Statistical mechanical theory for discotic liquid crystals Discotic nematic-isotropic transition properties

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Statistical mechanical theory for discotic liquid crystals
Discotic nematic–isotropic transition properties

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A statistical mechanical theory is applied to study the equilibrium properties of discotic nematic liquid crystals. We report the calculation of thermodynamic properties for a model system composed of molecules interacting through angle-dependent pair potentials which can be broken up into rapidly varying short-ranged repulsions and weak long-range attractions. The repulsive interaction is represented by a repulsion between hard oblate ellipsoids of revolution and is a short-range, rapidly-varying, potential. The influence of attractive potentials, represented by dispersion and quadrupole interactions on a variety of thermo-dynamic properties is analysed. It is found that the thermodynamic properties for the discotic nematic–isotropic transition are highly sensitive to the form of effective one-body orientational perturbation potential. The discontinuity in the transition properties is more pronounced in the case of quadrupole interaction than for anisotropic dispersion interaction. A remarkable symmetry in the transition properties between prolate ellipsoids (ordinary nematic) and oblate ellipsoids (discotic nematic) is observed.

1. Introduction

As is well accepted, a fundamental criterion to determine whether or not a substance exhibits a liquid-crystalline phase is the geometrical anisotropy of the molecule. The most generally accepted rule has been that the molecule must be elongated or rod like for mesomorphism to occur in non-amphiphilic systems. But about 10 years ago, exception to this rule was observed by Chandrasekhar and co-workers [1] who found that pure compounds composed of disc-shaped molecules may also form stable thermotropic liquid crystals. They have been shown to comprise a new class of liquid-crystalline phases, the discotic phases, some of which have been observed to exhibit a 'fluid' phase with only a long-range orientational order, i.e. a discotic nematic phase. Activities in this new kind of mesomorphism are quite intense because of the potential importance of such systems in applications and due to the very interesting physics of the mesophases themselves. A unique situation occurs in discotics: in one dimension the system has the properties of a liquid, and in the other two it is a solid, i.e. it is a system 'melted' in one dimension. This indicates the absence of correlations only in the arrangement of the centres of mass of the molecules along a straight line.

The purpose of this paper is to give a molecular description of the equilibrium properties of discotic phase by using the perturbation theory developed elsewhere [2, 3] for rod-like molecules. We assume that disc-shape molecules are oblate ellipsoids

of revolution parametrized by length-to-width ratio x. Considering the variation of x from values less than one (oblate molecules) to greater than one (prolate molecules) the results are considered for ordinary nematic (rod-shape) to discotic nematic. A brief account of the perturbation method and the working equations is given in §2. Results and discussions are presented in §3.

2. Theory and working equations

We consider a system composed of N axially symmetric nonspherical nematogenic molecules contained in a volume V at temperature T which interact through a pair potential function by

$$U_N(\bar{X}_1, \ldots, \bar{X}_N) = \sum_{1 \leqslant i < j \leqslant N} U_0(\bar{X}_i, \bar{X}_j) + \sum_{1 \leqslant i < j \leqslant N} U_P(\bar{X}_i, \bar{X}_j), \tag{1}$$

where the vector $\bar{X}_i = (\bar{r}_i, \Omega_i)$ represents both the position of centre of mass and orientation of the ith molecule. $U_0(\bar{X}_i, \bar{X}_j)$ represents the reference potential and is described by the repulsion between hard ellipsoids of revolution parametrized by the length to width ratio $x = a/b$, where $2a$ and $2b$ denote, respectively, lengths of major and minor axes of revolution. The perturbation potential $U_P(\bar{X}_i, \bar{X}_j)$ contains the more smoothly-varying, long-range, attractive part.

Assuming the pairwise additivity of the interaction potential and following the statistical mechanical machinery as outlined earlier [2], the perturbation series for the Helmholtz free-energy is written as

$$\frac{\beta A}{N} = \frac{\beta A_0}{N} + \sum_{s=1}^{\infty} \frac{\beta A^{(s)}}{N}, \tag{2}$$

where A_0 is the contribution of reference system and

$$\frac{\beta A^{(s)}}{N} = \beta \int f(\Omega_1) d\Omega_1 \psi^{(s)}(\Omega_1) \tag{3}$$

represents the perturbation terms. s denotes the order of perturbation, and $\psi^{(s)}(\Omega_1)$ is defined as an effective one-body orientational perturbation potential

$$\psi^{(s)}(\Omega_1) = \frac{1}{2s} \varrho \int d\Omega_2 f(\Omega_2) \int d\bar{r}_{12} U_P(\bar{r}_{12}, \Omega_1, \Omega_2) g^{(s-1)}(\bar{r}_{12}, \Omega_1, \Omega_2), \tag{4}$$

where $g^{(s-1)}(\bar{r}_{12}, \Omega_1, \Omega_2)$ is pair correlation function (PCF) for all s. For $s = 1$, $g^0(\bar{r}_{12}, \Omega_1, \Omega_2)$ represents the PCF for reference system. The first order perturbation term envolves hard ellipsoid's PCF $g^0(\bar{r}_{12}, \Omega_1, \Omega_2)$ only. The PCF is related to the probability of finding a hard ellipsoid with known orientation at a given distance from the reference hard ellipsoid whose position and orientation is known. All the other terms have their usual meaning [2].

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

$$\frac{\beta P_0}{\varrho} = 1 - \tfrac{1}{6} \beta \varrho \int d\bar{r}_{12} \int f(\Omega_1) d\Omega_1 \int f(\Omega_2) d\Omega_2$$

$$\times [\bar{r}_{12} \nabla U_0(\bar{r}_{12}, \Omega_{12})] g^{(0)}(\bar{r}_{12}, \Omega_1, \Omega_2). \tag{5}$$

Here the operator ∇ acts only on the $\hat{r}_{12}$ coordinates of $U_0(\bar{r}_{12}, \Omega_{12})$. The hard ellipsoid potential U_0 satisfies the relation

$$U_0(\bar{r}_{12}, \Omega_{12}) = U_0[\bar{r}_{12}/D(\Omega_{12})]$$

$$= U_0(r_{12}^*) = \begin{cases} \infty & \text{for} \quad r_{12}^* < 1, \\ 0 & \text{for} \quad r_{12}^* > 1, \end{cases} \tag{6}$$

where $D(\Omega_{12})$ $[\equiv D(\bar{r}_{12}, \Omega_1, \Omega_2)]$ is the distance of closest approach of two molecules with relative orientation Ω_{12}; $r_{12}^* = |\bar{r}_{12}|/D(\Omega_{12})$. It is pertinent to mention here that equation (5) involves the hard ellipsoid's pair correlation function (PCF), $g^{(0)}$. In general a detailed knowledge of PCF as a function of $r_{12}, \Omega_1, \Omega_2$ (in total five scalars: $r_{12}, \bar{r}_{12} \cdot \Omega_1, \bar{r}_{12} \cdot \Omega_2, \Omega_1 \cdot \Omega_2$ and $\Omega_1 \times \Omega_2 \cdot \bar{r}_{12}$) is needed for evaluating equation (5). However, in our present development we need to know only $\tilde{g}^0(\bar{r}_{12}, \Omega_{12})$ which is defined as

$$\tilde{g}^0(\bar{r}_{12}, \Omega_{12}) = \int d\hat{r}_{12} g^{(0)}(\bar{r}_{12}, \Omega_1, \Omega_2), \tag{7}$$

where $\hat{r}_{12}$ is unit vector along the axis joining the centres of the two ellipsoids. The integration in (7) is performed by keeping the relative orientation Ω_{12} between the two molecules fixed. Unfortunately, we know very little about $g^0(\bar{r}_{12}, \Omega_1, \Omega_2)$ and, therefore, about $\tilde{g}^0(\bar{r}_{12}, \Omega_{12})$. Following Parson [4] we, therefore, assume that $\tilde{g}^0(\bar{r}_{12}, \Omega_{12})$ can be approximated by $g^0[\bar{r}_{12}/D(\Omega_{12})]$ which decouples the orientational degrees of freedom from the translational ones to all orders in the density, i.e.

$$\tilde{g}^0(\bar{r}_{12}, \Omega_{12}) = g^0[r_{12}/D(\Omega_{12})]$$

$$= g_{HS}^0(r_{12}^*), \tag{8}$$

Using equation (7), we get

$$\frac{\beta P_0}{\varrho} = 1 + \tfrac{1}{2}\varrho g_{HS}(1) \int f(\Omega_1)d\Omega_1 \int f(\Omega_2)d\Omega_2 V_{exc}(\Omega_{12}), \tag{9}$$

where $V_{exc}(\Omega_{12})$ is the excluded volume, or co-volume, between the two ellipsoids of revolution

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

$$= 8V_0(1 - \chi^2)^{-1/2}(1 - \chi^2\cos^2\theta_{12})^{1/2}, \tag{10}$$

$g_{HS}(1)$ is the value of the hard sphere radial distribution at contact, V_0 the volume of a molecule, and

$$\chi = \frac{x^2 - 1}{x^2 + 1}.$$

Equation (9) now reduces to

$$\frac{\beta P_0}{\varrho} = 1 + \frac{2\eta(2 - \eta)}{(1 - \eta)^3}[F_0(\chi) - F_2(\chi)S_2^2], \tag{11}$$

where

$$\eta = \varrho V_0, \left. \begin{array}{c} \\ \end{array} \right\}$$

$$S_n = \int f(\Omega) d\Omega P_n (\cos \theta), \qquad (12)$$

$$F_0(\chi) = (1 - \chi^2)^{-1/2} [1 - \tfrac{1}{6}\chi^2 - \tfrac{1}{40}\chi^4 - \tfrac{1}{112}\chi^6 \cdots], \qquad (13)$$

$$F_2(\chi) = \tfrac{1}{3}\chi^2 (1 - \chi^2)^{-1/2} [1 + \tfrac{3}{14}\chi^2 + \tfrac{5}{56}\chi^4 + \tfrac{25}{528}\chi^6 + \ldots]. \qquad (14)$$

The Helmholtz free-energy per particle for the reference system can now be written as

$$\frac{\beta A_0}{N} = (\ln \varrho - 1) + \langle \ln [4\pi f(\Omega)] \rangle + \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} [F_0(\chi) - F_2(\chi)S_2^2]. \qquad (15)$$

The angular bracket $\langle \ \rangle$ denotes the ensemble average over the $N - 1$ particles of the system.

The Helmholtz free-energy in the first-order perturbation is given by

$$\frac{\beta A^{(1)}}{N} = \beta \int d\Omega_1 f(\Omega_1) \psi^{(1)}(\Omega_1), \qquad (16)$$

where

$$\psi^{(1)}(\Omega_1) = \tfrac{1}{2}\varrho \int d\Omega_2 f(\Omega_2) \int d\bar{r}_{12} U_P(\bar{r}_{12}, \Omega_1, \Omega_2) \tilde{g}^{(0)}(\bar{r}_{12}, \Omega_{12}). \qquad (17)$$

We approximate the perturbation potential by the relation

$$U_p(\bar{r}_{12}, \Omega_1, \Omega_2) = -r_{12}^{-6} [C_{id} + C_{ad} P_2 (\cos \theta_{12})]$$
$$- r_{12}^{-5} C_{aq} P_2 (\cos \theta_{12}) \quad \text{for} \quad r_{12} > D(\Omega_{12}), \qquad (18)$$

where C_{id} and C_{ad} are constants related with the isotropic and anisotropic dispersion interactions and C_{aq} represents the anisotropic quadrupole interaction strength. θ_{12} is the angle between the orientation of two molecules.

Reducing the distance variables in equation (17) with $D(\Omega_{12})$ and taking the Berne and Pechukas [5] expression for $D(\bar{r}_{12}, \Omega_{12})$,

$$D(\bar{r}_{12}, \Omega_{12}) = D_0 \left[1 - \chi \frac{(\hat{r}_{12} \cdot \hat{e}_1) + (\hat{r}_{12} \cdot \hat{e}_2) - 2\chi(\hat{r}_{12} \cdot \hat{e}_1)(\hat{r}_{12} \cdot \hat{e}_2)(\hat{e}_1 \cdot \hat{e}_2)}{1 - \chi^2(\tilde{e}_1 \cdot \tilde{e}_2)^2} \right]^{-1/2} \qquad (19)$$

where $D_0 = 2b$. We obtain the following expression for the effective one-body potential

$$\psi^{(1)}(\cos \theta_1) = -\phi_0 - \phi_2 S_2 P_2 (\cos \theta_1) - \phi_4 S_4 P_4 (\cos \theta_1) \qquad (20)$$

where

$$\phi_0 = LC_{id}^* N_0 + \tfrac{1}{5} M C_{aq}^* A_0^{(5)}, \qquad (21)$$

$$\phi_2 = LC_{id}^* N_2 + M C_{aq}^* Q_2, \qquad (22)$$

$$\phi_4 = LC_{id}^* N_4 + M C_{aq}^* Q_4, \qquad (23)$$

with

$$L = \left(\frac{\pi x}{12}\right)\eta I_6(\eta),$$

$$M = \frac{1}{2}\left(\frac{\pi x}{6}\right)^{2/3}\eta I_5(\eta),$$

$$N_0 = A_0^{(6)} + \frac{1}{5}\left(\frac{C_{ad}^*}{C_{id}^*}\right)A_2^{(6)},$$

$$N_2 = A_2^{(6)} + [A_0^{(6)} + \tfrac{2}{7}(A_2^{(6)})]\frac{C_{ad}^*}{C_{id}^*},$$

$$N_4 = A_4^{(6)} + [\tfrac{18}{35}A_2(6) + \tfrac{20}{77}A_4^{(6)}]\frac{C_{ad}^*}{C_{id}^*},$$

$$Q_2 = A_0^{(5)} + \tfrac{2}{7}(A_2^{(5)} + A_4^{(5)}),$$

$$Q_4 = \tfrac{18}{35}A_2^{(5)} + \tfrac{20}{77}A_4^{(5)},$$

$$C_{id}^* = C_{id}/V_0^2,$$

$$C_{ad}^* = C_{ad}/V_0^2,$$

$$C_{aq}^* = C_{aq}/V_0^{5/3}.$$

In equation (19) $\hat{e}_1$ and $\hat{e}_2$ are the unit vectors along the symmetry axes of two interacting ellipsoids. $A_0^{(n)}$, $A_2^{(n)}$ and $A_4^{(n)}$ (with $n = 5$ and 6) are constants appearing in the integral

$$I_n(\theta_{12}) = \int\frac{dr_{12}}{D^{n-3}(\Omega_{12})}.$$

We have evaluated this integral for fixed relative orientation $\hat{e}_1 \cdot \hat{e}_2 = \cos\theta_{12}$ and present our results in the following form

$$I_n(\theta_{12}) = \frac{1}{D_0^{n-3}}[A_0^{(n)} + A_2^{(n)}P_2\cos\theta_{12}) + A_4^{(n)}p_4(\cos\theta_{12}) + \ldots]. \qquad (24)$$

The values of constants $A_m^{(n)}$ ($m = 0, 2$ and $4, n = 5$ and 6) are evaluated as a function of x for a system of oblate ellipsoids ($x < 1.0$). These values are listed in table 1 and 2.

Table 1. The values of constants of equation (24) for the potential model of equation (18) with $C_{aq} = 0$ representing the dispersion interaction as function of length-to-width ratio x.

x	$A_0^{(6)}$	$A_2^{(6)}$	$A_4^{(6)}$	$A_6^{(6)}$	$A_8^{(6)}$	$A_{10}^{(6)}$	$A_{12}^{(6)}$
0·9	13·9717	0·1184	0·0006	0·0000	0·0000	0·0000	0·0000
0·8	15·7478	0·6205	0·0131	0·0002	0·0000	0·0000	0·0000
0·7	18·0497	1·8736	0·0999	0·0044	0·0002	0·0000	0·0000
0·6	21·1335	4·6049	0·4951	0·0438	0·0035	0·0003	0·0000
0·5	25·4555	10·3348	1·9851	0·3129	0·0450	0·0062	0·0008
0·4	31·9220	22·5211	7·1916	1·8787	0·4465	0·1061	0·0246
0·3	42·6367	50·1284	25·4296	10·5063	3·9442	1·6081	0·5904
0·2	63·8539	122·0767	95·4817	60·5488	35·5568	26·6541	14·2940
0·1	126·3784	390·2147	470·7925	476·2758	490·8973	731·2206	540·3548

Table 2.   The values of constants of equation (24) for the potential model of equation (18) with $C_{ad} = 0$ representing the isotropic dispersion and anisotropic quadrupole interaction as function of length-to-width ratio x.

x	$A_0^{(5)}$	$A_2^{(5)}$	$A_4^{(5)}$	$A_6^{(5)}$	$A_8^{(5)}$	$A_{10}^{(5)}$	$A_{12}^{(5)}$
0·9	13·4800	0·0686	0·0003	0·0000	0·0000	0·0000	0·0000
0·8	14·5743	0·3423	0·0058	0·0001	0·0000	0·0000	0·0000
0·7	15·9067	0·9760	0·0417	0·0016	0·0000	0·0000	0·0000
0·6	17·5621	2·2426	0·1925	0·0146	0·0010	0·0000	0·0000
0·5	19·6738	4·6400	0·7092	0·0957	0·0122	0·0015	0·0002
0·4	22·4657	9·1272	2·3116	0·5159	0·1088	0·0233	0·0050
0·3	26·3565	17·7095	7·1071	2·5063	0·8343	0·3029	0·1029
0·2	32·2732	35·1835	21·7728	11·7845	6·0938	3·9812	2·0031
0·1	43·0455	76·8215	73·0866	61·9298	54·4075	70·8097	47·1559

The integrals $I_5(\eta)$ and $I_6(\eta)$ as defined by the relation

$$I_n(\varrho, T) \;=\; \int dr_{12}^* r_{12}^{*2-n} g_{HS}^{(0)}(r_{12}^*) \tag{25}$$

are approximated from the series proposed by Larsen *et al.* [6]

$$I_n(\varrho^*) \;=\; J_{0,n} + J_{1,n}\varrho^* + J_{2,n}\varrho^{*2} + J_{3,n}\varrho^{*3} + J_{4,n}\varrho^{*4} + J_{5,n}\varrho^{*5}, \tag{26}$$

where

$$\varrho^* \;=\; \frac{6}{\pi} V_0.$$

The coefficients $J_{m,n}$s are listed by Larsen *et al.* [6] for several value of n $(= 0$ to 24).

The values of ϕ_0, ϕ_2 and ϕ_4 are given in table 3 for $x = 0.9, 0.8, 0.7$ and 0.6. We see from the table that the average contribution of ϕ_2 and ϕ_4 increases as x decreases.

Table 3.   The values of functions ϕ_0^*, ϕ_2^*, ϕ_4^* and ϕ_4^*/ϕ_2^* (as defined in equation (20)) as function of packing fraction η and length-to-width ratio x for the dispersion interaction (equation (18) with $C_{aq} = 0$) with $C_{id}^*/C_{ad}^* = 8$, $\phi_n^* = \phi_n/C_{id}^*$.

x	η	ϕ_0^*	ϕ_2^*	ϕ_4^*	ϕ_4^*/ϕ_2^*
0·9	0·4	0·7187	0·0961	0·0004	0·0438
	0·5	1·0063	0·1346	0·0006	0·0438
	0·6	1·3446	0·1798	0·0008	0·0438
	0·7	1·7329	0·2318	0·0010	0·0438
0·8	0·4	0·7206	0·1194	0·0024	0·0204
	0·5	1·0090	0·1672	0·0034	0·0204
	0·6	1·3482	0·2233	0·0045	0·0204
	0·7	1·7375	0·2879	0·0059	0·0204
0·7	0·4	0·7239	0·1680	0·0089	0·0532
	0·5	1·0136	0·2352	0·0125	0·0532
	0·6	1·3543	0·3143	0·0167	0·0532
	0·7	1·7454	0·4051	0·0216	0·0532
0·6	0·4	0·7285	0·2547	0·0276	0·1086
	0·5	1·0201	0·3566	0·0387	0·1086
	0·6	1·3630	0·4765	0·0518	0·1086
	0·7	1·7566	0·6141	0·0667	0·1086

Table 4. The values of functions ϕ_0^*, ϕ_2^*, ϕ_4^* and ϕ_4^*/ϕ_2^* (as defined in equation (20)) as function of packing fraction η and length to width ratio x for the isotropic dispersion and anisotropic quadrupole interactions (equation (18) with $C_{ad} = 0$) with $C_{id}^*/C_{aq}^* = 8$, $\phi_n^* = \phi_n/C_{id}^*$.

x	η	ϕ_0^*	ϕ_2^*	ϕ_4^*	ϕ_4^*/ϕ_2^*
0·9	0·4	0·7187	0·1537	0·0004	0·0027
	0·5	1·0063	0·2088	0·0006	0·0027
	0·6	1·3346	0·2708	0·0007	0·0027
	0·7	1·7329	0·3392	0·0009	0·0027
0·8	0·4	0·7206	0·1767	0·0024	0·0135
	0·5	1·0089	0·2409	0·0032	0·0135
	0·6	1·3481	0·3138	0·0043	0·0135
	0·7	1·7373	0·3945	0·0054	0·0135
0·7	0·4	0·7238	0·2248	0·0087	0·0388
	0·5	1·0134	0·3082	0·0120	0·0388
	0·6	1·3539	0·4035	0·0158	0·0388
	0·7	1·7448	0·5101	0·0201	0·0388
0·6	0·4	0·7283	0·3103	0·0270	0·0870
	0·5	1·0197	0·4278	0·0374	0·0870
	0·6	1·3622	0·5631	0·0494	0·0870
	0·7	1·7753	0·7157	0·0630	0·0870

The contribution of ϕ_4 is about 4 per cent of that from ϕ_2 for $x = 0·9$ and about 10 per cent for $x = 0·6$. Thus the contribution of ϕ_4 for $x \leqslant 0·6$ is substantial and cannot be neglected. A similar conclusion can also be drawn from table 4. The variations of ϕ_2^* and ϕ_4^* as a function of V^*, where $\phi_n^* = \phi_n/C_{id}^*$ and $V^* = I/\varrho^*$, are shown in figures 1 and 2 for several values of x. A linear volume dependence of ϕ_2 and ϕ_4 are seen. Similar dependences have been seen [2, 3] in case of prolate ellipsoids. In the present work we limit ourselves to the case $x \leqslant 0·6$ and approximate the effective one-body orientational protential $\psi(\Omega)$ by the first two terms of equation (20)

$$\psi(\Omega) = -\phi_0 - \phi_2 S P_2(\cos\theta_1). \tag{27}$$

Here and onward we drop the subscript 2 from S_2. Equation (16) for $x \leqslant 0·6$ now becomes

$$\frac{\beta A^{(1)}}{N} = -\beta\phi_0 - \beta\phi_2 S^2. \tag{28}$$

The excess configurational Helmholtz free-energy can be written as

$$\frac{\beta A}{N} = \langle \ln[4\pi f(\Omega)] \rangle + C_2 - B_2 S^2, \tag{29}$$

where

$$C_2 = \ln\varrho - 1 + \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} F_0(\chi) - \beta\phi_0 \tag{30}$$

and

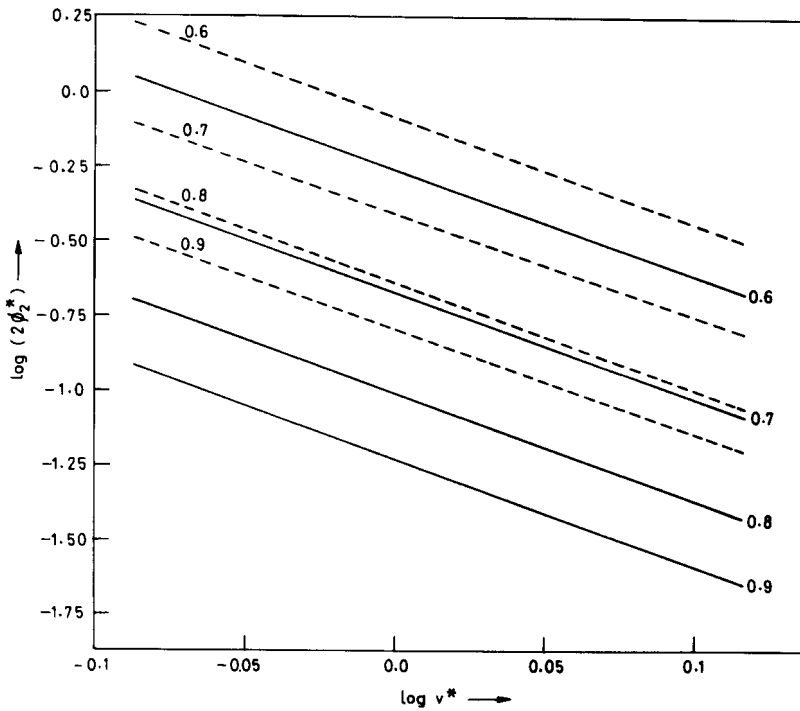$$B_2 = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} F_2(\chi) + \beta\phi_2. \tag{31}$$

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Figure 1. The volume dependence of the interaction parameter ψ_2^* for the effective one-body orientational potential for $C_{id}^*/C_{aq}^* = 8$. The number on the curve indicates x. Solid and dashed lines represent potential models given by equation (18) with $C_{aq} = 0$ and $C_{ad} = 0$ respectively.
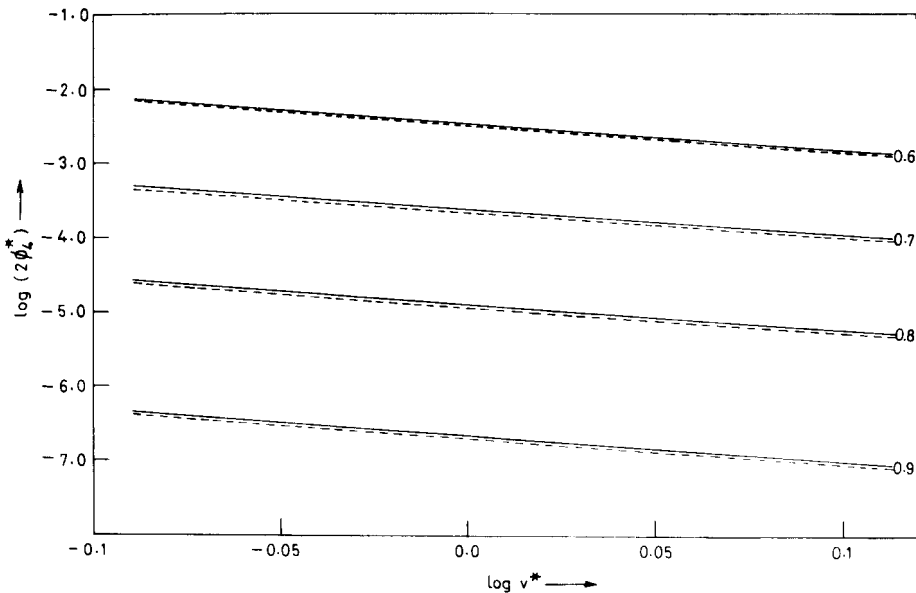

Figure 2. The volume dependence of the interaction parameter ϕ_4^* for the effective one-body orientational potential for $C_{id}^*/C_{aq}^* = 8$. The number on the curve indicates x. Solid and dashed lines represent potential models given by equation (18) with $C_{aq} = 0$ and $C_{ad} = 0$ respectively.

The minimization of the free-energy with respect to the variation of $f(\Omega)$, subject to the constraint

$$\int f(\Omega)d\Omega = 1 \tag{32}$$

determines the one-particle orientational distribution at a fixed temperature and pressure. From equation (29) and (32), $f(\Omega)$ can be written as

$$f(\Omega) = \frac{\exp\left[2B_2 S P_2(\cos\theta)\right]}{\int \exp\left[2B_2 S P_2(\cos\theta)\right]d\Omega}, \tag{33}$$

which leads to an equation for the lowest order parameter

$$S = \frac{\int \exp\left[2B_2 S P_2(\cos\theta)\right]P_2(\cos\theta)d\Omega}{\int \exp\left[2B_2 S P_2(\cos\theta)\right]d\Omega}. \tag{34}$$

The discotic nematic–isotropic (DNI) transition at constant pressure is located by equating the pressure and chemical potentials of the two phases

$$\left.\begin{aligned} p_{\text{nem}}(\eta_{nc}, T_c, S_c) &= p_{\text{iso}}(\eta_{ic}, T_c), \\ \mu_{\text{nem}}(\eta_{nc}, T_c, S_c) &= \mu_{\text{iso}}(\eta_{ic}, T_c). \end{aligned}\right\} \tag{35}$$

S_c is determined from equation (34). If we keep the pressure fixed, we get four equations involving four unknowns η_{nc}, η_{ic}, T_c and S_c. These unknowns can be determined by solving simultaneoulsy equations (34) and (35), with p_{iso} = fixed pressure.

3. Results and discussions

We investigate first the effects of length-to-width ratio x and potential parameters C_{id}, C_{ad} and C_{aq} as defined in equation (18) on the thermodynamic properties of nematic–isotropic phase transition of ordinary nematic as well as discotic nematic phases. Numerical calculations are done for two model potentials. The first model assumes $C_{aq} = 0$ in equation (18) whereas the second puts $C_{ad} = 0$. These choices enable us to investigate separately the effect of anisotropic dispersion and quadrupole interactions on the NI transition properties. The method and details of calculation are similar to that described by Singh and Singh [2, 3]. We compare the results obtained for these two model potentials.

The calculation has been made for systems of ellipsoids (prolate $x > 1$; oblate $x < 1$) by retaining up to the S_2 term only in equation (20). For a given x the potential parameters are selected so as to reproduce quantitatively the NI transition temperature $T_c \simeq 409\,\text{K}$ (for the ordinary nematic phase) and $\simeq 600\,\text{K}$ (for the discotic nematic phase). These values correspond, respectively, to the T_c of PAA (ordinary nematic) and hexa-η-hexyloxy benzoate of triphenylene (discotic phase). Other transition parameters are determined self consistently by an iterative procedure. However, the potential parameters can also be estimated from the latent heat of vaporization which is an experimentally measurable quantity. For PAA the value of C_{id} is $\simeq 1$–$2.5 \times 10^{-56}\,\text{erg}\,\text{cm}^6$.
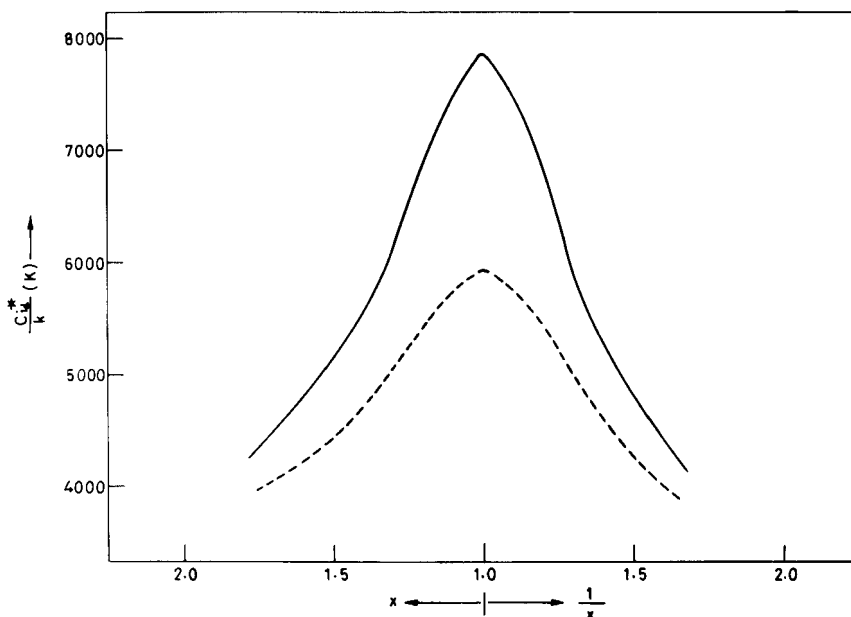
Figure 3.   Variation of C_{id}^*/k as a function of x (for prolate) and $1/x$ (for oblate) with $C_{id}^*/C_{ad}^* = 8\cdot0$. Solid and dashed lines are for dispersion and quadrupolar.

The variation of the interaction strength C_{id}^*/k as a function of x is plotted in figure 3. Figure 4 is a plot of packing fraction, order parameter and the relative change in density at the transition as a function of x. We see from the figure 3 that C_{id}^*/k takes a maximum value for $x = 1\cdot0$ and decreases on either side as the shape anisotropy increases. Further, as shown by figure 4 all the transition properties vary smoothly around $x \simeq 1\cdot0$; the packing fraction is maximum whereas the order parameter and relative change in density at the transition are minimum.

Figure 5 shows the variation of T_c with C_{id}^*/k for discotic nematic phase. In table 5 we list a number of transition properties at the discotic nematic–isotropic transition. In this table the parameter Γ is a measure of the relative sensitivity of the order parameter to volume change (at constant temperature) and temperature change (at constant volume). It is defined as

$$\Gamma = \frac{V}{T}\frac{(\partial s/\partial v)_T}{(\partial s/\partial T)_v} = -\left(\frac{\partial \ln T}{\partial \ln v}\right)_s = \left(\frac{\partial \ln T}{\partial \ln \varrho}\right)_s. \tag{36}$$

The pressure dependence of the transition temperature (dT/dp) is obtained by Clausius–Clapeyron's law. $\Delta\Sigma/Nk$ is a measure of the change in entropies at the transition. It can be observed from figure 4 and table 5 that, as physically expected for both the model potentials, the phase transition is shifted with increasing x to higher temperature with higher value of density and C_{id}^*/k but lower values of order parameter, relative change in density, entropy change, (dT_c/dp) and Γ. From numerical calculations we have also observed that the transition properties are not very sensitive to the ratio C_{id}^*/C_{ad}^*(or C_{id}^*/C_{aq}^*) if it is greater than 20. This is in accordance with the observation of Gelbart and Baron [7]. A comparison of the results in table 5 for both potential models shows that for a given x the quadrupole interaction leads to the smaller values for C_{id}^*/k, the packing fraction and Γ, whereas the values of
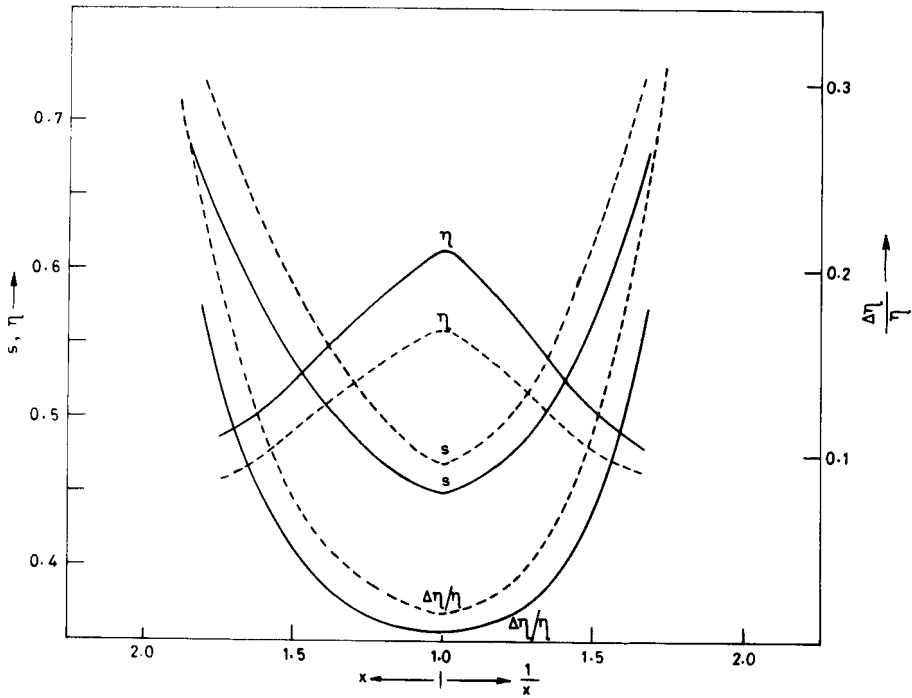
Figure 4. Order parameters S, packing fraction η (Discotic nematic phase) and change in density as a function of x and $1/x$ for given $C_{id}^{*}/k = 6000\,\mathrm{K}$. Line symbols are same as in figure 1.
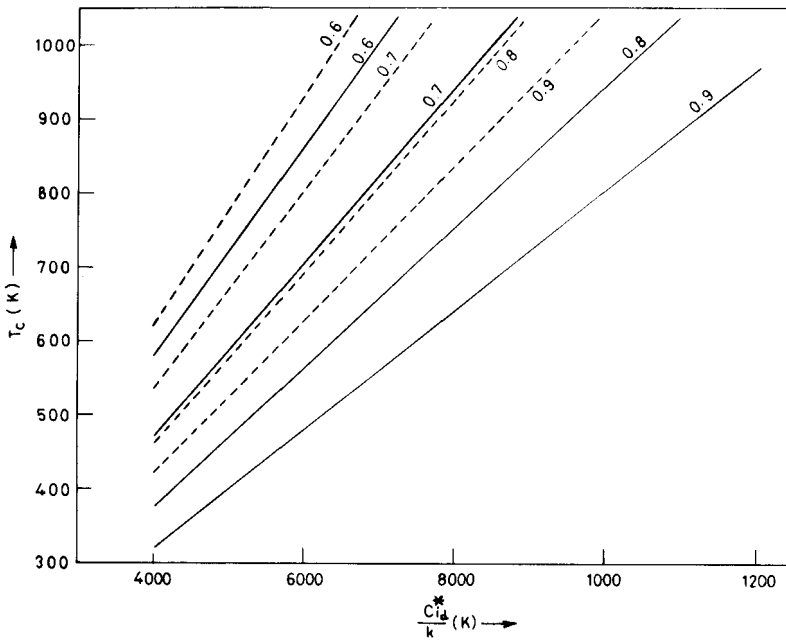

Figure 5. Variation of T_{c}^{*} as a function of C_{id}^{*}/k. Line symbols are the same as in figure 1.

Table 5. The discotic nematic–isotropic transition parameters for a system having disc type molecules. S_c is the order parameter, $\bar{\eta} = \frac{1}{2}(\eta + \eta_i)$, η and η_i are the discotic nematic and isotropic packing fractions, $(\Delta\Sigma/Nk)$ the transition entropy and $\Gamma(T_c)$ is defined in equation (36). The model parameters are chosen so as to reproduce the transition temperature $T_c \simeq 600\,\mathrm{K}$, with C_{id}^*/C_{ad}^* or $C_{il}/C_{aq}^* = 8$.

Potential model	x	$\dfrac{C_{id}^*}{k}$	$\bar{\eta}$	$\dfrac{\Delta\eta}{\eta}$	S_c	$\dfrac{\Delta\Sigma}{Nk}$	$\left(\dfrac{dT_c}{dp}\right)_{p=1\,\mathrm{bar}}$	$\Gamma(T_c)$
(1) Equation (18) with	0·9	7453·72	0·601	0·0092	0·458	0·727	35·33	1·67
$C_{aq} = 0$	0·8	6355·43	0·567	0·0163	0·479	0·845	57·28	1·76
	0·7	5110·07	0·509	0·0444	0·541	1·254	118·57	1·85
	0·6	4146·93	0·436	0·1797	0·686	2·784	273·74	1·93
(2) Equation (18) with	0·9	5733·82	0·544	0·0195	0·480	0·870	69·31	1·46
$C_{ad} = 0$	0·8	5191·85	0·512	0·0323	0·508	1·053	100·55	1·54
	0·7	4490·41	0·470	0·0812	0·587	1·665	180·33	1·66
	0·6	3870·39	0·397	0·3150	0·732	3·896	418·09	1·80

$\Delta\eta/\eta$, S, $\Delta\Sigma/Nk$ and dT_c/dp go up in comparison with the anisotropic dispersion interaction. Further, it can be seen that overall the discontinuity in transition properties is more pronounced for the anisotropic quadrupole interaction as compared to anisotropic dispersion interaction. A similar trend has been observed [2, 3] in the case of ordinary nematic phases also.

Figure 6 shows the variation of order parameter S with temperature at constant pressure ($p = 1$ bar). The theoretical result is not compared with experimental
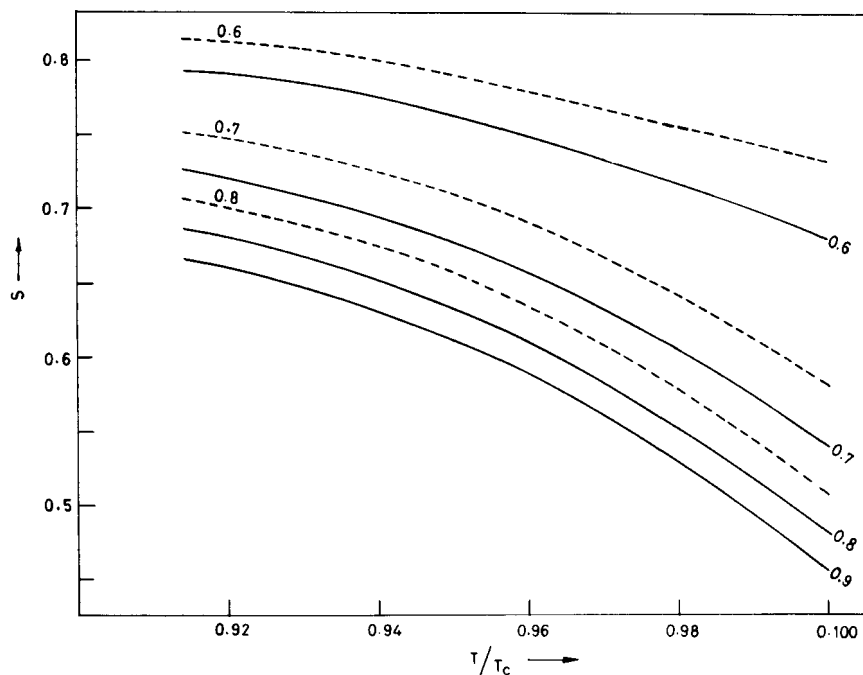

Figure 6. Temperature variation of the long-range orientational order parameters at constant pressure. C_{id}^*/k are chosen so as to reproduce nematic–isotropic transition temperature ($T_c = 409\,\mathrm{K}$ for ordinary nematic and $T_c = 600\,\mathrm{K}$ for discotic nematic). Line symbols are the same as figure 1.

data because such data are not available in the literature for the isotropic–discotic transition.

In conclusion, our calculation demonstrates remarkable symmetry between phase transition properties of rod like molecules (ordinary nematic) and disc-like molecules (discotic nematic) which is in agreement with Monte Carlo simulation of Frenkel and McTague [8] and with the result of Savithramma and Madhusudana [9]. This we physically expect because in ordinary nematics, the role of the director is played by the average orientation of the long axes of molecules while in the nematics consisting of discotic molecules, the director is the normal to the plane of the predominant orientation of molecules. Also, discotic nematic phase having symmetry, $D_{\infty h} \times T(3)$ is the analogue of the ordinary nematic phase. It is distinguished from nematic liquid crystals formed by rod shaped molecules only by indications of the anisotropy of the dielectric permittivity and other tensor characteristics. We have used the decoupling approximation to investigate the isotropic discotic nematic transition properties which introduces anisotropy in pair correlation function and is exact at very low density. It cannot be exact at liquid densities. It is easy to see that the decoupling approximation over emphasizes the anisotropy in PCF for parallel configurations and under estimates that for perpendicular configurations. However, the decoupling approximation has been found to yield the values of the compressibility factor in very good agreement with computer simulation results [8, 10]. Quantitative agreement between theory and experiment cannot be expected because the model system crudely simulates real system but the result of the simple approach described in this paper is hoped to provide a beginning molecular basis for the thermodynamics of discotic nematic liquid crystals.

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