Effect of External Fields on the Condensation of a Biaxial Nematic Liquid Crystal phase with Significant Coupling between Uniaxial and Biaxial Orders

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Abstract. Hamiltonian model describing general quadratic interactions among liquid crystal molecules (with positive dielectric anisotropy, and D_{2h} symmetry) is investigated in the presence of an external field E_a (coupling to their long axes), through Monte Carlo simulations. While the isotropic-to-uniaxial nematic (I-NU) transition temperature is enhanced with increasing field (attributed as due to the quenching of the primary director), the uniaxial-to-biaxial nematic transition on the other hand, seemingly concurrent with I-NU transition at E_a=0, is split, and occurs at progressively low temperatures with increasing field. By comparing our recent detailed investigations on this (zero-field) transition via a sampling procedure facilitating the computation of the density of states of the system [Latha *et. al., Phys. Rev. E*, 89 050501(R) (2014)], we infer that the applied field is effectively decreasing the degree of the mesoscopic inhomogeneity of the medium (with respect to the distribution of the orientational order), induced by the cross-coupling interactions among molecular tensor components. We argue that this facilitates an increasingly more evident role of the biaxial-biaxial tensor interactions among neighbours, so as to induce a condensation of a macroscopically biaxial medium at a lower temperature. These observations perhaps suggest that within this model, application of an appropriate external field might be effectively equivalent to a virtual shift of the system point (in the two-dimensional parameter space of the Hamiltonian) to facilitate possibly a ready condensation of the system into a biaxial phase.

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INTRODUCTION

Recently, detailed Monte Carlo simulations on the thermal behaviour of an assembly of liquid crystal molecules (with D_{2h} symmetry and described by a general pair-wise quadratic Hamiltonian) indicated that its mean-field phase diagram, predicted in the biaxially stable region of the Hamiltonian parameter space (γ, λ) [1], could qualitatively differ in certain regions, particularly in the presence of significant cross-coupling between the uniaxial and biaxial tensors of neighbouring molecules (quantified by γ) [2, 3]. It has been observed that a high degree of this interaction, relative to the biaxial-biaxial tensor interaction term, would induce mesoscopic inhomogeneity of the orientational order (so-called staggered configurations [4]), resulting in a biaxial phase of very low order. This qualitatively differs from another lower-temperature biaxial phase to which it transits, - the latter is macroscopically homogeneous promoting a normal growth of the biaxial order. In this context, we investigate the effect of an external field on the inhomogeneity in the sample, and consequent changes in the phase diagram, through Monte Carlo simulations.

DETAILS OF SIMULATION

The simulation box is simple cubic (40 x 40 x 40) with periodic boundaries on all the sides. Each interacting molecule is represented by a parallelepiped with major axis $\boldsymbol{m}$ and minor axes $\boldsymbol{e}$ and $\boldsymbol{e}_{\perp}$. They interact via the nearest neighbor potential given by [2, 3],

$$E = \varepsilon\begin{Bmatrix} -G_{33} + 2\gamma\left(G_{11} - G_{22}\right) - \\ \lambda\left[2\left(G_{11}+G_{22}\right) - G_{33}\right] \end{Bmatrix} - \varepsilon E_a^2 P_2\left(\boldsymbol{e}_a \cdot \boldsymbol{m}\right) \qquad (1)$$

where, {1, 2, 3} represent the molecular axes {***e***, ***e***⊥, ***m***} and $G_{jk}=P_2(\langle j|k\rangle)$. $\varepsilon > 0$ sets the temperature and energy scales. $|\gamma|$ and $|\lambda|$ are usually taken to be < 1. $\lambda=0$ implies the absence of a biaxial phase. E_a is the strength of the externally applied field along the direction $\boldsymbol{e}_a$. Canonical simulations are performed based on Metropolis importance sampling. In the present study we choose the Hamiltonian parameter values of the system, so as to make the pair-wise interaction exhibit D_{4h} symmetry (***e***-axis is the symmetry direction). Assuming that the medium is having a positive (dielectric) anisotropy, and by coupling an external field to the long axes of the molecules, we attempt to preferentially promote the degree of long range order of molecular ***m***-axes, and investigate its effect on the manifestations of the γ-term, by tracking the different transition temperatures.

RESULTS OF SIMULATION

For the chosen parameters set, (γ, λ) = (0.26, 0.16) it is observed that the field shifts the temperature of the transition from the isotropic to an essentially uniaxial nematic phase (T^*_{PN}) towards higher values, while the intermediate nematic to biaxial nematic transition temperature (T^*_{UB}) is suppressed, as shown in Figure 1. Here the transition temperatures are determined from the peaks of the susceptibility corresponding to the uniaxial (R^2_{00}) and biaxial (R^2_{22}) order parameters. The specific heat profile shows a single notable peak for the case of E_a=0. We have observed that as the contribution of γ is reduced progressively by decreasing its value, the specific heat profile shows two distinct peaks even at zero field.

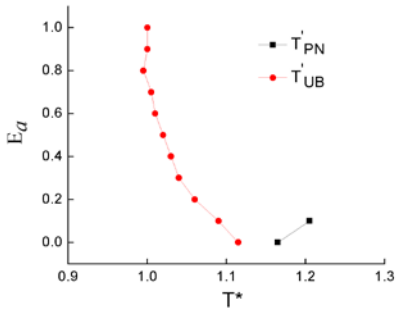

FIGURE 1. Variation of T^*_{PN} and T^*_{UB} for (γ, λ) = (0.26, 0.16) determined from the susceptibility peaks of uniaxial and biaxial order parameters respectively. It may be noted that the specific heat profile shows a single notable peak for E_a=0 case.

Temperature variation of the biaxial order parameter (R^2_{22}) for various values of field is shown in Figure 2. On cooling the system, the effect of field is to decrease the biaxial order initially, till another low-temperature transition to biaxial phase takes place.

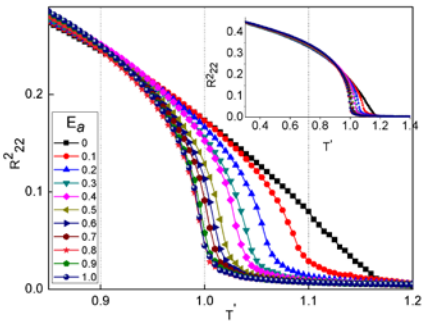

FIGURE 2. Temperature variation of the biaxial order parameter at various values of fields for (γ, λ) = (0.26, 0.16).

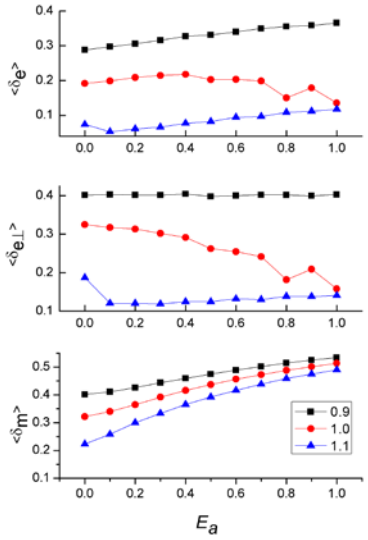

FIGURE 3. Field dependence on (δ_e, $\delta_{e\perp}$, δ_m) at different values of T' indicated in the legend.

Field dependence of the maximum eigen values corresponding to the ordering tensors of the three molecular axes (δ_e, $\delta_{e\perp}$, δ_m) at three temperatures bracketing the biaxial transitions are shown in Figure 3. It is seen that while δ_m increases monotonically with field at all temperatures, variation of δ_e, and $\delta_{e\perp}$, are curious especially at T'=1.0 and 1.1 which are above T^*_{UB}. A representation of this behaviour is also seen from the contour plots of the local orders exhibited by the molecular axes, as shown in Figure 4. The increase in the order along molecular ***m*** axis with applied field is readily observed, evidenced by an increase in the blue tones of the contour. Similarly the increase in the

red tones for the case of $\boldsymbol{e}_\perp$ and a relatively constant texture of the case of $\boldsymbol{e}$ may also be noted.

Hence the shift in T'_{UB} towards lower values on the application of the external field (Figure 1) appears to have a reasonable correlation with the changes in the local ordering of the minor axes, biaxial symmetry being its direct consequence. For (γ, λ) = (0.0, 0.16), our simulations show that both the transition temperatures increase with field, emphasizing the interesting role of γ in pointedly influencing the phase transition behaviour in biaxial systems. These observations are also in agreement with the predictions based on Landau-de-Gennes theory [5, 6] wherein T'_{UB} is found to get enhanced or suppressed with field, depending on the choice of the expansion parameters.

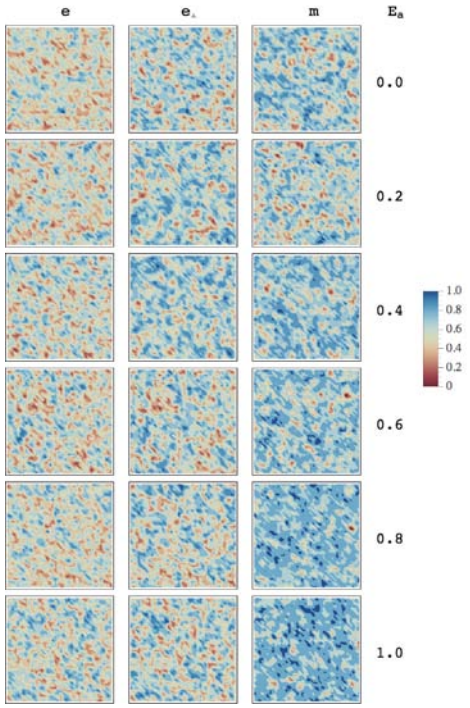

FIGURE 4. Contour plots of the local orders along the molecular axes in a plane of the system at T'=1.0.

DISCUSSION

For liquid crystal systems hosting uniaxial molecules with positive dielectric anisotropy, experiments indicate that T'_{PN} is enhanced with increase of the field, with a linear initial response followed by a quadratic behaviour, with field [7]. These were explained as due to a field-induced quenching of the director modes. High resolution Monte Carlo simulations [8], while supporting the experimental observations, established the robustness of the lattice model to deal with consequences expected of hydrodynamic considerations. In biaxial systems the transition from isotropic to biaxial phase could occur in one or two stages. Effect of an external field on the Hamiltonian model (eq (1)) in certain regions of biaxial stability has been studied recently [9]. For the values of (γ, λ) used in this study the mean-field treatment predicts, supported by Metropolis-based Boltzmann sampling methods, a direct transition from isotropic to biaxial phase. Our present results show that this transition is split on the application of the field, and the intermediate phase is another biaxial phase of low order. Progressive increase of the applied field seems to make the medium relatively more homogeneous. The variation of the biaxial order, in particular its suppression on the application of the field (Figure 2) is reminiscent of the efforts of entropic sampling procedure to estimate an accurate density of states, in the process overcoming the free energy barriers due to structural inhomogeneity. We also find that at high enough fields, the biaxial order of the intermediate phase decreases significantly, practically making the medium uniaxial. Finally, it appears that the application of a suitable field (in real systems with inherently significant γ) has the desirable result of effectively lowering its influence on the condensation of the biaxial phase, thereby yielding a possible chance for the onset of a homogeneous biaxial order mediated by the biaxial interactions (λ term in eqn (1)).

The computations are carried out at the computing clusters of Manipal Centre for Natural Sciences, Manipal University and at the Centre for Modelling Simulation and Design, University of Hyderabad.

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