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

The effect of pressure on the discotic nematic-isotropic transition properties

T. K. Lahiri[a]; S. Singh[a]; K. Singh[b]
[a] Department of Physics, Banaras Hindu University, Varanasi, India [b] Department of Physics and Electronics, Awadh University, Faizabad, India

To cite this Article Lahiri, T. K. , Singh, S. and Singh, K.(1990) 'The effect of pressure on the discotic nematic-isotropic transition properties', Liquid Crystals, 7: 3, 395 — 398

To link to this Article: DOI: 10.1080/02678299008033815

URL: http://dx.doi.org/10.1080/02678299008033815

LIQUID CRYSTALS, 1990, VOL. 7, NO. 3, 395–398

The effect of pressure on the discotic nematic–isotropic transition properties

by T. K. LAHIRI and S. SINGH

Department of Physics, Banaras Hindu University, Varanasi-221005, India

K. SINGH

Department of Physics and Electronics, Awadh University, Faizabad, India

(*Received 13th July 1989; accepted 31 October 1989*)

We study the influence of pressure on the stability, ordering and thermodynamic properties of the discotic nematic–isotropic transition. In the present calculation we include both the second and fourth Legendre polynomial order parameters in the evaluation of the angle-dependent term in the expression of the excluded volume and the perturbation term.

Recently we applied [1], (referred to as I), a perturbation expansion method [2] to examine the relationship between the intermolecular forces and the thermodynamic and orientational properties of the discotic nematic–isotropic (DNI) phase transition [3] as revealed by the second Legendre polynomial order parameter values obtained from theory. In the present paper, we consider an investigation similar to that of I to analyse the thermodynamic and orientational phase transition behaviours under pressure. In addition, the present calculation includes both second and fourth Legendre polynomial order parameters in the evaluation of the angle-dependent term in the expression for the excluded volume and the perturbation term.

We consider a system of N-axially symmetric discotic molecules contained in a volume V_0 at temperature T. Assuming that the total interaction potential can be written as the sum of pair interactions and adopting the procedure as outlined in I, the total Helmholtz free-energy of the system is written as

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

where A_0 is the contribution of reference system and $A^{(t)}$ represents the perturbation terms arising from the attractive potential. Here it has been assumed that the molecules interact via a pair potential which has a reference hard part and an attractive part, and that the former is described by the repulsion between the hard ellipsoids of revolution parameterized by the length-to-width ratio x $(=2a/2b)$. The perturbation potential, which is a function only of centre of mass distance r_{12} and the relative orientation Ω_{12} between two molecules, is written as

$$U_p(r_{12}, \Omega_{12}) = -r_{12}^{-6}(C_i + C_a P_2(\cos\theta_{12})); \quad \text{for} \quad r_{12} > D(\Omega_{12}). \tag{2}$$

Here C_i and C_a are constants related to the isotropic and anisotropic dispersion interactions, θ_{12} is the angle between the symmetry axes of two molecules and $D(\Omega_{12})$ is the distance of closest approach of two molecules having relative orientation Ω_{12}.

0267-8292/90 $3.00 © 1990 Taylor & Francis Ltd

Following Parson [4] we approximate the reference system pair correlation function $g^0(r_{12},\Omega_{12})$ by $g^0(r_{12}/D(\Omega_{12}))$, which decouples the orientational degrees of freedom from the translational ones to all orders in density, and obtain, in the first-order perturbation,

$$\frac{\beta A_0}{N} = \ln\rho - 1 + \ln\langle 4\pi f(\Omega)\rangle + \frac{\eta(4-3\eta)}{(1-v)^2}\left(F_0(\chi) - F_2(\chi)\bar{P}_2^2 - F_4(\chi)\bar{P}_4^2\right) \tag{3}$$

and

$$\frac{\beta A^{(1)}}{N} = \beta(-\phi_0 - \phi_2\bar{P}_2^2 - \phi_4\bar{P}_4^2), \tag{4}$$

where

$$\eta = \rho v_0, \tag{4a}$$

$$\bar{P}_n = \int d\Omega f(\Omega)P_n(\cos\theta), \tag{4b}$$

$$F_0(\chi) = (1-\chi^2)^{-1/2}(1 - \tfrac{1}{6}\chi^2 - \tfrac{1}{40}\chi^4 - \tfrac{1}{112}\chi^6 - \cdots), \tag{4c}$$

$$F_2(\chi) = \tfrac{1}{3}\chi^2(1-\chi^2)^{-1/2}(1 + \tfrac{3}{14}\chi^2 + \tfrac{5}{56}\chi^4 + \tfrac{25}{528}\chi^6 + \cdots), \tag{4d}$$

$$F_4(\chi) = \tfrac{1}{35}\chi^4(1-\chi^2)^{-1/2}(1 + \tfrac{15}{22}\chi^2 + \tfrac{525}{1184}\chi^4 + \cdots), \tag{4e}$$

$$\phi_0 = \tfrac{1}{12}\pi\eta I_6(\eta)xC_i^*\left(A_0 + \frac{1}{5}\frac{C_a}{C_i}A_2\right), \tag{4f}$$

$$\phi_2 = \tfrac{1}{12}\pi\eta I_6(\eta)xC_i^*\left[A_2 + (\tfrac{2}{7}A_2 + \tfrac{2}{7}A_4)\frac{C_a}{C_i}\right], \tag{4g}$$

$$\phi_4 = \tfrac{1}{12}\pi\eta I_6(\eta)xC_i^*\left[A_4 + (\tfrac{18}{35}A_2 + \tfrac{20}{77}A_4)\frac{C_a}{C_i}\right], \tag{4h}$$

with

$$C_i^* = C_i/v_0^2, \tag{4i}$$

$$I_6(\eta) = 0{\cdot}333334 + 0{\cdot}429911\eta + 0{\cdot}241818\eta^2 + 0{\cdot}017573\eta^3 + 0{\cdot}090841\eta^4 - 0{\cdot}171067\eta^5, \tag{4j}$$

$$\chi = (x^2-1)/(x^2+1). \tag{4k}$$

A_0, A_2 and A_4 are the constants which are tabulated in I. Expressions for pressure, chemical potential and other thermodynamic properties can be derived from equations (3) and (4) using standard thermodynamic relations. The one particle orientational distribution function $f(\Omega)$ at a specified temperature and pressure is determined by minimizing the free-energy with respect to the variation of $f(\Omega)$ subject to the constraint

$$\int f(\Omega)\,d\Omega = 1.$$

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

Table 1. The DNI transition parameters under high pressure, $\bar{P}_{2c}$ and $\bar{P}_{4c}$ are order parameters; η is the discotic nematic packing fraction, $\Delta\eta/\eta$ the density discontinuity, $\Delta\Sigma/NK$ the transition entropy, $\Gamma(T_c) = (\partial \ln T/\partial \ln \rho)_{\bar{P}_2}$, and (dT_c/dp) is the pressure dependence of the transition temperature T_c. $C_i/C_a = 8$

x	C_i^*/k	P/bar	T_c	η	$\Delta\eta/\eta$	$\bar{P}_{2c}$	$\bar{P}_{4c}$	$\Delta\Sigma/Nk$	(dT_c/dp)	$\Gamma(T_c)$
0·6	4500·00	1	658·4	0·486	0·206	0·7351	0·4021	3·259	274·43	1·951
		100	683·6	0·481	0·146	0·7001	0·3576	2·551	233·62	1·955
		200	705·9	0·480	0·113	0·6719	0·3250	2·137	208·94	1·965
		300	726·2	0·481	0·092	0·6485	0·2999	1·858	190·62	1·978
		400	744·7	0·482	0·078	0·6305	0·2816	1·665	175·76	1·994
		500	761·3	0·485	0·068	0·6189	0·2703	1·539	163·08	2·012
0·8	6500·00	1	614·5	0·571	0·0169	0·4863	0·1565	0·872	57·41	1·763
		100	619·7	0·574	0·0158	0·4866	0·1567	0·858	54·49	1·769
		200	625·0	0·576	0·0149	0·4853	0·1558	0·841	61·93	1·774
		300	629·9	0·578	0·0141	0·4854	0·1559	0·830	49·60	1·779
		400	634·8	0·581	0·0133	0·4837	0·1548	0·814	47·55	1·784
		500	640·0	0·583	0·0124	0·4769	0·1503	0·782	45·80	1·788
0·9	7500·00	1	604·95	0·603	0·0088	0·4485	0·1315	0·695	35·52	1·669
		100	607·11	0·606	0·0089	0·4614	0·1393	0·729	34·02	1·671
		200	612·38	0·607	0·0078	0·4399	0·1264	0·656	33·06	1·672
		300	613·98	0·609	0·0081	0·4572	0·1367	0·704	31·73	1·675
		400	617·03	0·611	0·0078	0·4573	0·1368	0·699	30·69	1·676
		500	619·92	0·613	0·0075	0·4580	0·1373	0·696	29·72	1·678

The DNI transition parameters are determined at various constant values of pressure ranging from 1 bar to 500 bar in a way similar to that described in I. The present work includes both $\bar{P}_2$ and $\bar{P}_4$ terms in equations (3) and (4) whereas in I only the $\bar{P}_2$ term is included. For a given x, at the atmospheric pressure $p = 1$ bar, we selected the potential parameters C_i^*/k and C_i/C_a so as to reproduce quantitatively the DNI transition temperature $T_c \simeq 600$ K which corresponds to the T_c of hexa-η-hexyloxy benzoate of triphenylene. Other transition parameters are determined self-consistently by an iterative procedure [1]. From the numerical results it is observed that in both cases in I, as well as in the present work, the relative density change at the transition decreases as the ratio C_i/C_a increases for a given value of C_i^*/k. A very slow increase in the value of packing fraction η is observed with increasing C_i/C_a. For $C_i/C_a > 20$ the phase transition quantities are not very sensitive to the C_i/C_a. Comparing the results obtained here with the corresponding results obtained in I, we observe for $x \leqslant 0{\cdot}8$ an increase in the value of the packing fraction η, relative density change $\Delta\eta/\eta$, second Legendre polynomial order parameter $\bar{P}_{2c}$, transition entropy and dT_c/dp due to the inclusion of the fourth Legendra polynomial order parameter $\bar{P}_{4c}$. For $x > 0{\cdot}8$ no noticeable change in the transition parameters is seen.

The table summarizes a number of thermodynamic properties at the DNI transition. From the table it can be observed that for a given x and the interaction parameter, the phase transition shifts to higher temperature and the density increases very slightly and the fractional volume change decreases as pressure increases. A decrease in the value of the transition entropy, order parameters and dT_c/dp is found whereas the parameter Γ increases very slightly. A similar variation of the transition properties is observed at a given pressure and with increasing ratio C_i/C_a. We also observed that the range of stability of the discotic nematic phase is considerably larger at constant density as compared to its stability range at constant pressure.

References

[1] Singh, K, Singh, U. P., and Singh, S., 1988, *Liq. Crystals*, **3**, 617.
[2] Singh, S., and Singh, Y., 1982, *Molec. Crystals liq. Crystals*, **87**, 211.
[3] Chandrasekhar, S., Sadashiv, R. K., and Suresh, K. A., 1977, *Pramana* **9**, 471.
[4] Parson, J. D., 1979, *Phys. Rev.* A, **19**, 1225.