



Structure and orientational ordering in a fluid of elongated quadrupolar molecules



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ABSTRACT

A second-order density-functional theory is used to study the effect of quadrupolar interactions on the isotropic–nematic transition in a system of fluids of elongated molecules interacting via the Gay–Berne potential. The direct pair–correlation functions of the coexisting isotropic fluid that enter in the theory as input information are obtained by solving the Ornstein–Zernike equation using the Percus–Yevick integral equation theory in the (reduced) temperature range of $1.6 \leq T^* \leq 3.0$ for different densities, temperatures and quadrupole moments. Using the harmonic coefficients of the direct pair–correlation functions, isotropic–nematic phase coexistence and thermodynamic parameters have been calculated. The theoretical results have been compared with the available computer simulation results.

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1. Introduction

Liquid crystals exhibit a rich variety of phases with varying degrees of positional and orientational order between the isotropic fluid and the crystalline phase. The main characteristics of liquid crystals, and what makes them particularly difficult to study and simulate, is the existence of orientational and possibly positional order and the presence of transitions between phases where some of these order parameters vanish. A transition of particular importance is the isotropic–nematic (I–N) one, where the order parameters vanish in the isotropic phase, is nonzero in the liquid crystal phases and is unity in the limit of complete orientational ordering. Elongated particles, in particular, undergo a phase transition from a phase in which particle orientations and positions are disordered (isotropic phase) to a phase in which orientations are aligned and positions are disordered (nematic phase). The isotropic–nematic phase transition, which is believed to be weakly first order in nature with certain characteristics of the continuous transition, has been the subject of immense attention in condensed matter physics and material sciences.

Fluids of elongated or rod-like molecules are an important class of mesogens with relevant technological and biological applications and, therefore, different models have been introduced in order to explore their properties. For instance, a number of continuous potential models for fluids of nonspherical molecules have been proposed. These include the Kihara potential [1], the site–site potential [2], the Gaussian overlap model [3], etc. One of the most useful molecular models that incorporate explicitly anisotropy in both the attractive and repulsive interactions was long ago proposed by Gay and Berne [4]. The Gay–Berne (GB) model has become nowadays a standard model to the study of thermotropic liquid crystals.

The intermolecular pair potential $u(1, 2)$ between the molecules is modelled by a uniaxial potential comprising an anisotropic GB potential together with an embedded quadrupole, located at the centre of the molecule, and takes the form:

$$u(1, 2) = U(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}) = U_{GB}(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}) + U_{QQ}(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}), \quad (1.1)$$

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where

$$U_{GB}(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}) = 4\varepsilon(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}) (R^{-12} - R^{-6}), \quad (1.2)$$

$$R = \frac{r_{12} - \sigma(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}) + \sigma_0}{\sigma_0},$$

and

$$U_{QQ}(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}) = \frac{3}{4} \frac{Q^2}{r^5} [1 - 5(c_1^2 + c_2^2 + 3c_1^2 c_2^2) + 2(s_1 s_2 c' - 4c_1 c_2)^2]. \quad (1.3)$$

Here $r_{12} = |\mathbf{r}_{12}|$ is the length of the separation vector and $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/r_{12}$ is its orientation. U_{QQ} [5] in Eq. (1.3) is the potential due to the electrostatic interactions such as the quadrupole–quadrupole interaction, $c_i = \cos \theta_i$, $s_i = \sin \theta_i$, $c' = \cos(\varphi_1 - \varphi_2)$ and Q is the permanent quadrupole moment. The quadrupole moment can be expressed in terms of reduced quantity as $Q^* = Q/\sqrt{4\pi\varepsilon_0\sigma_0^5}$. The quadrupole–quadrupole interactions decay as r^{-5} , which is sufficiently rapid to neglect very long range contributions to the total energy.

The orientation-dependent molecular shape parameter $\sigma(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12})$ represents the distance (for given molecular orientations) at which the intermolecular potential vanishes, and is given by

$$\sigma(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}) = \sigma_0 \left(1 - \frac{1}{2} \chi \left[\frac{(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{e}}_1 + \hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{e}}_2)^2}{1 + \chi(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2)} + \frac{(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{e}}_1 - \hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{e}}_2)^2}{1 - \chi(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2)} \right] \right)^{-1/2}, \quad (1.4)$$

where the parameter χ is a function of the length-to-breadth ratio $x_0 (\equiv \sigma_e/\sigma_s)$, which is defined in terms of the contact distances when the molecules are end-to-end (e) and side-by-side (s) configurations, $\chi = (x_0^2 - 1)/(x_0^2 + 1)$. This vanishes for a sphere and tends to the limiting value of unity for an infinitely long rod. $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ are the unit vectors along the symmetry axis of two interacting molecules.

The energy parameter $\varepsilon(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12})$ in Eq. (1.2) represents the strength of the interactions, and its dependence upon the molecular orientation is given by

$$\varepsilon(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}) = \varepsilon^v(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2) \varepsilon'^\mu(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}), \quad (1.5)$$

and

$$\varepsilon(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2) = \varepsilon_0 [1 - \chi^2(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2)^2]^{-1/2}, \quad (1.6)$$

$$\varepsilon'(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{r}}_{12}) = 1 - \frac{1}{2} \chi' \left[\frac{(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{e}}_1 + \hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{e}}_2)^2}{1 + \chi'(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2)} + \frac{(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{e}}_1 - \hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{e}}_2)^2}{1 - \chi'(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2)} \right]. \quad (1.7)$$

The anisotropy parameter χ' is related to the potential well depths ratios k' for the side-by-side (s) and end-to-end (e) arrangement and is defined as $\chi' = (k'^{1/2} - 1)/(k'^{1/2} + 1)$. ε_0 and σ_0 are constants and, in some ways, provide a measure of the attractive interactions and the size of the molecules. The first function of Eq. (1.5) favours the parallel alignment of the particles and so aids liquid crystal formation and the second function favours the side-by-side arrangement over the end-to-end and so encourages the formation of smectic phases. Note that the potential of Eq. (1.2) reduces to the spherical Lennard-Jones (12–6) potential with parameters σ_0 and ε_0 , when both x_0 and k' are equal to unity.

The GB potential for a certain choice of parameters is conveniently indicated by the notation $GB(x_0, k', \mu, \nu)$ proposed by Bates and Luckhurst [6]. The potential contains four adjustable parameters (x_0, k', μ, ν) which control the anisotropy in the repulsive and attractive interactions in addition to two parameters (σ_0, ε_0) that scale the distance and energy, respectively. Though x_0 measures the anisotropy of the repulsive core, it also determines the difference in the depth of the attractive well between the side-by-side and the cross configurations. Both x_0 and k' play important role in stabilising the liquid crystalline phases. The exact role of the other two parameters μ and ν is not very obvious, though they appear to affect the anisotropic attractive forces in a subtle way. Bates and Luckhurst [6] have used the isothermal-isobaric Monte Carlo simulations and have shown that the mesogen $GB(4.4, 20.0, 1, 1)$ exhibits isotropic, nematic, smectic-A and smectic-B phases, depending upon the choice of the pressure. Most liquid crystals of technological interest are formed by highly elongated molecules. The original $GB(3, 5, 2, 1)$ parametrisation has been widely used in computer simulation to study the phase behaviour, liquid crystal properties [7–14] and also in theoretical studies [15–23].

As far as a theoretical description of the liquid crystalline phase behaviour of GB molecules is concerned, comparatively fewer studies have been reported, probably as a result of the complicated anisotropic form of the potential [15,16,18,24–26]. A very limited number of computer studies have been made to examine the effect of quadrupolar interactions on the ordered phases of Gay–Berne molecules [27–30]. To our knowledge no theoretical investigation of the liquid crystalline phase diagram for quadrupolar $GB(4.4, 20.0, 1, 1)$ has been made; some limited work has appeared on the structure and phase transition study of $GB(3, 5, 2, 1)$ [31,32]. This work is an attempt to fill this gap.

The goal of this work is to examine the effect of quadrupolar interactions on the isotropic–nematic transition of Gay–Berne mesogens with embedded quadrupoles making comparisons with the simulation data wherever possible. We do not treat states with positional order in this study, and examine only orientational ordering. The scheme of the paper is as

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