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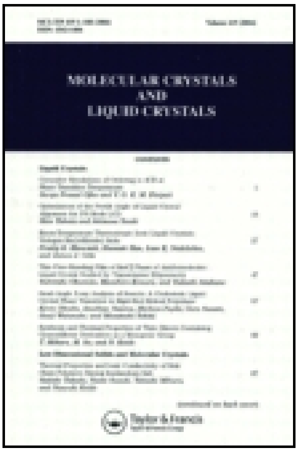

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Landau-de Gennes Theory of Thermotropic Biaxial Nematics: A Role of Fluctuations

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Landau-de Gennes Theory of Thermotropic Biaxial Nematics: A Role of Fluctuations

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We generalize the phenomenological Landau-de Gennes theory of biaxial nematics by including fluctuations of the tensor order parameter. Then, using real-space Monte Carlo simulations we study how these fluctuations affect relative stability of the isotropic phase, the uniaxial nematic phase and the biaxial nematic phase of D_{2h} symmetry. Results are confronted with earlier predictions of Landau-de Gennes theory.

Keywords Fluctuations; Landau-Ginzburg-de Gennes theory; Monte Carlo simulation; tensor order parameter; thermotropic biaxial nematics

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1. Introduction

Recent experimental observation that the biaxial nematic phase can be made stable in bent-core systems [1,2] and for tetrapode like molecules [3,4], has raised a considerable excitement in the field of thermotropic biaxial nematics. In particular, a phenomenological Landau-de Gennes (LdeG) theory worked out some time ago by Gramsbergen, Longa and de Jeu [5] has been reexamined [6] to identify all distinct classes of the phase diagrams the model can predict.The works [5,6] are extended here to look into the effect of thermal fluctuations on stability of the isotropic and the nematic phases at the level of phenomenological LdeG theory. More specifically, the effect of thermal fluctuations is studied by including elastic terms in the LdeG theory out to sixth order in the order parameter field and by applying Monte Carlo simulations to the resulting Landau-Ginzburg-de Gennes (LGdeG) model. The outcome is that the order parameter fluctuations can considerably alter the phenomenological phase diagrams [6], with the results being dependent on relative importance of bulk and elastic terms.

2. Model

The starting point of our considerations is the Landau-Ginzburg-de Gennes free energy functional, F, for biaxial nematics of D_{2h} symmetry (see e.g., [5,6]). It is

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constructed as an $O(3)$ – symmetric expansion in terms of the symmetric and traceless alignment tensor field $\mathbf{Q}(\vec{\mathbf{r}})$ and its derivatives $Q_{\alpha\beta,\gamma}(\vec{\mathbf{r}})$. In the absence of electric and magnetic fields the expansion is composed of the bulk term, F_{bulk}, and the elastic term, F_{el}: $F = F_{bulk} + F_{el}$, which are given by [5,6]

$$F_{bulk} = e\int_V d^3\mathbf{r}\left\{\frac{a}{2}\,Tr[\mathbf{Q}^2(\vec{\mathbf{r}})] - \frac{\sqrt{6}b}{3}\,Tr[\mathbf{Q}^3(\vec{\mathbf{r}})] + \frac{c}{4}\,Tr[\mathbf{Q}^2(\vec{\mathbf{r}})]^2 + \frac{\sqrt{6}d}{5}\,Tr[\mathbf{Q}^2(\vec{\mathbf{r}})]\,Tr[\mathbf{Q}^3(\vec{\mathbf{r}})] + \frac{1}{6}\,Tr[\mathbf{Q}^2(\vec{\mathbf{r}})]^3 + (f-1)\,Tr[\mathbf{Q}^3(\vec{\mathbf{r}})^2]\right\} \tag{1}$$

and

$$F_{el} = L_1\int_V\left[\frac{1}{2}\,Q_{ij,k}(\vec{\mathbf{r}})\,Q_{ij,k}(\vec{\mathbf{r}}) + \frac{1}{2}\,\varrho\,Q_{ij,j}(\vec{\mathbf{r}})\,Q_{ij,k}(\vec{\mathbf{r}})\right]. \tag{2}$$

Note that the bulk expansion (1) has to be taken up to sixth order with respect to $\mathbf{Q}(\vec{\mathbf{r}})$ to account for the stable biaxial nematic phase. The elastic part (2) contains, up to a surface term, the lowest order linearly independent terms in derivatives $Q_{ij,k}(\vec{\mathbf{r}})$, where $Q_{ij,k}(\vec{\mathbf{r}}) \equiv \partial_k\,Q_{ij}(\vec{\mathbf{r}}) = \frac{\partial Q_{ij}(\vec{\mathbf{r}})}{\partial x_k}$, and where the Einstein's summation convention over repeated indices is assumed. The stability of the expansion F with respect to an unlimited growth of $\mathbf{Q}(\vec{\mathbf{r}})$ and $Q_{\alpha\beta,\gamma}(\vec{r})$ requires that $e > 0$, f> 0, $L_1 > 0$ and $1 + \frac{3}{2}\varrho > 0$. The coefficients of the expansion generally depend on temperature and other thermodynamic control parameters. In what follows only the coefficient $a = a_0\,(\mathrm{T} - T^*)$ ($a_0 > 0$), with T being the absolute temperature, is assumed to be explicitly temperature dependent. The temperature T^* represents the spinodal temperature for the first-order phase transition from isotropic to nematic phase and the transition temperature for the second-order phase transition from the isotropic phase. The material parameters a, T^*, b, c, d, e, f, L_1 and ρ are treated as constants.

Three states are stabilized *locally* by the expansion F. When all three eigenvalues of $\mathbf{Q}(\vec{\mathbf{r}})$ are equal, which yields $\mathbf{Q}(\vec{\mathbf{r}}) = 0$, this would be the isotropic state. For the $D_{\infty h}$-symmetric uniaxial states two out of the three eigenvalues of $\mathbf{Q}(\vec{\mathbf{r}})$ are equal and, finally, for the D_{2h}-symmetric biaxial states all the three eigenvalues are different.

Analysis of all possible ground state structures coming from the bulk free energy (1) was performed in [6]. Adding F_{el}, Eq. (2), does not change the structures identified in [6] for the elastic terms are minimized when the structures are homogenous. In the present work we extend the LGdeG model by including fluctuations of the field $\mathbf{Q}(\vec{\mathbf{r}})$. We also carry out an exemplary simulation to examine how fluctuations can influence stability of the nematic phases. Full outcome of the model will be presented elsewhere.

For a fluctuating field $\mathbf{Q}(\vec{\mathbf{r}})$ the probability of finding a given field's configuration is given by

$$P[\mathbf{Q}(\vec{\mathbf{r}})] = Z^{-1}\,e^{-\beta F[\mathbf{Q}(\vec{\mathbf{r}})]}, \tag{3}$$

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where

$$Z = \int D\mathbf{Q}(\overrightarrow{\mathbf{r}})\, e^{-\beta F[\mathbf{Q}(\overrightarrow{\mathbf{r}})]} \tag{4}$$

is the partition function, $\beta^{-1} = k_B T$, and $\int D\mathbf{Q}(\overrightarrow{\mathbf{r}})$ is the functional integral over all possible fields $\mathbf{Q}(\overrightarrow{\mathbf{r}})$. The probability distribution function has been determined from Monte Carlo simulations in the following way. We divided the system with volume V into a cubic grid of $\mathrm{N} = 20 \times 20 \times 20 = 8000$ grid nodes taken as reference points and assumed periodic boundary conditions. With tensor $\boldsymbol{Q}$ specified at each node the integration in the exponent in (4) was approximated by a finite sum, and the derivatives replaced by finite differences. Then Z, Eq. (4), and $F[Q, Q_{\alpha\beta,\ \gamma}]$ become replaced by their (real space) discretized versions

$$Z \approx \prod_{\alpha\delta}^{\prime} \prod_{I=1}^{N} \int_{-\infty}^{\infty} d\, Q_{\alpha\delta}(\overrightarrow{\mathbf{r}}_I)\, \exp\left[-T^{-1} \sum_{J=1}^{N} F\left[\mathbf{Q}(\overrightarrow{\mathbf{r}}_j),\, \mathbf{Q}(\overrightarrow{\mathbf{r}}_j) - \mathbf{Q}(\overrightarrow{\mathbf{r}}_{j+nn})\right]\right],$$

where I,J run over the grid, while nn refers to nodes that are neighbours of J. $\prod_{\alpha\delta}$ runs over all α, β that enumerate the independent components of $\boldsymbol{Q}$.

Out of all material parameters entering (3), three are setting a scale for F (or temperature in (Eq. (3)), $\boldsymbol{Q}$ and for $\overrightarrow{\mathbf{r}}$, and can be set equal to 1. We choose $e = 1$ and $c = 0$. Note that the discretization introduces a grid constant (real space cutoff) as an extra parameter which, along with k_B, we also set equal to 1. This exhausts the freedom in reparameterizing (4) that does not affect qualitative predictions of the theory.

Consequently, the phase diagrams in the a, b plane are functions of d, f, r, ρ, and L_1. Also please note that the free energy is invariant with respect to the transformation: $\{b, d, \boldsymbol{Q}\} \to \{-b, -d, -\boldsymbol{Q}\}$, which limits d to $d \geq 0$. The diagrams for $d < 0$ are obtained as mirror images with respect to the $b = 0$ line of those for $d > 0$.

3. Results

Inclusion of fluctuations into LGdeG theory introduces competition between elastic and bulk terms in (4), which can be measured by a dimensionless ratio of L_1 and e. In the present work we limit ourselves to the case when $L_1 = 1$ and $e = 1$. Exemplary simulations are carried out for $c = 0$, $d = 0$, $f = 1.5$, $a_0 = 1$, $T^* = 1$ and $\rho = 1$. The results of simulations are compared with a saddle point value of the partition function (4), which gives the most probable value $\mathbf{Q_{sp}}$ of the field $\mathbf{Q}(\overrightarrow{\mathbf{r}})$. The homogeneous field $\mathbf{Q_{sp}}$ recovers the results of the original LdeG theory, worked out in [6].

In simulations we monitor the mean alignment tensor $\langle \mathbf{Q}(\overrightarrow{\mathbf{r}}) \rangle$ and $\langle F \rangle$. A diagonalisation of $\langle \mathbf{Q}(\overrightarrow{\mathbf{r}}) \rangle$ allows to identify the directors and the corresponding structures. For high temperatures (*see* Figures 1–3) all eigenvalues of $\langle \mathbf{Q}(\overrightarrow{\mathbf{r}}) \rangle$ are equal up to fluctuations, which correspond to the isotropic phase.

When temperature is lowered the eigenvalues became nonzero with two of them being equal. This corresponds to uniaxial prolate ($b > 0$) or uniaxial oblate ($b < 0$) nematic phase. Lowering temperature further removes degeneracy and the system enters into the biaxial nematic phase. The phase diagram and the exemplary

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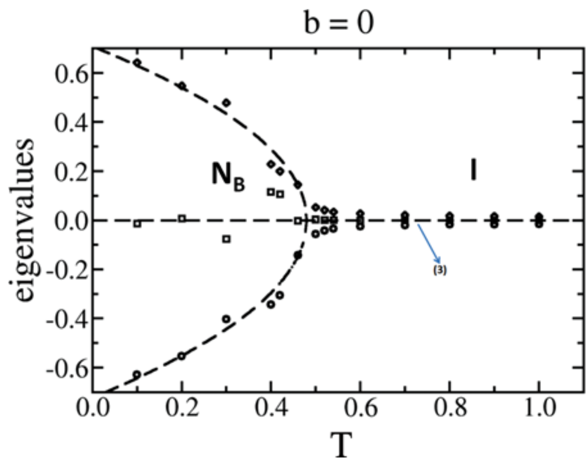

Figure 1. Eigenvalues of the mean tensor $\langle \mathbf{Q}(\overrightarrow{\mathbf{r}})\rangle$ versus temperature for $c = 0$, $d = 0$, $f = 1.5$, $a_0 = 1$, $T^* = 1$, $L_1 = 1$, $e = 1$, $\varrho = 1$ and $b = 0$. Number in curly brackets denotes degeneracy of the eigenvalues. Note a direct isotropic (**I**)-biaxial nematic ($\mathbf{N_B}$) phase transition. (Figure appears in color online.)

(averaged over directors orientation) pair correlation function $G(|\mathbf{r}|) = < Tr\ (\mathbf{Q}\ (\mathbf{r}' + \mathbf{r})\ \mathbf{Q}\ (r')) >$ are shown in Figures 4 and 5, respectively. Note that the phase diagram is symmetric with respect to the line b = 0 for the chosen set of the expansion parameters.

As it turns out the fluctuations cause the transition temperatures to considerably diminish as compared to their Landau values [6] (roughly by 100% for the parameters chosen in Fig. 4) and bending of the nematic uniaxial-nematic biaxial line is opposite to that predicted by Landau-de Gennes theory. We also observe considerable biaxial fluctuations in the vicinity of isotropic to nematic phase transition, especially for small *b*. The correlation function dies out very fast away from

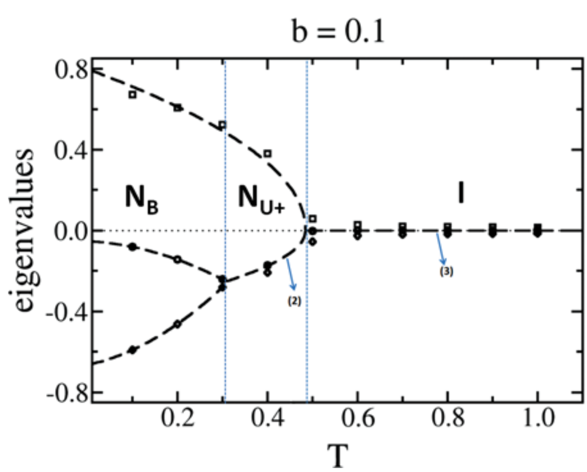

Figure 2. As Figure 1, but for $b = 0.1$. Here we observe a sequence of phase transitions: isotropic (**I**)-uniaxial nematic prolate ($\mathbf{N_{U+}}$)-biaxial nematic ($\mathbf{N_B}$). (Figure appears in color online.)

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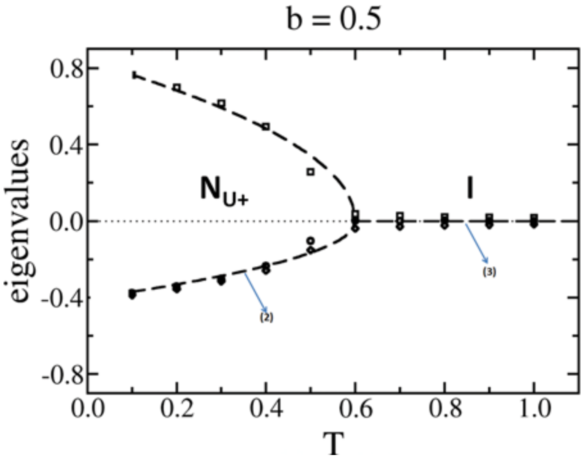

Figure 3. As Figures 1 and 2, but for $b = 0.5$. Note that the biaxial nematic phase does not show up until $T = 0.1$. Parameters and symbols are the same as in previous figures. (Figure appears in color online.)

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transition. For large distances it approaches the value of $Tr(\langle \mathbf{Q}(\overrightarrow{\mathbf{r}}) \rangle)^2)$, consistent with the direct averages of the alignment tensor. Another interesting observation are small heat capacities about transition points, but we need to carry out more systematic studies before conclusions can be drawn.

We should add that the starting point of the present analysis is the original Landau-de Gennes model, where it is explicitly assumed that the biaxial nematic phase is of D_{2h} symmetry. In principle the biaxial nematic phases studied experimentally could be of lower symmetry [7] in which case the tensor $\boldsymbol{Q}$ must be supplemented by additional tensor/vector order parameters. At present there is no direct symmetry assignment to the cases studied experimentally; here we just assume the

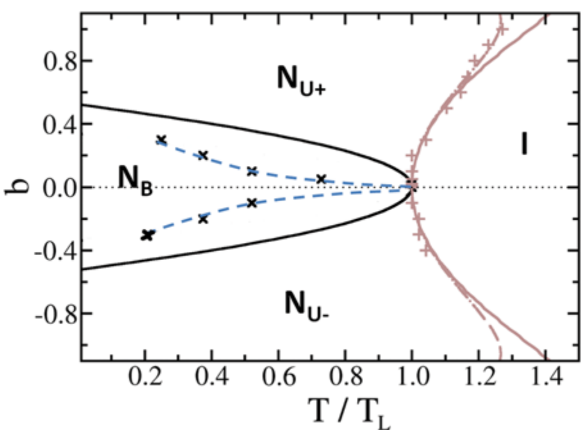

Figure 4. Phase diagram found from simulations (crosses) vs the reference Landau-de Gennes phase diagram [6] (continuous lines). Dashed lines are fits to experimental data.$T_L = 1$ is given by the Landau-deGennes theory [6] while in simulations $T_L = 0.5$. Parameters are taken the same as in Figure 1. The dashed lines are guide to the eyes. (Figure appears in color online.)

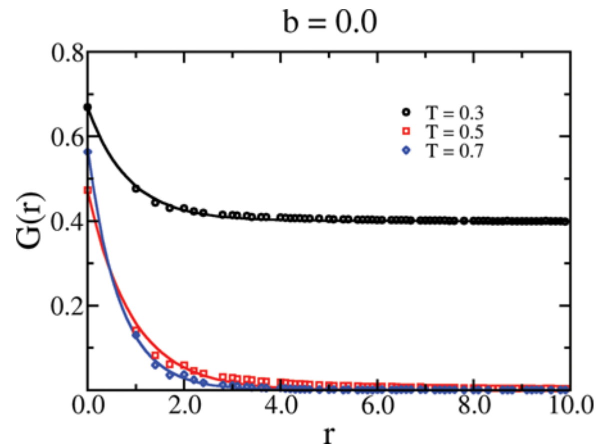

Figure 5. The simplest of pair correlation functions for the same set of parameters as figure 1. Note that the long-range order appears for $T \leq 0.5$. (Figure appears in color online.)

simplest possibility, namely D_{2h} symmetry although one of recent experimental reports [8] indicates on a possibility of a biaxial ferroelectric nematic phase.

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