High accuracy Monte Carlo study of dispersion model of biaxial liquid crystals

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Abstract

We present a high accuracy Monte Carlo simulation study of the Isotropic - Nematic phase transition of a lattice dispersion model of biaxial liquid crystals. The NI coexistence curve terminating at the Landau critical point have been determined using multiple histogram reweighting technique. A close investigation reveals a sharp departure in the nature of the N-I coexistence curve in 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 molecular biaxiality.

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1 INTRODUCTION

In recent years, a great deal of attention has been devoted to investigations of the phase transformations in the thermotropic liquid crystals composed of bent-core molecules [1, 2]. Such molecules can be assumed to possess $D_{2h}$ symmetry and are commonly referred as biaxial molecules in contrast to the conventional uniaxial nematogenic molecules having $D_{\infty h}$ symmetry. It is well known from Landau-deGennes (LDG) [3] and Maier-Saupe mean field theories that the isotropic to nematic phase transition in thermotropic liquid crystals 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. In their study [8] they measured a very low stability limit of the isotropic phase of their bent-core compounds by measuring $T_{NI} - T^* \approx 0.4^\circ C$, $T^*$ being the super-cooling limit, compared to the typical calamitic (rod-shaped) liquid crystals for which $T_{NI} - T^* \geq 1^\circ C$.

Bent-core molecules have exhibited other diverse effects such as formation of chiral phases in achiral molecules [9], indication of possible biaxial nematic order ($N_B$) in thermotropic LCs [10, 11] etc. Formation of microscopic clusters of bent-core molecules in isotropic phase and high degree of molecular biaxiality of this new class of nematics are the primary factors for these unconventional behaviours as has been stated in Ref. [8]. (The biaxial nature of the constituent bent-core molecules is relevant specifically for the present study and this issue will be addressed later.)

The possible effects of molecular biaxiality on nematic order have been studied theoretically using a number of techniques. These include molecular field treatments [12, 13, 14, 15, 16, 17, 18, 19], computer simulation studies of lattice dispersion models [20, 21, 22, 23] and off-lattice biaxial Gay-Berne model [24, 25]. All these studies predict sequences of phase transitions, from $I$ to $N_U$ at a higher temperature and from $N_U$ to $N_B$ at a lower temperature. Also a direct $I$ to $N_B$ transition is predicted at a particular molecular geometry.

Apart from the above observations, molecular field studies [17, 19] have shown that the increase of degree of molecular biaxiality influences the $I$ - $N_U$ transition in a number of ways. First, as molecular biaxiality parameter increases the nematic order parameter $S$
at the phase transition becomes smaller and thus the jump in $S$ at the $I - N_U$ transition decreases. Second, the transition temperature $T_{NI}$ decreases monotonically with increase in $\lambda$. Third, the difference between the $I - N_U$ transition temperature and the orientational spinodal temperature ($T^*$) decreases monotonically with increasing $\lambda$ and finally, these two temperatures merges as $\lambda$ approaches its critical value $\lambda = \lambda_C = 1/\sqrt{6}$.

More recently, a Monte Carlo (MC) simulation study [26] based on a lattice dispersion model has investigated the influences of molecular biaxiality on $I - N_U$ transition using multiple histogram reweighting technique [27] and the relevant part of the free energy has been generated for two different systems - one composed of uniaxial molecules and the other of biaxial molecules. Although the work reported in Ref. [26] emphasized on the effect of an external field on uniaxial and biaxial molecules, however, from free energy analysis it established (pointed out) an important fact that molecular biaxiality weakens further the weak first order $I - N_U$ transition. The investigations presented in Ref. [26] were limited to a single value of molecular biaxiality parameter and also the aim of the study was different, namely the effects of field on nematic order. So far, there is no other simulations which were able to investigate the influence of biaxiality on $I - N_U$ transition. The limited number of studies in this area is due to the lack of accuracy in conventional simulation technique necessary to explore the influences of deviation from cylindrical symmetry of nematogenic molecules on pretransitional behaviours in $I - N_U$ transition.

In this paper we present an MC study using powerful reweighting technique [27] on a lattice dispersion model to investigate the influences of molecular biaxiality on $I - N_U$ transition. We have found that after a certain value of the molecular biaxiality parameter, $\lambda$ (to be elaborated later), the nematic-isotropic phase transition temperature behaves anomalously. We thus report on an unprecedented biaxiality-induced change of curvature of the isotropic-nematic co-existence curve in temperature - biaxiality parameter phase diagram for a widely studied dispersion model of biaxial molecules [20, 21].

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.
Here we consider a system of biaxial prolate molecules possessing $D_{2h}$ symmetry (board-like), whose centres of mass are associated with a simple-cubic lattice. We use the dispersion potential \[ U_{ij}^{\text{disp}} = -\epsilon_{ij} \{ R_{00}^2(\Omega_{ij}) + 2\lambda [R_{02}^2(\Omega_{ij}) + R_{20}^2(\Omega_{ij})] + 4\lambda^2 R_{22}^2(\Omega_{ij}) \} \]. (1)

Here $\Omega_{ij} = \{ \phi_{ij}, \theta_{ij}, \psi_{ij} \}$ denotes the triplet of Euler angles defining the relative orientation of $i^{th}$ and $j^{th}$ molecules; we have used the convention used by Rose \[28\] in defining the Euler angles. $\epsilon_{ij}$ is the strength parameter which is assumed to be a positive constant ($\epsilon$) when the particles $i$ and $j$ are nearest neighbours and zero otherwise. $R_{mn}^{L}$ are combinations of symmetry-adapted ($D_{2h}$) Wigner functions

\[ R_{00}^2 = \frac{3}{2} \cos^2 \theta - \frac{1}{2}, \]

\[ R_{02}^2 = \frac{\sqrt{6}}{4} \sin^2 \theta \cos 2\psi, \] (3)

\[ R_{20}^2 = \frac{\sqrt{6}}{4} \sin^2 \theta \cos 2\phi, \] (4)

\[ R_{22}^2 = \frac{1}{4} (1 + \cos^2 \theta) \cos 2\phi \cos 2\psi - \frac{1}{2} \cos \theta \sin 2\phi \sin 2\psi. \] (5)

The parameter $\lambda$ is a measure of the molecular biaxiality and for the dispersion interactions, it can be expressed in terms of the eigenvalues ($\rho_1$, $\rho_2$, $\rho_3$) of the polarizability tensor $\rho$ of the biaxial molecule $\lambda = \sqrt{3/2(\rho_2 - \rho_1)/(2\rho_3 - \rho_2 - \rho_1)}$. The condition for the maximum biaxiality (also known as the self-dual geometry) 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. This dispersion model can successfully reproduce both the uniaxial and the biaxial orientational orders and various order-disorder transitions as a function of temperature and molecular biaxiality \[20\] \[21\].

In our simulations we consider a range of values of biaxiality parameter. For $\lambda = 0$ the pair potential takes the usual Lebwohl-Lasher (LL) form \[29\] for nematic liquid crystals of perfectly uniaxial molecules which has been extensively studied by Zhang \textit{et al.} \[6\]. $0 < \lambda \leq 0.40325$ represents biaxial systems composed of prolate biaxial molecules. For the LL model there is a single weak first-order $I - N_U$ transition at a dimensionless temperature ($T_{NI} = kT_K/\epsilon$, $T_K$ being the temperature measured in Kelvin and $k$ the Boltzmann’s
constant) $T = 1.1232 \pm 0.0001$ [6, 26] ($T = 1.1232 \pm 0.0006$ [30]). From the Monte Carlo results, as reported in [21, 31], the biaxial model ($0 < \lambda < 0.40325$) is found to exhibit a biaxial-uniaxial phase transition at lower temperature and a uniaxial-isotropic transition at higher temperature ($T \approx 1.1$). The biaxial nematic-uniaxial nematic transition is known to be second order while the uniaxial nematic-isotropic transition is known to be first order. We restrict our simulations within a narrow range of temperature around the $I - NU$ transition as discussed below.

3 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 $L = 64$ ($N = L^3$) have been performed. The system size chosen in our simulations is sufficiently large so that finite size corrections are negligible. We have used a range of values of molecular biaxiality parameter, $\lambda$ (0, 0.150, 0.200, 0.250, 0.300, 0.325, 0.350, 0.375, and 0.40825). An orientational move was attempted following the Barker-Watts method [32]. For a given value of $\lambda$ the simulation at the lowest temperature studied was started from the perfectly ordered state. The simulations at the other temperatures for the same $\lambda$ run in cascade starting from an equilibrium configuration at a nearby lower temperature.

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 ($\Delta E = 1.0$). In our simulations $10^6$ sweeps or MCS (Monte Carlo steps per site) for the equilibration and $3 \times 10^6$ 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 total run was divided into several (100) blocks by performing independent simulations so that we could compute the jackknife errors [33].

In order to analyze the orientational order we have calculated the second rank order parameters $\langle R^2_{mn} \rangle$ following the procedure described by Vieillard-Baron [34]. 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 $Q_{\alpha\beta}(w) =$
\[ \langle (3w_\alpha w_\beta - \delta_{\alpha\beta})/2 \rangle, \]

where the average is taken over the configurations and the subscripts \( \alpha \) and \( \beta \) label Cartesian components of \( w \) with respective 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 \( \langle R_{00}^2 \rangle, \langle R_{02}^2 \rangle, \langle R_{20}^2 \rangle \) and \( \langle R_{22}^2 \rangle \) with respect to the director frame \[^{35}\]. Out of these four second rank order parameters the usual uniaxial order parameter \( \langle R_{00}^2 \rangle \) (or, \( S \)) which measures the alignment of the longest molecular symmetry axis with the primary director (\( n \)), is involved in our study because we 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 \( \chi \) from fluctuations in the order parameter:

\[
\chi = \frac{L^3(\langle R_{00}^2 \rangle) - (\langle R_{00}^2 \rangle)^2}{T}.
\]

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 \[^{36}\] 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 \[^{37},^{38}\] \( P(E) \) using the relation \( A(E) = -\ln P(E), \)

where the normalized histogram count \( P(E) = h(E)/\Sigma_E h(E) \).

4 RESULTS

We first present temperature dependence of nematic order parameter (Fig.1). As the degree of the molecular biaxiality increases the jump in the order parameter decreases and the transition shifts towards lower temperature till \( \lambda = 0.300 \). From \( \lambda = 0.325 \) the transition shifts towards right. We have studied the system till \( \lambda = 1/\sqrt{6} \). The jump at lower biaxialities signifies a first order transition, and the diminishing jump as \( \lambda \) gets closer to \( 1/\sqrt{6} \) implies a weaker first order transition. At \( \lambda = 1/\sqrt{6} \) a crossover is observed as expected and the transition is of second order.

The variation of susceptibility with reduced temperature for different degrees of molec-
Figure 1: Variation of order parameter with reduced temperature for different degrees of molecular biaxiality.

ular 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 $N \rightarrow I$ transition occurs decreases until $\lambda = 0.3$ and thereafter increases again.

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 $\lambda$ 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 $N \rightarrow I$ transition temperature and supercooling temperature for four different values of the biaxiality parameter (Fig. 3). In each plot two different ordinates have been 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 ordinate on the right corresponds to the free energy vs energy curve at $T^*$. Figures are plotted column first, with
Figure 2: Variation of susceptibility with reduced temperature for different degrees of molecular biaxiality. Peak height of the susceptibility curve decreases with increasing biaxiality. Also, the $N - I$ transition temperature decreases with increasing biaxiality until $\lambda = 0.30$ and increases again.

$\lambda$ values 0, 0.25, 0.30, and 0.325. We can see, from the curves corresponding to $T_{NI}$, as the value of biaxiality parameter increases, the depth of the free energy well decreases, taking the transition closer to being second order.

The change in energy, which corresponds to change of entropy at the transition, also decreases with increasing biaxiality parameter. For $\lambda$ values greater than 0.325 the depth of the free energy well at transition becomes so small that the structure of the well becomes non-discernible from random fluctuations.

Finally, in Fig.4 we present the coexistence line and the orientational spinodal line in the $\lambda - T$ plane. We see that both $T_{NI}$ and $T^*$ first decrease with increasing value of the biaxiality parameter and then increase with increasing $\lambda$. Another important observation is that the gap between these curves decreases monotonically and finally vanishes as $\lambda$ approaches $\lambda_C$. A similar qualitative feature was found in the molecular-field theory study of To et al. [19].
5 CONCLUSION

In conclusion we have shown that the NI coexistence curve of the dispersion model of biaxial molecules is substantially modified. Previous computer simulation studies [20, 21, 22, 23] on this model could not explore such behaviour at and around the I - N\textsubscript{U} transition. This high resolution investigation reveals a sharp deviation in the nature of the nematic-isotropic coexistence curve in temperature-biaxiality parameter phase diagram. The coexistence curve shows a change in curvature with increasing value of the degree molecular biaxiality. A possible reason for the deviation with increasing value of the degree of molecular biaxiality may be due to the corresponding increase of strength of interactions among the transverse axes of the biaxial molecules.

Other pretransitional phenomena such as, dependence of super cooling temperature on molecular biaxiality etc., have also been observed.

Our study, although, is based on a simple lattice model which neglects other degrees of freedom such as, translational or vibrational i.e. the molecular flexibility and considers only the orientational movement, is expected to help understand the important role of molecular biaxiality that plays in nematic - isotropic transition in bent-core systems as has
Figure 4: $T_{NI}$ vs. $\lambda$ Phase diagram for the nematic isotropic transition. Dependence of transition temperature on degree of biaxiality. The co-existence curve slopes downwards till $\lambda = 0.30$ and then slopes upwards till $\lambda = 1/\sqrt{6}$.

been observed in the experimental investigation of Wiant et al. [8].

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References

[1] G. R. Luckhurst and T. J. Sluckin (Editors), Biaxial Nematic Liquid Crystals (Wiley, UK, 2015).
Table 1: NI transition temperatures for different values of the biaxiality parameter $\lambda$ for the biaxial systems. Estimates of orientational spinodal temperature $T^*$ are also listed for the systems having lower $\lambda$. The estimated (jackknife) error in each temperature is within $\pm 0.0001$.

| $\lambda$ | $T_{NI}(\text{from } \chi vs T)$ | $T_{NI}(\text{from } F(E) vs T)$ | $T^*$  |
|-----------|----------------------------------|----------------------------------|--------|
| 0         | 1.1227                           | 1.1226                           | 1.1224 |
| 0.075     | 1.1187                           | 1.1186                           | 1.1221 |
| 0.150     | 1.1187                           | 1.1186                           | 1.1221 |
| 0.200     | 1.1163                           | 1.1162                           | 1.1221 |
| 0.250     | 1.1140                           | 1.1139                           | 1.1221 |
| 0.300     | 1.1130                           | 1.1130                           | 1.1221 |
| 0.325     | 1.1136                           | 1.1135                           | 1.1221 |
| 0.350     | 1.1151                           | 1.1151                           | 1.1221 |
| 0.375     | 1.1185                           | 1.1186                           | 1.1221 |
| 0.40825   | 1.1224                           |                                  |        |

[2] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, J. Mater. Chem., 6, 1231 (1996).

[3] P. G. de Gennes and J. Prost, The Physics of Liquid Crystals, (Oxford Science, Oxford, 1993).

[4] T. W. Stinson and J. D. Litster, Phys. Rev. Lett. 25, 503 (1970).

[5] E. F. Gramsbergen, L. Longa, and W. H. de Jeu, Phys. Rep. 135, 195 (1986).

[6] Z. Zhang, O. G. Mouritsen, and M. J. Zuckermann, Phys. Rev. Lett. 69, 2803 (1992).

[7] U. Fabbri and C. Zannoni, Mol. Phys. 58, 763 (1986).

[8] D. Wiant, S. Stojadinovic, S. Sharma, K. Fodor-Csorba, A. Jakli, J. T. Gleeson, and S. Sprunt, Phys. Rev. E 73, 030703(R) (2006).
[9] D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Korblova, and D. M. Walba, Science **278**, 1924 (1997).

[10] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Phys. Rev. Lett. **92**, 145505 (2004).

[11] B. R. Acharya, A. Primak, and S. Kumar, Phys. Rev. Lett. **92**, 145506 (2004).

[12] M. J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).

[13] R. Alben, Phys. Rev. Lett. **30**, 778 (1973).

[14] J. P. Straley, Phys. Rev. A **10**, 1881 (1974).

[15] G. R. Luckhurst, C. Zannoni, P. L. Nordio and U. Segre, Mol. Phys. **30**, 1345 (1975).

[16] N. Boccara, R. Mejdani and L. de Seze, J. Phys. **38**, 149 (1977).

[17] D. K. Remler and A. D. J. Haymet, J. Phys. Chem. **90**, 5426 (1986).

[18] A. M. Sonnet, E. G. Virga, and G. E. Durand, Phys. Rev. E **67**, 061701 (2003).

[19] T. B. T. To, T. J. Sluckin, and G. R. Luckhurst, Phys. Rev. E **88**, 062506 (2013).

[20] G. R. Luckhurst and S. Romano, Mol. Phys. **40**, 129 (1980).

[21] F. Biscarini, C. Chiccoli, P. Pasini, F. Semeria, and C. Zannoni, Phys. Rev. Lett. **75**, 1803 (1995).

[22] S. Romano, Physica A, **337**, 505 (2004).

[23] M. A. Bates and G. R. Luckhurst, Phys. Rev. E **72**, 051702 (2005).

[24] R. Berardi and C. Zannoni, J. Chem. Phys., **113**, 5971 (2000).

[25] R. Berardi and C. Zannoni, Mol. Cryst. Liq. Cryst., **396**, 177 (2003).

[26] N. Ghoshal, K. Mukhopadhyay, and S. K. Roy, Phys. Rev. E **89**, 042505 (2014).

[27] A. M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. **61**, 2635 (1988); **63**, 1195 (1989).
[28] M. E. Rose, *Elementary Theory of Angular Momentum*, (Wiley, New York, 1957).

[29] P. A. Lebwohl and G. Lasher, Phys. Rev. A 6, 426 (1972).

[30] U. Fabbri and C. Zannoni, Mol. Phys. 58, 763 (1986).

[31] N. Ghoshal, K. Mukhopadhyay and S. K. Roy, Liq. Cryst. 39, 1381 (2012).

[32] J. A. Barker and R. O. Watts, Chem. Phys. Lett. 3, 144 (1969).

[33] M. E. J. Newman and G. T. Barkema, *Monte Carlo Methods in Statistical Physics*, (Clarendon press, Oxford, 1999).

[34] J. Vieillard-Baron, J. Chem. Phys. 56, 4729 (1972).

[35] P. J. Camp and M. P. Allen, J. Chem. Phys. 106, 6681 (1997).

[36] P. Peczak, A. M. Ferrenberg and D. P. Landau, Phys. Rev. B 43, 6087 (1991).

[37] J. Lee and J. M. Kosterlitz, Phys. Rev. Lett. 65, 137 (1990).

[38] J. Lee and J. M. Kosterlitz, Phys. Rev. B 43, 3265 (1991).