Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Singh, Kalyan , Pandey, N. S. and Lahiri, T. K.(1999) 'Perturbation theory for discotic nematic liquid crystals of axially symmetric molecules: effect of dispersion interaction', Liquid Crystals, 26: 7, 999 — 1005
To link to this Article: DOI: 10.1080/026782999204345
URL: http://dx.doi.org/10.1080/026782999204345

LIQUID CRYSTALS, 1999, VOL. 26, NO. 7, 999–1005

Perturbation theory for discotic nematic liquid crystals of axially symmetric molecules: effect of dispersion interaction

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(*Received 6 August 1997; accepted 1 May 1998*)

We investigate the influence of dispersion interaction on a variety of thermodynamic properties of discotic nematic liquid crystals at the discotic nematic–isotropic transition. We report calculations for a hard oblate ellipsoidal system, superposed with an attractive interaction represented by dispersion interaction subjected to different external pressures ranging from 1 to 300 bar. We consider a model system (which simulates a discotic nematic liquid crystal) in which molecules are assumed to interact via a pair potential having both repulsive and attractive parts. The repulsion part is represented by a repulsion between hard oblate ellipsoids of revolution and is a short range, rapidly varying potential. The attractive potential, a function of centre of mass distance and relative orientation between two molecules, is represented by dispersion interaction. The properties of the reference system and first order perturbation term are evaluated using a decoupling approximation which decouples orientational from translational degrees of freedom. The inclusion of fourth and sixth rank orientational order parameters in the calculation slightly improves the result. The role of pressure on phase transition parameters has also been studied.

1. Introduction

Molecules consisting of hard ellipsoids of revolution (HER) and other similar hard-core molecules such as hard sphero-cylinders (HSC) and hard dumbells (HD) have long served as some of the most important models for phase transitions in condensed matter consisting of nonspherical molecules. There are two reasons for the importance of hard-core models. First, they can be used to test molecular theories for static and dynamic properties of liquid crystals; secondly, they may provide a starting point for thermodynamic perturbation theories. Onsager made a major contribution to our understanding of the nematic phase with his simple theory [1] of the isotropic–nematic (I–N) transition in the HSC system. The isotropic to nematic liquid crystal transition could be predicted on the basis of a virial expansion for the Helmholtz free energy and this expansion had only to include the lowest order interaction term arising from the second virial coefficient. As a particle becomes more elongated, the higher virial coefficients become progressively less important and so only the second virial is necessary for a quantitatively accurate prediction of a phase transition density [2]. Among extensive work [2–4] on hard ellipsoid molecules, based on Onsager like theory, Samborsk *et al.* treat the second and the third virial coefficients in the same way, but the fourth and higher virials, are re-summed in a manner consistent with the Carnahan–Starling equation of state for hard spheres. This work provides analytical expressions for the free energy and direct correlation function in terms of the second and third virial coefficients, along with other results.

Several authors [5–8] have used a density functional theory (DFT) to study the first order I–N transition and the freezing transition with fair success. In the DFT of Singh and Singh [5] for hard ellipsoids, one starts from a DFT expression for the free energy of the ordered (nematic) phase and expands it around the disordered (isotropic) phase to third order in the local density change. The I–N transition for hard ellipsoids is found to occur at lower densities than predicted by the other approach. The DFT of Colot and coworkers [6] has an explicit oblate–prolate symmetry and leads to simple analytic expressions, e.g. for the equation of state of the isotropic phase. The results of the theory of Colot *et al.* produce all the qualitative features provided by the computer simulation of Frenkel and Mulder in the case

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Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd
http://www.tandf.co.uk/JNLS/lct.htm
http://www.taylorandfrancis.com/JNLS/lct.htm

of the isotropic phase, and fair agreement for the nematic phase and the isotropic–nematic coexistence.

Allen and Frenkel [3(*c*)] have carried out the first molecular dynamics simulations of a system of prolate HER, near the I–N phase transition. Computer simulations [2–4] have shown that a system of hard ellipsoids does exhibit some liquid crystal phases and can thus be used as a simple reference system for the study of nonspherical molecules. The simulations have also shown that liquid crystal phases can be formed both by prolate (rod-like) and by oblate (disc-like) hard ellipsoids. These facts indicate that the hard ellipsoids system can be expected to provide a good reference system for a perturbational treatment [9] of a more realistic system of dislike molecules.

We have applied a perturbation expansion method [10] of a rod-shaped system to study a molecular description of the equilibrium properties of discotic nematogens [11]. We assume that disc-shaped molecules are oblate ellipsoids of revolution parameterized by their length to width ratio x_0 ($=2a/2b$, where $2a$ and $2b$ denote, respectively, the lengths of major and minor axes of the ellipsoids) which is less than one for oblate ellipsoids. This work is similar to that of our previous publication [12] in which the effects of dispersion and quadrupolar interaction were separately considered on discotic nematic–isotropic (DN–I) transition properties of the discotic nematic phase close to transition. But the numerical results in [12] are limited to only the second order orientational order parameter, whereas the importance of higher order orientational order parameters has been demonstrated experimentally [13]. In this paper we extend the calculation of equilibrium properties of discotic nematics, retaining second, fourth and sixth rank long range orientational order parameters ($\mathbf{P}_2$, $\mathbf{P}_4$ and $\mathbf{P}_6$) in the evaluation of the angle-dependent term in the expression of excluded volume and perturbation term. The influence of pressure on stability, ordering and thermodynamic properties, for suitably chosen potential parameters, is also analysed at the DN–I transition. In the following section a brief account of the theory is given and working equations are summarized. Results and discussions are given in §3.

2. Theory and working equations

We consider a system composed of N axially symmetric discotic nematic molecules in a volume V at temperature T, interacting through a potential function given by

$$U_N(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \sum_{1 \leqslant i < j \leqslant N} [U_o(\mathbf{x}_i, \mathbf{x}_j) + U_p(\mathbf{x}_i, \mathbf{x}_j)] \tag{1}$$

where vector $\mathbf{x}_i$ [$\equiv (\mathbf{r}_i, \Omega_i)$] represents both the position of centre of mass of the ith molecule and its relative orientation Ω_i described by Euler's angles θ_i, ϕ_i and ψ_i. $U_o(\mathbf{x}_i, \mathbf{x}_j)$ represents the reference potential which is described by the repulsion between the hard oblate ellipsoids of revolution, and satisfies the relation

$$\begin{aligned} U_o(\mathbf{r}_{12}, \Omega_1, \Omega_2) \equiv U_o(\mathbf{r}_{12}, \Omega_{12}) &= U_o[\mathbf{r}_{12}/D(\Omega_{12})] \\ &= U_o(r^*_{12}) = \begin{cases} \infty & \text{for } r^*_{12} < 1 \\ 0 & \text{for } r^*_{12} > 1. \end{cases} \end{aligned} \tag{2}$$

Here $D(\Omega_{12})$ [$\equiv D(\mathbf{r}_{12}, \Omega_1, \Omega_2)$] is the distance of closest approach between two molecules with relative orientation Ω_{12}, $\mathbf{r}_{12}$ is a vector joining the centres of mass of two molecules and $r^*_{12} = |\mathbf{r}_{12}|/D(\Omega_{12})$. For $D(\Omega_{12})$, we use the expression given by the Gaussian overlap model of Berne and Pechukas [14].

The perturbation potential $U_p(\mathbf{x}_i, \mathbf{x}_j)$ contains the more smoothly varying long-range attractive part. It is a function of only the centres of mass distance and the relative orientation between two molecules, and is approximated by the interaction arising from the dispersion force between two asymmetric molecules. We adopt the following form for the perturbation potential:

$$\begin{aligned} U_p(\mathbf{r}_{12}, \Omega_1, \Omega_2) = -r_{12}^{-6}[C_i + C_a P_2(\cos\theta_{12})], \\ \text{for } r_{12} > D(\Omega_{12}). \end{aligned} \tag{3}$$

Here C_i and C_a are constants related to isotropic and anisotropic dispersion interactions and θ_{12} is the angle between the axes of two molecules. The perturbation potential so chosen is certainly an oversimplification of the intermolecular potential of real liquid crystals but this is in accordance with Maier–Saupe theory [15].

Adopting the procedure as outlined in [10], we write the total Helmholtz free energy A of the system as

$$\frac{\beta A}{N} = \frac{\beta A_o}{N} + \sum_{s=1}^{\infty} \frac{\beta A^{(s)}}{N} \tag{4a}$$

where $\beta = 1/kT$ and A_o is the contribution of the reference system. The second term of equation (4*a*) is a perturbation series with s as a perturbation order.

In order to calculate the thermodynamic properties of the reference system (hard ellipsoids) we start with the pressure equation

$$\begin{aligned} \frac{\beta p_o}{\rho} = 1 - \frac{1}{6}\beta\rho \int \mathrm{d}\mathbf{r}_{12} \int f(\Omega_1)\,\mathrm{d}\Omega_1 \int f(\Omega_2)\,\mathrm{d}\Omega_2 \\ \times [\mathbf{r}_{12}\nabla u_o(\mathbf{r}_{12}, \Omega_{12}) g^o(\mathbf{r}_{12}, \Omega_{12})]. \end{aligned} \tag{4b}$$

Here the operator ∇ acts only on $\mathbf{r}_{12}$ coordinates of $U_o(\mathbf{r}_{12}, \Omega_{12})$. Following Parsons [16], we approximate the reference system pair correlation function

$g^{\circ}(\mathbf{r}_{12}, \Omega_{12})$ as

$$g^{\circ}(\mathbf{r}_{12}, \Omega_{12}) = g^{\circ}[\mathbf{r}_{12}/D(\Omega_{12})] = g^{\circ}(r^{*}_{12}). \qquad (4c)$$

This approximation completely decouples the orientational and positional degrees of freedom. We consider excluded volume or co-volume between the two ellipsoids of revolution as

$$V_{\mathrm{exc}} = \frac{1}{3}\int D^{3}(\Omega_{12})\,\mathrm{d}\mathbf{r}_{12}$$

$$= 8v_{\mathrm{o}}(1-\chi^{2})^{-1/2}(1-\chi^{2}\cos^{2}\theta_{12})^{1/2} \qquad (4d)$$

where v_{o} is the volume of a molecule and $\chi = x_{\mathrm{o}}^{2} - 1/x_{\mathrm{o}}^{2} + 1$.

Taking the Berne and Pechukas [14] relation for $D(\mathbf{r}_{12}, \Omega_{12})$ and reducing the distance variable with $D(\mathbf{r}_{12}, \Omega_{12})$ and using equations $(4c)$ and $(4d)$, we get

$$\frac{\beta p_{\mathrm{o}}}{\rho} = \frac{1+2\eta(2-\eta)}{(1-\eta)^{3}}[F_{0}(\chi) - F_{2}(\chi)\mathbf{P}_{2}^{2}$$

$$- F_{4}(\chi)\mathbf{P}_{4}^{2} - F_{6}(\chi)\mathbf{P}_{6}^{2}] \qquad (4e)$$

where

$$\eta = \rho v_{0}$$

$$F_{0}(\chi) = (1-\chi^{2})^{-1/2}\left(1 - \frac{1}{6}\chi^{2} - \frac{1}{40}\chi^{4} - \frac{1}{112}\chi^{6} - \ldots\right)$$

$$F_{2}(\chi) = \frac{\chi^{2}}{3}(1-\chi^{2})^{-1/2}\left(1 + \frac{3}{14}\chi^{2} + \frac{5}{56}\chi^{4} + \frac{25}{528}\chi^{6} + \ldots\right)$$

$$F_{4}(\chi) = \frac{\chi^{4}}{35}(1-\chi^{2})^{-1/2}\left(1 + \frac{15}{22}\chi^{2} + \frac{525}{1144}\chi^{4} + \ldots\right)$$

$$F_{6}(\chi) = \frac{\chi^{6}}{231}(1-\chi^{2})^{-1/2}\left(1 + \frac{7}{6}\chi^{2} + \frac{147}{136}\chi^{4} + \ldots\right).$$

The orientational order parameter can be written

$$\mathbf{P}_{n} = \int \mathrm{d}\Omega f(\Omega) P_{n}(\cos\theta). \qquad (5)$$

The Helmholtz free energy per particle for the reference system can now be evaluated using the standard thermodynamic relation and we write

$$\frac{\beta A_{\mathrm{o}}}{N} = (\ln\rho - 1) + \langle \ln[4\pi f(\Omega)]\rangle + \frac{\eta(4-3\eta)}{(1-\eta)^{2}}$$

$$\times [F_{0}(\chi) - F_{2}(\chi)\mathbf{P}_{2}^{2} - F_{4}(\chi)\mathbf{P}_{4}^{2} - F_{6}(\chi)\mathbf{P}_{6}^{2}]. \qquad (6)$$

The angular bracket $\langle \ldots \rangle$ in equation (6) 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 non-interacting molecules, the third is the excess free energy arising from the inter-particle interaction. One finds that the expression (6) is similar to the corresponding equations derived by Vroege and Lekkerkerker [17] and Samborsk *et al.* [4].

The first order perturbation to the Helmholtz free energy is given by

$$\frac{\beta A^{(1)}}{N} = \beta\int \mathrm{d}\Omega_{1}\, f(\Omega_{1})\,\psi^{(1)}(\Omega_{1}). \qquad (7)$$

The term $\psi^{(1)}(\Omega_{1})$ is defined as an effective one-body orientational perturbation potential and is given by

$$\psi^{(1)}(\Omega_{1}) = \frac{1}{2}\rho\int \mathrm{d}\Omega_{2}\, f(\Omega_{2})\int \mathrm{d}\mathbf{r}_{12}\, u_{\mathrm{p}}$$

$$\times (\mathbf{r}_{12}, \Omega_{1}, \Omega_{2})\, g^{\circ}(\mathbf{r}_{12}, \Omega_{12}). \qquad (8)$$

By reducing the distance variables in equation (8) with $D(\mathbf{r}_{12}, \Omega_{12})$, applying the decoupling approximation and solving the integrals involved, we get finally

$$\frac{\beta A^{(1)}}{N} = -\beta\phi_{0} - \beta\phi_{2}\mathbf{P}_{2}^{2} - \beta\phi_{4}\mathbf{P}_{4}^{2} - \beta\phi_{6}\mathbf{P}_{6}^{2} \qquad (9)$$

where

$$\phi_{k} = \left(\frac{\pi}{12}x_{0}\right)\eta I_{6}(\eta) C_{\mathrm{i}}^{*}\, N_{k} \qquad k = 0, 2, 4 \text{ and } 6$$

$$N_{0} = A_{0} + \frac{1}{5}A_{2}\, C_{\mathrm{a}}^{*}/C_{\mathrm{i}}^{*}$$

$$N_{2} = A_{2} + \left(A_{0} + \frac{2}{7}A_{2} + \frac{2}{7}A_{4}\right)C_{\mathrm{a}}^{*}/C_{\mathrm{i}}^{*}$$

$$N_{4} = A_{4} + \left(\frac{18}{35}A_{2} + \frac{20}{77}A_{4}\right)C_{\mathrm{a}}^{*}/C_{\mathrm{i}}^{*}$$

$$N_{6} = A_{6} + \left(\frac{5}{11}A_{4} + \frac{14}{55}A_{6}\right)C_{\mathrm{a}}^{*}/C_{\mathrm{i}}^{*}$$

$$C_{\mathrm{i}}^{*} = C_{\mathrm{i}}/v_{0}^{2} \quad \text{and} \quad C_{\mathrm{a}}^{*} = C_{\mathrm{a}}/v_{0}^{2}.$$

A_{0}, A_{2}, A_{4} and A_{6} are constants appearing in the integral $I_{6}(\eta)$ which is defined as

$$I_{6}(\rho, T) = \int_{0}^{\infty} r_{12}^{*\,-4}\, g_{\mathrm{hs}}^{(0)}(r_{12}^{*})\,\mathrm{d}r_{12}^{*} \qquad (10)$$

and evaluated from the series proposed by Larsen *et al.* [18].

The total configurational Helmholtz free energy is obtained by adding equations (6) and (9).

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

$$\int f(\Omega)\,\mathrm{d}\Omega = 1. \qquad (11)$$

The exact expression of $f(\Omega)$ leads directly to the transcendental equations for the second, fourth and sixth rank order parameters as defined by equation (5).

The DN–I transition properties are located by equating the pressure and chemical potentials of the two phases—discotic nematic and isotropic.

3. Results and discussion

We study first the effects of length to width ratio x_0 and potential parameters C_i^*/k and C_i^*/C_a^* on the thermodynamic properties of the DN–I phase transition. The method and details of calculation are the same as described by Singh and Singh [10]. The calculation has been done for a system of oblate ellipsoids (which crudely simulates a discotic nematic phase) retaining terms up to $\mathbf{P}_6$ in the expansion of the one-body effective potential $\psi^{(1)}(\Omega)$ defined by equation (8). For a given x_0 the potential parameters are such as to reproduce quantitatively the DN–I transition temperature $T_{NI} \simeq 600$ K which corresponds to the hexa-*n*-hexyloxybenzoate of triphenylene. The volume of a molecule is taken 230 Å^3. Other transition parameters are determined selfconsistently by an iterative procedure.

The variation of interaction strength C_i^*/k as a function of x_0 is plotted in figure 1. We observe from the figure that C_i^*/k decreases as the shape anisotropy increases and its value reaches maximum at $x_0 \simeq 1.0$. Figure 2 shows the variation of transition temperature T_c with C_i^*/k for the discotic nematic phase at different values of x_0. It is observed that the transition temperature shifts to higher values with increase of anisotropy and also with increase of the strength parameter of attractive interaction. In figure 3, we show the variation of transition temperature as a function of C_i^*/C_a^*. It is evident from this figure that for $C_i^*/C_a^* > 20$, the phase transition temperature is not very sensitive to the value of C_i^*/C_a^*.

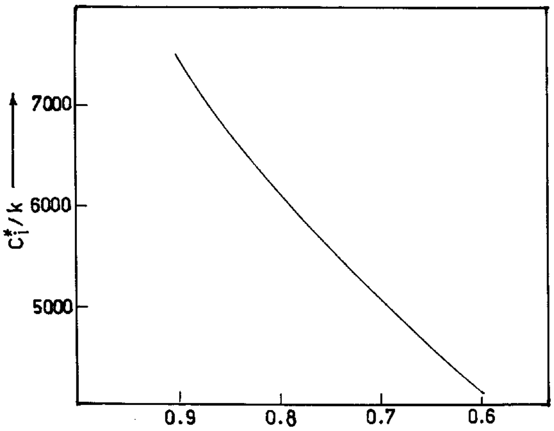

Figure 1. Variation of C_i^*/k (which yields the transition temperature of 600 K) as a function of x_0 (for oblate ellipsoids) with $C_i^*/C_a^* = 8$.

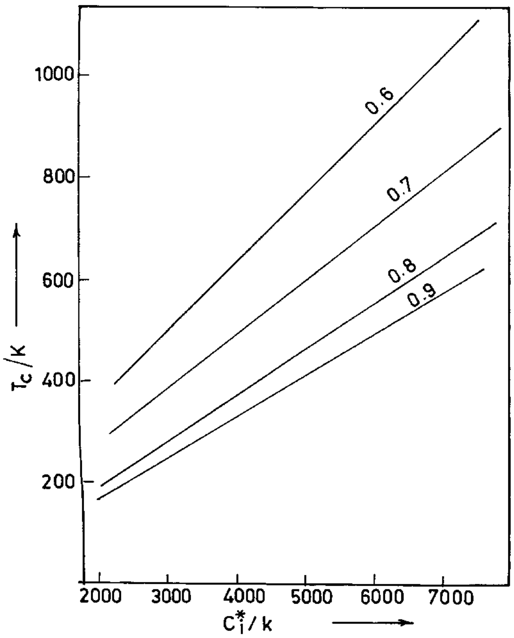

Figure 2. Variation of the DN–I transition temperature T_c as a function of C_i^*/k for $C_i^*/C_a^* = 8$. The number on the curves indicates the value of x_0.

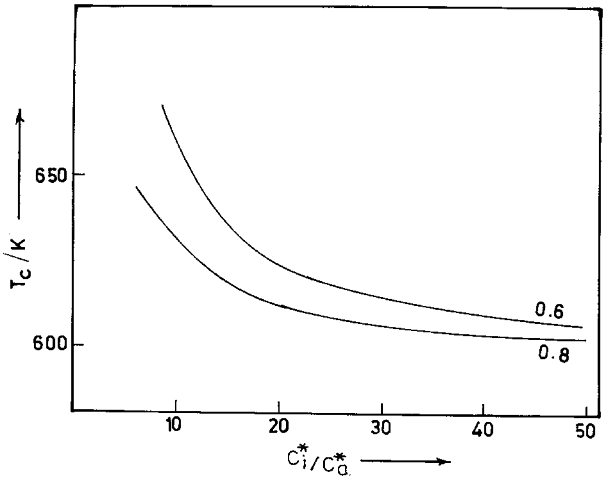

Figure 3. Variation of the DN–I transition temperature T_c as a function of C_i^*/C_a^* for a fixed value of C_i^*/k. The number on the curves indicates the value of x_0.

The variation of packing fraction η, and relative change in density $\Delta\eta/\eta$ for $x_0 = 0.6$ and 0.7 as a function of C_i^*/C_a^*, is shown in figure 4. There is a jump in the values of η and $\Delta\eta/\eta$ with the change in the values of x_0. For a fixed value of x_0, η increases and $\Delta\eta/\eta$ decreases with C_i^*/C_a^*. But again changes are small for $C_i^*/C_a^* > 20$. This trend for the discotic nematic is similar

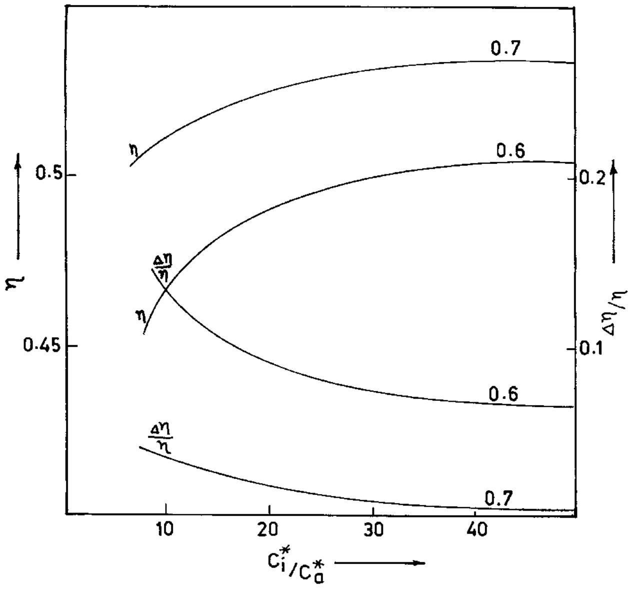

Figure 4. The variation of packing fraction η and relative change in density $\Delta\eta/\eta$ at the transition as a function of C_i^*/C_a^*. C_i^*/k are chosen to reproduce the DN–I transition temperature $T_c \simeq 600$ K. The number on the curve indicates the value of x_0.

to that for the ordinary nematic (prolate ellipsoids) which is in accordance with the observations of Gelbert and Baron [19].

In table 1, we list a number of thermodynamic quantities at the DN–I transition at a constant pressure equal to 1 bar. The parameter Γ listed in the table measures the sensitivity of the order parameter to volume change (at constant temperature) and the temperature change (at constant volume),

$$\Gamma = \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_{\mathbf{P}_2}. \tag{12}$$

The pressure dependence of the transition temperature $(\mathrm{d}T/\mathrm{d}P)$ is determined by the Clausius–Clapeyron law. $\Delta\Sigma/Nk$ measures the entropy change at the transition. Comparing with the results obtained by Singh *et al.* [12] we find that the inclusion of $\mathbf{P}_4$ and $\mathbf{P}_6$ terms in the calculation leads to a slight change in thermodynamic quantities: $\mathbf{P}_2$, $\Delta\eta/\eta$, η, $\Delta\Sigma/Nk$, $(\mathrm{d}T_c/\mathrm{d}P)$ and Γ increase slightly. The change is not very significant but the importance of higher orientational order parameters cannot be neglected.

In table 2, we summarize a number of thermodynamic properties at the DN–I transition at high pressures ranging from 1 to 300 bar for dispersion interaction. From the table it can be seen that for a given x_0 and interaction parameters, as pressure increases the phase transition shifts to a higher temperature and the fractional change in volume $(\Delta V/V)$ decreases. V^* is the reduced volume given by $V^* = \pi/(6\eta)$. The order parameters ($\mathbf{P}_2$, $\mathbf{P}_4$ and $\mathbf{P}_6$), reduced volume V^*, transition entropy $\Delta\Sigma/Nk$ and $\mathrm{d}T_c/\mathrm{d}P$ decrease with increasing pressure. Γ measures the relative sensitivity of order parameter ($\mathbf{P}_2$) to volume change, and increases slightly with pressure. It is also observed that the range of stability of the discotic nematic phase is considerably larger at constant density than at constant pressure.

Figures 5 and 6 show the variation of order parameters ($\mathbf{P}_2$, $\mathbf{P}_4$ and $\mathbf{P}_6$) as a function of T/T_c and C_i^*/C_a^*, respectively. From figure 5 it is evident that $\mathbf{P}_2$, $\mathbf{P}_4$ and $\mathbf{P}_6$ decrease with increasing T/T_c, but at a given T/T_c value they increase with increase in shape anisotropy.

4. Conclusion

A statistical mechanical theory has been applied within mean-field approximation to analyse the influence of dispersion interaction on the thermodynamic and orientational properties of the DN–I phase transition,

Table 1. The discotic nematic–isotropic transition parameter for a system having oblate molecules. $\mathbf{P}_2$, $\mathbf{P}_4$ and $\mathbf{P}_6$ are order parameters; $\eta = (1/2)(\eta + \eta_i)$, η and η_i are the discotic nematic and isotropic packing fractions; $\Delta\Sigma/Nk$ is the transition entropy and $\Gamma(T_c)$ is defined in equation (12). The model parameters are chosen so as to reproduce the transition temperature $T_c \approx 600$ K with $C_i^*/C_a^* = 8$.

x_0	C_i^*/k	η	$\Delta\eta/\eta$	$\mathbf{P}_2$	$\mathbf{P}_4$	$\mathbf{P}_6$	$\Delta\Sigma/Nk$	$(\mathrm{d}T_c/\mathrm{d}P)_{P=1\ \mathrm{bar}}$	$\Gamma(T_c)$
0.9	[a] 7455.04	0.6011	0.0093	0.462	0.140	0.031	0.741	35.302	1.67
	[b] 7453.72	0.6010	0.0092	0.458	—	—	0.727	35.300	1.67
0.8	[a] 6365.15	0.5680	0.0179	0.503	0.168	0.041	0.934	57.857	1.77
	[b] 6355.43	0.5670	0.0163	0.479	—	—	0.845	57.280	1.76
0.7	[a] 5091.17	0.5090	0.0487	0.565	0.218	0.063	1.376	118.690	1.85
	[b] 5110.07	0.5090	0.0444	0.541	—	—	1.254	118.570	1.85
0.6	[a] 4098.11	0.4360	0.2078	0.735	0.404	0.176	3.269	275.190	1.95
	[b] 4146.93	0.4360	0.1797	0.686	—	—	2.784	273.740	1.93

[a] Our calculation including $\mathbf{P}_2$, $\mathbf{P}_4$ and $\mathbf{P}_6$.
[b] Results of Singh, *et al.* [12], limited to $\mathbf{P}_2$.

Table 2. The discotic nematic isotropic transition parameters under high pressure. $\mathbf{P}_2$, $\mathbf{P}_4$ and $\mathbf{P}_6$ are order parameters; $\Delta\Sigma/Nk$ is the transition entropy and $\Gamma(T_c)$ is defined in equation (12). The model parameters are chosen so as to reproduce the transition temperature $T_c \approx 600$ K at $P = 1$ bar, $V^* = \pi/6\eta$, $\Delta V/V$ is the fractional change in volume and $C_i^*/C_a^* = 8$.

x_0	C_i^*/k	P/bar	T_c/k	V^*	$\Delta V/V$	$\mathbf{P}_2$	$\mathbf{P}_4$	$\mathbf{P}_6$	$\Delta\Sigma/Nk$	$\Gamma(T_c)$	dT_c/dP
0.8	6365.15	1	612.71	0.922	0.017	0.503	0.168	0.041	0.93	1.765	56.86
		100	619.62	0.919	0.015	0.488	0.157	0.037	0.86	1.769	54.45
		200	624.84	0.914	0.014	0.487	0.157	0.037	0.84	1.774	51.88
		300	631.43	0.911	0.013	0.470	0.146	0.033	0.77	1.778	49.94
0.7	5091.17	1	648.18	1.028	0.048	0.565	0.217	0.063	1.37	1.853	118.69
		100	659.02	1.018	0.042	0.558	0.212	0.061	1.28	1.864	109.31
		200	670.33	1.010	0.036	0.543	0.200	0.055	1.17	1.874	102.24
		300	679.79	1.002	0.033	0.540	0.198	0.054	1.12	1.886	95.56
0.6	4098.11	1	658.84	1.201	0.207	0.735	0.403	0.176	3.26	1.951	275.19
		100	683.53	1.173	0.147	0.702	0.361	0.146	2.57	1.956	233.03
		200	706.53	1.157	0.113	0.670	0.324	0.123	2.13	1.964	209.60
		300	725.45	1.140	0.094	0.654	0.307	0.112	1.89	1.981	189.51

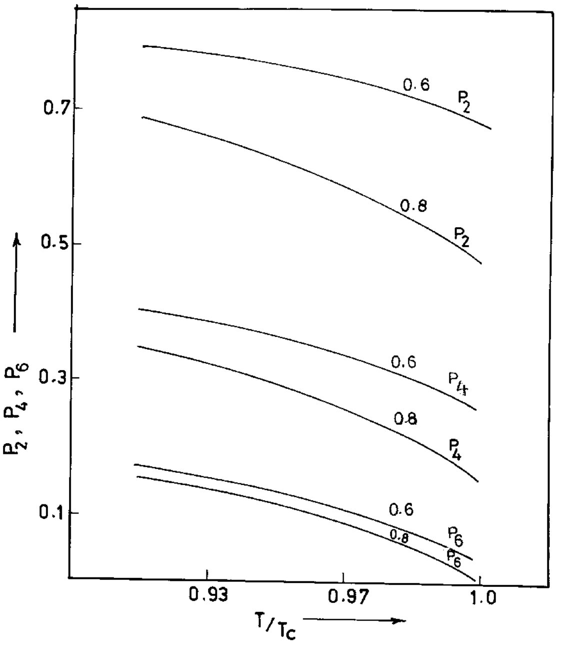

Figure 5. Temperature variation of the long range orientational order parameters at constant pressure. C_i^*/k are chosen so as to reproduce the DN–I transition temperature $T_c \simeq 600$ K.

and to study the role of pressure on the phase transition. Basic to this theory is the recognition that the predominant factor in determining the mesophase stability is geometric. The thermodynamic properties have been calculated for a model system composed of nonspherical molecules interacting via a pair potential having both repulsive and attractive components. Our calculation with second, fourth and sixth rank order parameters for phase transition properties of disc-like molecules shows similar trends to that for an ordinary nematic, which is

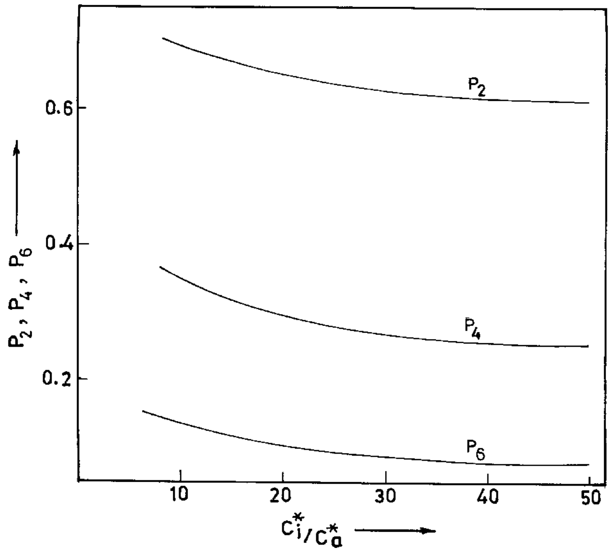

Figure 6. The variation of order parameters $\mathbf{P}_2$, $\mathbf{P}_4$ and $\mathbf{P}_6$ at the transition as a function of C_i^*/C_a^*. C_i^*/k are chosen to reproduce the transition temperature $T_c \simeq 600$ K. Order parameters are plotted for $x_0 = 0.6$.

in agreement with the Monte Carlo simulation of Frenkel *et al.* [3(*a*)].

Quantitative agreement between theory and experiment can not be really expected, since our model system only crudely simulates a real system. However, we expect that this simple approach to a study of the thermodynamic properties at the DN–I transition will certainly provide a molecular basis for the study of discotic nematic liquids. Further, we plan to use this approach to study the results [20] of experimental data on temperature dependence of the orientational order of discotic nematic liquid crystals. This will be the subject of a future communication.

We are grateful to Prof. S. Singh for helpful discussion. K. S. is also grateful to UGC, India for financial support.

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