1/\sqrt{6}$) is found to exhibit a N_B-N_U phase transition at lower temperature and a N_U-I transition at higher temperature ($T \approx 1.1$) [18,27]. The N_B-N_U transition is known to be of second order while the N_U-I transition is of first order. We restrict our simulations within a narrow range of temperatures around the N_U-I transition as discussed below.

III. COMPUTATIONAL DETAILS

A series of Monte Carlo (MC) simulations using the conventional Metropolis algorithm on a periodically repeated simple cubic lattice, for the system size $L = 64$ ($N = L^3$) were performed. The system size chosen in our simulations is sufficiently large so that finite size corrections are negligible. We used a range of values of molecular biaxiality parameter λ (0, 0.075, 0.150, 0.200, 0.250, 0.300, 0.325, 0.350, 0.375, and 0.408). An orientational move was attempted following the Barker-Watts method [28]. For a given value of λ the simulation at the lowest temperature studied was started from the perfectly ordered state. The simulations at the other temperatures for the same λ were run in cascade starting from an equilibrium configuration at a nearby lower temperature. To check for presence of hysteresis effects, we also performed the same experiment in a cooling sequence for $\lambda = 0$, i.e., starting from a random configuration at a higher temperature and using the corresponding equilibrated configuration as initial state for the next lower temperature. No such hysteresis effect was observed, perhaps due to the weak first-order nature of the transition.

In each simulation, histograms of energy, $h(E)$, were accumulated. For this we divided the continuous energy range (from $-3.0L^3$ to 0) with a sufficiently small bin width per particle ($\delta E = 0.001$). In our simulations 10^6 sweeps or MCS (Monte Carlo steps per site) for the equilibration and 3×10^6 MCS for the production run were used. For the lattice size ($L = 64$), the total run length is more than 10 000 times the correlation time. The correlation time was computed from the energy autocorrelation function for a given temperature using the method described in Ref. [29]. For example, the correlation time for $\lambda = 0.25$ and $T = 1.116$ is 2.5×10^7 moves, which is approximately 100 MCS. The total run was divided into several (100) blocks by performing independent simulations so that we could compute the jackknife errors [30].

In order to analyze the orientational order we calculated the second-rank order parameters $\langle R^2_{mn}\rangle$ following the procedure described by Vieillard-Baron [31]. According to this, a **Q** tensor is defined for the molecular axes associated with a reference molecule. For an arbitrary unit vector **w**, the elements of the **Q** tensor are defined as $Q_{\alpha\beta}(\mathbf{w}) = \langle(3w_\alpha w_\beta - \delta_{\alpha\beta})/2\rangle$, where the average is taken over the configurations and the subscripts α and β label Cartesian components of **w** with respect to an arbitrary laboratory frame. By diagonalizing the matrix, one obtains nine eigenvalues and nine eigenvectors which are then recombined to give the four order parameters $\langle R^2_{00}\rangle$, $\langle R^2_{02}\rangle$, $\langle R^2_{20}\rangle$, and $\langle R^2_{22}\rangle$ with respect to the director frame [32]. Out of these four second-rank order parameters the usual uniaxial order parameter $\langle R^2_{00}\rangle$ (or S), which measures the alignment of the longest molecular symmetry axis with the primary director (**n**), is involved in our study since we

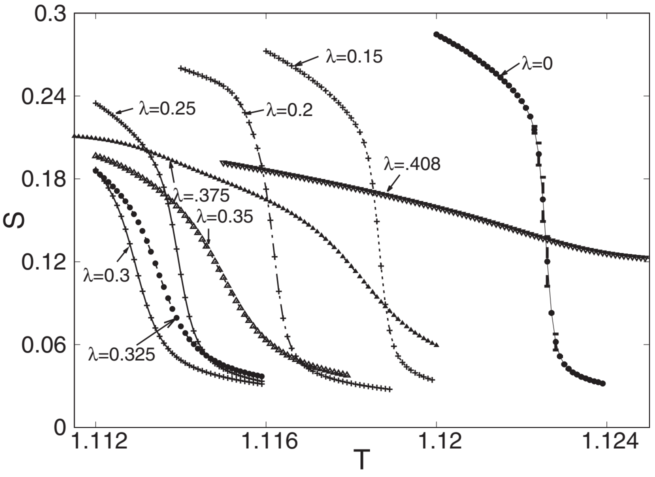

FIG. 1. Variation of order parameter with reduced temperature for different degrees of molecular biaxiality. Vertical bars on the plot corresponding to $\lambda = 0$ indicate the errors estimated by the jackknife method.

have simulated a very short temperature range (1.110–1.125) around T_{NI} within which no biaxial phase occurs. The full set of order parameters are required to describe completely the biaxial nematic phase of a system of biaxial molecules.

We have calculated the ordering susceptibility χ from fluctuations in the order parameter: $\chi = \frac{L^3(\langle (R^2_{00})^2\rangle - \langle R^2_{00}\rangle^2)}{T}$. In order to determine the order parameter and the ordering susceptibility one needs to generate a two-dimensional histogram of energy and order parameter. An alternative approach [33] is to estimate the constant-energy averages (corresponding to each energy bin) of the order parameter and its square from the simulation data. These averages are used to evaluate the order parameter and the corresponding susceptibility as a function of temperature using the reweighting method.

We have derived the relevant part of the free-energy-like functions $A(E)$ from the energy distribution functions $P(E)$ using the relation $A(E) = -\ln P(E)$ [34,35], where the normalized histogram count $P(E) = h(E)/\Sigma_E h(E)$.

IV. RESULTS

We first present the temperature dependence of the nematic order parameter (Fig. 1). As the degree of molecular biaxiality increases, the jump in the order parameter decreases and the transition shifts towards lower temperature till $\lambda = 0.3$. From $\lambda = 0.325$ the transition shifts towards right. We have studied the system till $\lambda = 0.408$. The jump at lower biaxialities signifies a first-order transition, and the diminishing jump as λ gets closer to $1/\sqrt{6}$ implies a weaker first-order transition. At $\lambda = 0.408$ a crossover is observed as expected and the transition is of second order.The variation of susceptibility with reduced temperature for different degrees of molecular biaxiality is given in Fig. 2. We observe that peak height of the susceptibility curve decreases with increasing biaxiality, which shows again the softening of the first-order transition. The temperature at which the N_U-I transition occurs decreases until $\lambda = 0.3$ and thereafter increases again.

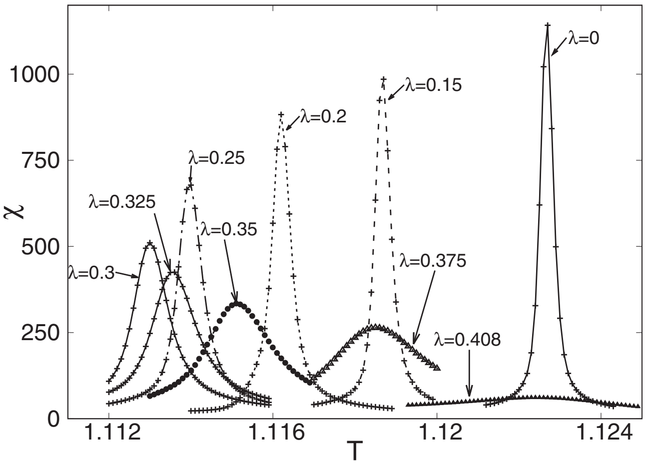

FIG. 2. Variation of susceptibility with reduced temperature for different degrees of molecular biaxiality. The peak height of the susceptibility curve decreases with increasing biaxiality. Also, the N_U-I transition temperature decreases with increasing biaxiality until $\lambda = 0.3$ and increases thereafter.

We now discuss the pretransitional effects for this model and the influences of molecular biaxiality on these effects. The derived free energy functions $A(T, L)$ provide a detailed picture of the stability limits of both the N_U phase and the I phase. Here we shall present the stability limit of the I phase only since both the limits are symmetric around the equilibrium transition for this model. The orientational spinodal temperature, $T^-(L)$, for different values of λ is estimated as the temperature where the second local minimum of $A(T, L)$ just vanishes as T is gradually lowered below T_{NI}. The free energy vs energy plots at N_U-I transition temperature and supercooling temperature for four different values of the biaxiality parameter are shown in Fig. 3. In each plot two different ordinates are used to represent the curves corresponding to T_{NI} and T^- on the same plot. The ordinate on the left of each plot corresponds to the free energy vs energy curve at T_{NI} and the

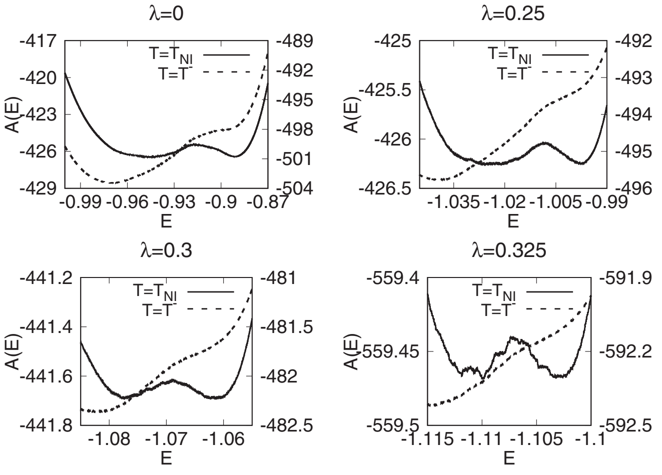

FIG. 3. Free energy vs energy at N-I transition for four different degrees of molecular biaxiality, $\lambda = 0$, 0.25, 0.3, and 0.325. The dashed curves show the spinodal behavior of the model.

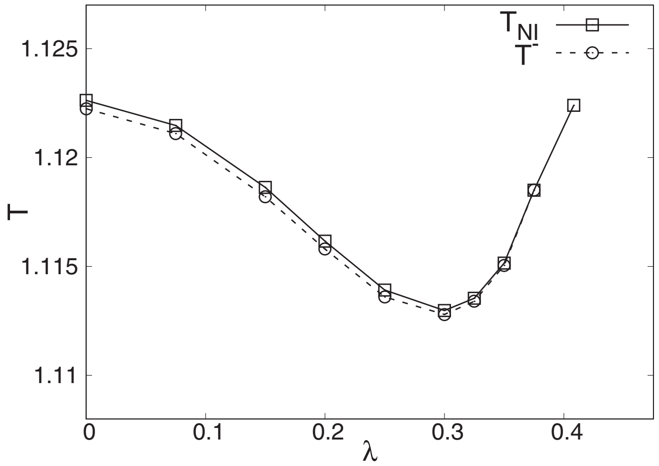

FIG. 4. T_{NI} vs λ phase diagram for the nematic-isotropic transition. The coexistence curve slopes downwards till $\lambda = 0.3$ and then slopes upwards till $\lambda = 1/\sqrt{6}$. The dashed curve represents orientational spinodal line. The error bars are smaller than the point size.

ordinate on the right corresponds to the free energy vs energy curve at T^-. Figures are plotted for λ values 0, 0.25, 0.3, and 0.325. We can see from the curves corresponding to T_{NI} that, as the value of biaxiality parameter increases, the depth of the free energy well decreases, taking the transition closer to being second order. For λ greater than 0.325 the depth of the free energy well at transition becomes so small that the structure of the well becomes nondiscernible from random fluctuations.

Investigators have also used the Lee and Kosterlitz finite size scaling method [34] to obtain the N_U-I temperature for $\lambda = 0$. Priezjev and Pelcovits [36] studied system sizes up to 70^3 using the single histogram reweighting technique [24] and obtained $T_{NI} = 1.1225 \pm 0.0001$ in the thermodynamic limit. This result is very close to what we obtained in the present study, namely $T_{NI} = 1.1226 \pm 0.0001$ for a system size 64^3. More recently Shekhar *et al.* [37] reported $T_{NI} = 1.1229 \pm 0.00015$ in a study similar to that of Priezjev and Pelcovits [36], but with relatively smaller system sizes (upto 40^3). Perhaps the use of smaller system sizes resulted in a slightly different value of T_{NI} obtained in this work. It may also be noted that, besides the transition temperature, our estimate of the depth in the free energy well (for $\lambda = 0$) is in close agreement with the finding of Priezjev and Pelcovits [36], namely of the order of 1.0ϵ.

Finally, in Fig. 4, we present the coexistence line and the orientational spinodal line in the λ-T plane. We see that both T_{NI} and T^- first decrease with increasing value of the biaxiality parameter and then increase with increasing λ. This observation deviates from the prediction of MF theory, which shows a monotonic nature of the T_{NI} vs λ curve, i.e., no change of curvature. While earlier MC simulations show no perceivable effect of molecular biaxiality upon T_{NI}. It should be noted that the exact nature of T_{NI} vs λ curve is revealed when T_{NI} is computed with sufficiently high temperature resolution Table I.

TABLE I. N-I transition temperatures for different values of the biaxiality parameter λ for the biaxial systems. Estimates of orientational spinodal temperature T^- are also listed for the systems having lower λ. The estimated (jackknife) error in each temperature is within ±0.0001.

λ	T_{NI} [from χ vs T]	T_{NI} [from $F(E)$ vs T]	T^-
0	1.1227	1.1226	1.1222
0.075	1.1215	1.1214	1.1211
0.150	1.1187	1.1186	1.1182
0.200	1.1163	1.1162	1.1158
0.250	1.1140	1.1139	1.1136
0.300	1.1130	1.1130	1.1128
0.325	1.1136	1.1135	1.1134
0.350	1.1151	1.1151	1.1150
0.375	1.1185	1.1186	1.1185
0.408	1.1224		

Another important observation is that the gap between these curves decreases monotonically and finally vanishes as λ approaches λ_C. A similar qualitative feature was found in the molecular-field theory study of To *et al.* [16].

V. CONCLUSION

We have reported the results of a MC study of a uniaxial nematic system composed of biaxial molecules. The temperature resolution used in this work is more than what is available in previous MC studies. The peculiar nature manifested in the change of curvature of the T_{NI}-λ curve exhibited in Fig. 4, to our knowledge not obtained in any previous MC work or MF studies, is the main finding of our work and needs to be explained by rigorous theoretical methods.

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