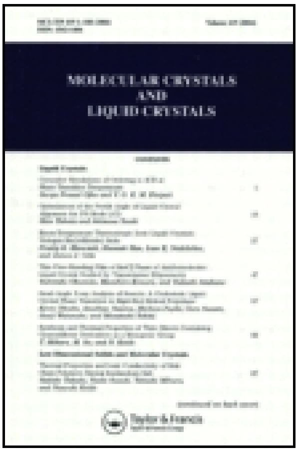

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Discotic Nematic-Isotropic Phase Transition Properties for a Disc-Like Mesogen

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A statistical mechanical perturbation theory has been used to describe discotic nematic-isotropic phase transition for a discotic liquid crystal, hexa(p-octyl phenyl ethynyl)benzene. We have employed the decoupling approximation, which introduces anisotropy in the pair correlation function, to investigate the discotic nematic-isotropic transition properties. The variation of second rank orientational order parameter with temperature has been computed and it shows qualitatively similar behavior to that of experimental studies of Aver'yanov [1]. However, the numerical value of order parameter at the transition found in the present work is larger than that of Aver'yanov's. The various thermodynamic properties have also been calculated at the transition.

Keywords Discotic liquid crystals; discotic nematic-isotropic transition; order parameter

Introduction

For the last couple of years there has been rapid progress in the development of conducting columnar systems and controlling the orientation of discotic mesophases. Molecules forming discotic nematic liquid crystals generally consist of a rigid planar core with four to eight flexible tails or chains. The structural features associated with both the flexible chains and the rigid core are of great importance for understanding the mesomorphism of the discotic materials [2–7]. Various experimental investigations using x-rays have revealed the complexity of the ordering of core versus tails in a columnar phase of disc-shaped liquid crystals. Also, discotic molecules with very large aromatic cores continue to attract particular attention because they are associated with high charge-carrier mobilities and hence improved conduction properties. In addition to these experimental works, there are some simulations studies with hard particle models by Allen and Frenkel [8] and Samborsk *et al.* [9] on ellipsoids, platelets, and cut spheres. The first Monte Carlo simulations on a system of cut spheres for length to diameter ratio $(L/D) = 0.1$ by Frenkel provided strong evidence that the system can form four distinct phases: isotropic, discotic nematic, columnar, and solid [10]. The range of stability of these phases was estimated [11]. Other simulations studies have been performed to investigate the influence of attractive interaction (polar and Gay-Berne potentials) on the phase behavior of discogens. The theory for

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the nematic phase in the vicinity of phase transitions has taken several directions [12–17]. One of the approaches is van der Waals (vdW)-type theories. The mesophase molecules possess a strong anistropy in both intermolecular repulsions and attractions. So, a molecular theory should incorporate both short-range repulsion and long-range attractive forces. In addition, the real complication one faces in the construction of a theory is dealing with both the spatial and angular variables of the molecules. Basic to these works is the recognition that the predominant factor in determining the liquid-crystalline stability is geometric and that of role of the attractive interactions is, to a first approximation, merely to provide a negative, spatially uniform mean field in which the molecules move. It can be shown [17] that all vdW theories can be derived from the statistical mechanical perturbation theory as developed by us [18].

The aim of this article is to study the characteristic features of discotic nematic-to-isotropic (N_D-I) transition properties and the temperature variation of the orientational order parameter of the discotic liquid crystal hexa(p-octyl phenyl ethynyl)benzene by using the perturbation expansion method. In addition, we obtain the numerical results on the various thermodynamic properties at N_D-I transition. A brief account of the perturbation expansion method and the working equations are given in the following section. Results and discussions are the presented, and the article ends with the conclusions.

Theory and Working Equations

We use a perturbation molecular-statistical approach, within the mean field approximation, to describe the equilibrium properties of discotic nematics for a model system composed of N axially symmetric nonspherical discotic molecules contained in volume V at temperature T. A model system composed of molecules interacting via a pair potential having both repulsive and attractive parts is considered. The repulsive interaction is represented by a repulsion between hard ellipsoids of revolution. The attractive potential, a function of only the center of mass distance and the relative orientation between two molecules, is approximated by the interaction arising from the dispersion interaction between the asymmetric molecules. We represent the discotic molecules by oblate ellipsoids of revolution parameterized by their length-to-width ratio $x < 1$ (here $x = 2a/2b$, where 2a and 2b denote, respectively, the lengths of major and minor axes of the ellipsoid). The total potential energy of interaction of this system is approximated as the sum of the interaction energies of pairs given by $U_N(\mathbf{x_1}, \mathbf{x_2}) = \Sigma_{1 \le i < j \le N}\ [U_0(\mathbf{x_i}, \mathbf{x_j}) + U_p(\mathbf{x_i}, \mathbf{x_j})]$ where the vector $\mathbf{x_i}[\equiv(\mathbf{r_i}, \Omega_i)]$ represents both the location $\mathbf{r_i}$ of the center of mass of the ith molecule and its relative orientation Ω_i described by Euler's angeles θ_i, ϕ_i, and ψ_i. The reference potential U_0 is described by the repulsion between the hard ellipsoids of revolution and satisfies the relation $U_0[(\mathbf{x_1}, \mathbf{x_2}) = U_{her}(\mathbf{x_1}, \mathbf{x_2}) = \infty$, for $\mathbf{r_{12}} \le D(\widehat{\mathbf{r_{12}}}, \Omega_{12})$ and 0 when $\mathbf{r_{12}} > D(\widehat{\mathbf{r_{12}}}, \Omega_{12})$. U_p represents the perturbation potential, which contains a smoothly varying long-range attractive part and is described by the dispersion interaction,

$$U_p(\mathbf{x_1}, \mathbf{x_2}) = U_P(\mathbf{r_{12}}, \Omega_1, \Omega_2) = \begin{cases} r_{12}^{-6}[C_i + C_a P_2(\widehat{\mathbf{e_1}} \cdot \widehat{\mathbf{e_2}})] & \text{for } \mathbf{r_{12}} > D(\widehat{\mathbf{r_{12}}}, \Omega_{12}) \\ 0 & \text{for } \mathbf{r_{12}} \le D(\widehat{\mathbf{r_{12}}}, \Omega_{12}) \end{cases} \tag{1}$$

Here $\mathbf{r_{12}}$ is the center-of-mass vector of two molecules and $D(\widehat{\mathbf{r_{12}}}, \Omega_{12})$ is the distance of the closest approach between two molecules with relative orientation Ω_{12}. Also, $\widehat{\mathbf{r_{12}}}$

and $\widehat{\mathbf{e}_1}$, $\widehat{\mathbf{e}_2}$ are, respectively, unit vectors along the intermolecular axis and along the symmetry axes of two interacting molecules. C_i and C_a are constants related to the isotropic and anisotropic dispersion interactions. We use the expression given by the Gaussian overlap model of Berne and Pechukas for $D(\widehat{\mathbf{r}_{12}}, \Omega_{12})$ [19].

We write the total Helmholtz free energy A in first-order perturbation as $\beta A/N = \beta A^0/N + \beta A^1/N$ where A^0 is the contribution of reference system and $\beta A^1/N = \beta \int d\Omega_1 f(\Omega_1)\psi^{(1)}(\Omega_1)$ represents the perturbation term. $f(\Omega_1)$ is the one-particle orientational distribution function, and $\psi^{(1)}$ may be defined as an effective one-body orientational perturbation potential.

$$\psi^{(s)}(\Omega_1) = \frac{1}{2s}\rho \int d\Omega_2 f(\Omega_2) \int d\mathbf{r}_{12} U_p(\mathbf{r}_{12}, \Omega_1, \Omega_2) g^{(s-1)}(\mathbf{r}_{12}, \Omega_1, \Omega_2) \tag{2}$$

Here $g^{(s-1)}$ $(\mathbf{r}_{12}, \Omega_1, \Omega_2)$ is the pair correlation function (PCF) for all s. For $s = 1$, $g^{(0)}$ $(\mathbf{r}_{12}, \Omega_1, \Omega_2)$ represents the PCF for the reference system.

In order to calculate the thermodynamic properties of a system of hard ellipsoids, we start with the pressure relation

$$\frac{\beta p_0}{\rho} = 1 - \frac{\beta\rho}{6}\int d\mathbf{r}_{12} \int d\Omega_1 f(\Omega_1) \int d\Omega_2 f(\Omega_2)[\mathbf{r}_{12}\nabla U_{her}(\mathbf{r}_{12}, \Omega_1, \Omega_2) g^{(0)}(\mathbf{r}_{12}, \Omega_{12})] \tag{3}$$

Here the operator ∇ acts on the $\mathbf{r}_{12}$ coordinates of $U_{her}(\mathbf{r}_{12}, \Omega_1, \Omega_2)$ only. It is pertinent to mention here that Eq. (3) involves the hard ellipsoid's PCF, $g^{(0)}$. In general, a detailed knowledge of PCF as function of r_{12}, Ω_1, Ω_2 is needed for determining Eq. (3). However, in our present development [18,20] we need to know only $g^{(0)}(\mathbf{r}_{12}, \Omega_{12})$. Following Parsons [21], we approximate the reference system pair correlation function as

$$\begin{aligned} g^{(0)}(\mathbf{r}_{12}, \Omega_{12}) &= g^{(0)}\left[\frac{r_{12}}{D(\widehat{\mathbf{r}_{12}}, \Omega_{12})}\right] \\ &= g^{(0)}(r_{12}^*) \end{aligned} \tag{4}$$

Here $(r_{12}^*) = r_{12}/D(\widehat{\mathbf{r}_{12}}, \Omega_{12})$. This approximation completely decouples the orientational and positional degrees of freedom. The error introduced in using Eq. (4) at liquid density is difficult to assess but is similar to a mean-field approximation for orientational part of the interaction [20]. Also, in solving Eq. (3) we consider excluded volume or co-volume between the two ellipsoids of revolution as

$$V_{exc}(\Omega_{12}) = \frac{1}{3}\int D^3(\widehat{\mathbf{r}_{12}}, \Omega_{12}) d\mathbf{r}_{12} = 8v_0(1-\chi^2)^{-\frac{1}{2}}(1-\chi^2\cos^2\theta_{12})^{\frac{1}{2}} \tag{5}$$

where v_0 is the volume of a molecule, θ_{12} is the angle between axes of molecules, and $\chi = x^2 - 1/x^2 + 1$. Considering the relation for $D(\widehat{\mathbf{r}_{12}}, \Omega_{12})$ and reducing the distance variable with $D(\widehat{\mathbf{r}_{12}}, \Omega_{12})$ and using Eq. (4) and (5), we get

$$\frac{\beta p_0}{\rho} = 1 + \frac{2\eta(2-\eta)}{(1-\eta)^3}[F_0(\chi) - F_2(\chi)\overline{P}_2^2] \tag{6}$$

where $\eta = \rho v_0$, η is the packing fraction, and ρ is number density.

$$F_0(\chi) = (1-\chi^2)^{-\frac{1}{2}}\left[1 - \frac{1}{6}\chi^2 - \frac{1}{40}\chi^4 - \frac{1}{112}\chi^6 \cdots\right] \tag{7}$$

$$F_2(\chi) = \frac{1}{3}\chi^2(1-\chi^2)^{-\frac{1}{2}}\left[1 + \frac{3}{14}\chi^2 + \frac{5}{56}\chi^4 + \frac{25}{528}\chi^6 + \cdots\right] \tag{8}$$

The orientational order parameter $\overline{P}_2$ is defined as

$$\overline{P}_2 = \int d\Omega\, f(\Omega) P_2(\cos\,\theta) \tag{9}$$

It is pertinent to mention here that for the hard sphere system ($x = 1$) Eq. (6) reduces to the Carnahan-Stirling (CS) equation of state [22]:

$$\frac{\beta p_0}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \tag{10}$$

The CS equation of state agrees remarkably well with molecular dynamics results over the entire fluid range. The Helmholtz free-energy per particle for the reference system can be written by using standard thermodynamic relation and we finally get

$$\frac{\beta A^0}{N} = (\ln\rho - 1) + \langle \ln[4\pi f(\Omega)] \rangle + \frac{\eta(4-3\eta)}{(1-\eta)^2}[F_0(\chi) - F_2(\chi)\overline{P}_2^2] \tag{11}$$

The angular bracket $\langle \cdots \rangle$ in Eq. (11) denotes the ensemble average over the (N – 1) particles of the system. Here the first two terms represent the free energy of a gas of noninteracting molecules and the third is the excess free energy arising from the interparticle interaction. One finds that expression (11) is similar to the corresponding equations derived by Vroege and Lekkerkerker [23] and Samborsk *et al.* [9].

The Helmholtz free energy in the first-order perturbation is

$$\frac{\beta A^{(1)}}{N} = \beta \int d\Omega_1 f(\Omega_1)\psi^{(1)}(\Omega_1) \tag{12}$$

where $\psi^{(1)}$ (Ω_1) is given by Eq. (2) and U_p by Eq. (1). Let

$$Y(\Omega_{12}) = \int d\mathbf{r_{12}} \frac{1}{r_{12}^6}[C_i + C_a P_2(\cos\theta_{12})]g^{(0)}(\mathbf{r_{12}}, \Omega_{12}) \tag{13}$$

Reducing the distance variables with $D(\widehat{\mathbf{r_{12}}},\ \Omega_{12})$, we get

$$Y(\Omega_{12}) = -\int_0^\infty dr_{12}^* r_{12}^{*\,-4}[C_i + C_a P_2(\cos\theta_{12})]g^{(0)}(r_{12}^*)\int \frac{d\widehat{\mathbf{r_{12}}}}{D^3(\widehat{\mathbf{r_{12}}},\ \Omega_{12})} \tag{14}$$

Considering the expression for $D(\widehat{\mathbf{r_{12}}},\Omega_{12})$ [18] and evaluating the second integral of the above equation for fixed relative orientation $\widehat{\mathbf{e_1}}\cdot\widehat{\mathbf{e_2}}=\cos\theta_{12}$, we can write our result as an expansion in the Legendre functions

$$\int\frac{d\widehat{\mathbf{r_{12}}}}{D^3(\widehat{\mathbf{r_{12}}},\Omega_{12})}=[D_0^{-3}][A_0+A_2P_2(\cos\theta_{12})+A_4P_4(\cos\theta_{12})+\cdots] \tag{15}$$

Here $D_0=2b$ [18] and one can calculate the values of the constants A_n, $n=0, 2, \ldots$ as a function of length-width ratio x [18]. With the help of Eqs. (14) and (15), we can write

$$\begin{aligned}Y(\Omega_{12})=-[D_0^{-3}][C_i+C_aP_2(\cos\theta_{12})][A_0+A_2P_2(\cos\theta_{12})\\+A_4P_4(\cos\theta_{12})+\cdots]I(\rho,T)\end{aligned} \tag{16}$$

where $I(\rho, T)$ is

$$I(\rho,T)=\int_0^\infty {r_{12}^*}^{-4}g_{hs}^{(0)}(r_{12}^*)dr_{12}^* \tag{17}$$

The above integral can be evaluated using the exact radial distribution function for hard spheres obtained from computer simulations. Combining the known density expansion for $g_{hs}^{(0)}(r_{12}^*)$ with Monte Carlo values, Larsen *et al.* have proposed the following extended series [24]:

$$I(\rho^*)=J_0+J_1\rho^*+J_2\rho^{*2}+J_3\rho^{*3}+\cdots \tag{18}$$

where $\rho^*=6\rho v_0/\pi$. The coefficients Js are tabulated [24] by Larsen *et al.* Using Eqs. (14) to (17) for $\psi^1(\Omega)$ we can express Eq. (12) as

$$\frac{\beta A^{(1)}}{N}=\beta(-\phi_0-\phi_2\overline{P}_2^2) \tag{19}$$

where

$$\phi_0=\left(\frac{\pi x}{12}\right)\eta I_6(\eta)C_i^*\left[A_0+\frac{1}{5}\left(\frac{C_a^*}{C_i^*}\right)A_2\right] \tag{20}$$

$$\phi_2=\left(\frac{\pi x}{12}\right)\eta I_6(\eta)C_i^*\left[A_2+\left(A_0+\frac{2}{7}A_2\right)\frac{C_a^*}{C_i^*}\right] \tag{21}$$

with $C_i^*=C_i/v_0^2$ and $C_a^*=C_a/v_0^2$. $I_6(\eta)$ is defined by the relation as given in Eq. (17). With the help of Eqs. (11) and (19), the total configurational Helmholtz free energy can be written as

$$\frac{\beta A}{N}=B_0(\eta,T)+\frac{\beta A_{orient}}{N} \tag{22}$$

B_0 is the orientation independent contribution,

$$B_0(\eta, T) = \ln \rho - 1 + \frac{\eta(4-3\eta)}{(1-\eta)^2} F_0(\chi) - \beta\phi_0 \tag{23}$$

and A_{orient} refers to the orientational free energy,

$$\frac{\beta A_{orient}}{N} = \langle \ln[4\pi f(\Omega)] \rangle - B_2(\eta, T)\overline{P}_2^2 \tag{24}$$

where $B_2(\eta, T) = \eta(4-3\eta)/(1-\eta)^2 F_2(\chi) + \beta\phi_2$. The one-particle orientational distribution function $f(\Omega)$ at a specified temperature and pressure is determined by minimizing the free energy with respect to variation of $f(\Omega)$ subject to the constraint $\int d\Omega f(\Omega) = 1$. The exact expression of $f(\Omega)$ leads directly to the transcedental equations for the second rank orientational order parameter as defined by Eq. (9). The N_D-I transition properties are located by equating the pressure and chemical potentials of the two phases—discotic nematic and isotropic.

Results and Discussion

We have used our theory to analyze the variation of order parameter with temperature for the molecule hexa(p-octyl phenyl ethynyl) benzene, a compound for which first experimental studies [1] on the temperature variation of orientational order parameter were reported by Aver'yanov. The volume of the molecule is taken as 322 cubic angstrom. For a given $x = 0.9$, the potential parameters C_i^*/k and C_i^*/C_a^* are chosen such that they quantitatively reproduce the N_D-I transition temperature $T_c = 372.3$ K. This is very close to the transition temperature 372.6 K as obtained by Aver'yanov. Other transition parameters are determined self-consistently by an iterative procedure. The variation of the order parameter with temperatue is shown in Figure 1. Our calculation yields the value of the order parameter as 0.48 at the transition, larger

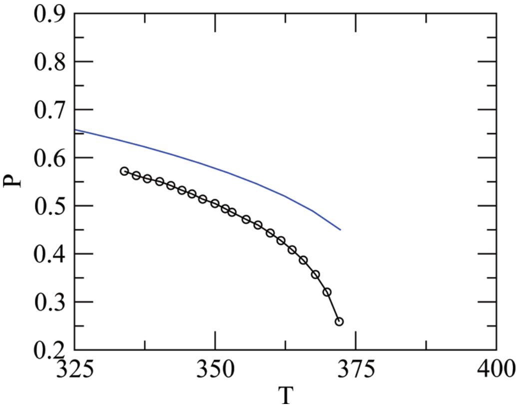

Figure 1. Temperature variation of the order parameter $\overline{P}_2$. The lower curve with circles represents the experimental values and the upper solid line curve represents the theoretical result corresponding to $x = 0.9$, $C_i^*/k = 4800$ K, and $C_i^*/C_a^* = 8.56$.

Table 1. Discotic nematic-isotropic transition parameters for $x = 0.9$, $C_i^*/k = 4800\,\mathrm{K}$, and $C_i^*/C_a^* = 8.56$ for hexa(p-octyl phenyl ethynyl)benzene

S. no.	Transition quantities	Values
1.	Long-range order parameter $(\overline{P}_2)$	0.48
2.	Nematic packing fraction (η_n)	0.61
3.	Isotropic packing fraction (η_i)	0.605
4.	Transition entropy $(\Delta\Sigma/N_k)$	0.68
5.	Relative density change $(\Delta\eta/\eta)$	0.002
6.	Γ as defined in text, $\Gamma = (\partial \ln T/\partial \ln p)_{\overline{P}_2}$	1.67

than that of Aver'yanov. No simulation result is available for this mesogen. But we can refer to Emerson *et al.* [25] for a molecular dynamics simulation work for the system of oblate molecules. By considering suitable parameterization for Gay-Berne potential, the value of order parameter at the transition was found to be 0.7. It is obvious that the present result qualitatively agrees with the simulation studies giving rise to a finite value of the order parameter at the transition. The molecules have a rigid, strongly polarized aromatic core and flexible end chains $(C_nH_{(2n+1)})$, which are orientationally melted at the transition temperature. The resulting values of order parameter thus characterize the orientational order of rigid molecular cores. Table 1 summarizes a number of thermodynamic quantities calculated at the N_D-I transition at a constant pressure of one bar with the interaction strength $C_i^*/k = 4800\,\mathrm{K}$ and $C_i^*/C_a^* = 8.56$. These values are reported here for our particular molecule under consideration. Similar values of the force parameters have been used in calculation of the nematic-isotropic transition of para-azoxyanisole (PAA) by several workers [14,26,27]. The variations of packing fraction η and relative change in density $\Delta\eta/\eta$ for $x = 0.9$ are calculated. The parameter Γ listed in Table 1 measures the sensitivity of the order parameter to volume change (at constant temperature) and the temperature change (at constant volume); that is, $\Gamma = (\partial \ln T/\partial \ln \rho)_{\overline{P}_2}$. The pressure dependence of the transition temperature dT/dP is determind by the Clausius-Clapeyron law, whereas $\Delta\Sigma/N_k$ measures the entropy change at the transition. All these values are consistent with discotic mesogens [18].

Conclusions

In order to study the variation of the long-range orientational order parameter $(\overline{P}_2)$ with temperature and to investigate the influence of dispersion interaction on a variety of thermodynamic properties of discotic nematic liquid crystal, hexa(p-octyl phenyl ethynyl)benzene, at the discotic nematic isotropic transition, we have applied a perturbation expansion method. Our model system is one in which molecules are assumed to interact via a pair potential having both repulsive and attractive parts. The properties of the reference system and the first-order perturbation term are evaluated by assuming that an angle-dependent range parameter scales the pair correlation function such that it decouples the orientational degrees of freedom from a translational one. The decoupling approximation has been found to yield values of the compressibility factor that are in very good agreement with computer simulation results [28]. The various transition parameters are determined self-consistently by an iterative procedure. In fact, realistic intermolecular interaction potentials for mesogenic molecules can be very complex and generally unknown. Also, we have presented our model system, which simulates a real system and so one cannot expect a perfect agreement with experiments. Notwithstanding, it is observed that our theoretical approach based on a simple model potential offers good qualitative solutions for the variation of the order parameter with temperature and the values of various thermodynamic properties at the transiton for the discogen considered here.

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