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K. Singh [a] & S. Singh [a]
[a] Department of Physics, Banaras Hindu University, Varanasi, 221005, India

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Perturbation Theory for Nematic Liquid Crystals of Axially Symmetric Molecules: Extension of Calculations to High Pressures

K. SINGH AND S. SINGH†
Department of Physics, Banaras Hindu University, Varanasi-221005, India

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We have applied a statistical mechanical perturbation theory to study the thermodynamic properties of nematic liquid crystals under pressure. In this theory the reference potential function is nonspherical and consists of the short range rapidly varying repulsive part of the pair potential. We report calculations on the nematic-isotropic (NI) transition properties for a hard spherocylindrical system superposed with an attractive potential, which is a function of only the centre of mass distance and the relative orientation between the two molecules, and subjected to different external pressures. The interaction arising from dispersion interaction between two asymmetric molecules represents the attractive interaction. The influence of pressure on the stability, ordering and thermodynamic functions for the NI transition is analysed. It is found that the theoretical predictions are in accordance with the experimental observations.

1. INTRODUCTION

The molecular theories of the liquid crystalline phase are best tested by experimental data on basic thermodynamic quantities at and in the vicinity of their phase transitions. Experimental quantities of interest,

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†Present Address: Department of Physics, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

particularly for the first-order phase transitions, are transition temperatures, transition entropy, transition densities and fractional density changes, order parameters, etc. The data which are obtained by measurements under high pressure[1] are of more use for several reasons. Such measurements can generate data on previously mentioned variables along with the information on pressure derivatives, order parameter behaviour at constant volume, and the volume dependence of the mean-field potential. McColl and Shih[2] made the first attempt to measure the second rank orientational order parameter as a function of both temperature and pressure at constant volume in the nematic substance *p*-azoxyanisole (PAA). At a constant molar volume of 221 cm^3 their observed values of the temperature and pressure for nematic–isotropic (NI) transition are, respectively, 437.5 °K and 640 bar. Such determination is of particular importance because it enables comparisons between theoretical predictions and the results of computer simulations which are normally available for systems at constant volume.[3] In addition, how the conformational distributions of the flexible alkyl chains which are expected to change with volume influence the orientational order of the mesogen can be studied.[4] There are also known compounds[1] which at atmospheric pressure do not form liquid crystals but as the pressure is raised they exhibit mesophase. The re-entrant nematic phase was discovered[5] by studying *N*-*n*-octyloxy-4′-cyanobiphenyl as a function of temperature and pressure. Pressure plays an important role in monitoring the character of the phase transition; for example, the smectic A–nematic transition can pass from being first order to second order on increasing the pressure which enables in locating the tricritical point.[6] The Lifshitz point, at which three transitions, smectic C–smectic A, smectic A–nematic and smectic C–nematic coincide, was observed by Shashidhar *et al.*[7] by treating both pressure and temperature as variables.

The recent attempts to study the orientational ordering in liquid crystals at high pressure are that of Horn and Faber[8] in two nematic, Keyes and Daniels[9] in three nematic and one cholesteric and of Emsley *et al.*[10] in one nematic liquid crystals. Pollmann and Scherer[11] investigated the phase transition via P-V-T measurements in cholesteric and smectic liquid crystals. These measurements under pressure have been done on liquid crystals from various homologous series. Transfield and Collings[12] were first to report thermodynamic measurements under pressure for the first six members of the same homologous series of di-alkoxyazoxybenzenes. They have measured the thermodynamic quantities throughout the nematic phase at constant volume as well as constant temperature near the NI phase transition. From the measured data they investigated the role of end chain flexibility in a specific molecular geometry.

Recently, Savithramma and Madhusudana[13] have used the van der Waals approach and scaled particle theory to predict the properties of the NI transition at high pressure from 1 bar to 6.5 kbar. For a spherocylindrical system superposed with an attractive potential represented by isotropic dispersion and anisotropic quadrupole forces, more recently, the influence of pressure on the stability, ordering and thermodynamic functions for the NI transition has been analysed by Singh and Singh.[14]

In a previous publication, Singh and Singh[15] (referred to as I) have developed a statistical mechanical perturbation theory to describe the equilibrium properties of nematic liquid crystals. Basic to this theory is the recognition that the predominant factor in determining the mesophase stability is geometric. Thermodynamic properties were calculated for a trial system composed of molecules interacting via a pair potential having both repulsive and attractive parts. The repulsive interaction was represented by a repulsion between hard spherocylinders. The attractive potential, a function of only the centre of mass distance and the relative orientation between the two molecules, was approximated by the interaction arising from the dispersion interaction between two asymmetric molecules. The relative influence of length to width ratio of molecular hard-core and the anisotropy in their correlation function on the NI transition properties at constant pressure was investigated. It was found that the effects of spatial and orientational pair correlations on the thermodynamic properties are quite large and the properties are extremely sensitive to the values of molecular parameters.

In the present paper, the same type of investigation as that of I has been extended to analyse the thermodynamic and orientational behaviours of nematogens close to NI phase transition under high pressures. In the following section the working equations are summarized. The results and discussions are presented in Sec. 3.

2. WORKING EQUATIONS

We consider a system of N axially symmetric nonspherical nematogenic molecules contained in a volume V at temperature T. Assuming the pairwise additivity of the interaction potential and following the statistical mechanical machinery as outlined in I, we write the perturbation series for the Helmholtz free-energy as

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

where A_0 is the reference system contribution to A and

$$\frac{\beta A^{(r)}}{N} = \beta \int f(\Omega_p)\, d\Omega_p \psi^{(r)}(\Omega_p) \tag{2}$$

represents the perturbation terms, r denotes the order of perturbation and $\psi(\Omega_p)$ is defined as the effective one-body orientational perturbation potential by the relation

$$\psi^{(r)}(\Omega_p) = \frac{1}{2r}\rho \int d\Omega_{p'} f(\Omega_{p'}) \int d\bar{r}\, u_p(\bar{r}, \Omega_p, \Omega_{p'}) \times g^{(r-1)}(\bar{r}, \Omega_p, \Omega_{p'}) \tag{3}$$

The zeroth order terms refer to quantities corresponding to the reference system and all the other symbols have their usual meaning.[15]

In order to calculate the thermodynamic properties of a system of hard spherocylinders interacting via the pair potential $u_0(\bar{r}_{12}, \Omega_{12})$ which satisfy the relation:

$$\begin{aligned} u_0(\bar{r}_{12}, \Omega_{12}) &= u_0[\bar{r}_{12}/D(\hat{\gamma}_{12}, \Omega_{12})] \\ &= u_0(r_{12}^*) = \begin{matrix} \infty & \text{for } r_{12}^* < 1 \\ 0 & \text{for } r_{12}^* > 1 \end{matrix} \end{aligned} \tag{4}$$

where $D(\hat{\gamma}_{12}, \Omega_{12})$ is the distance of closest approach of two molecules having relative orientations Ω_{12}, $\hat{r}_{12} = \bar{r}_{12}/|\bar{r}_{12}|$, we use the decoupling approximation[16] which decouples the orientational degrees of freedom from the translational ones and derive the relation

$$\frac{\beta A_0}{N} = (\ln \rho - 1) + \langle \ln[4\pi f(\Omega)] \rangle + \frac{\eta(4 - 3\eta)}{(1 - \eta)^2}[F_1(\chi) - F_2(\chi)S^2] \tag{5}$$

where

$$\eta = \rho V_0$$

$$F_1(\chi) = (1-\chi^2)^{-1/2}(1 - \tfrac{1}{6}\chi^2 - \tfrac{1}{40}\chi^4 - \tfrac{1}{112}\chi^6 - \cdots) \qquad (6)$$

$$F_2(\chi) = \tfrac{1}{3}\chi^2(1-\chi^2)^{-1/2}(1 + \tfrac{3}{14}\chi^2 + \tfrac{5}{56}\chi^4 + \cdots) \qquad (7)$$

with

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

V_0 is the volume of a molecule and x the length-to-width ratio of a hard spherocylinder. The first two terms of Eq. (5) represent the free-energy of a gas of non-interacting rods and the last term is the excess free-energy which arises due to the interparticle interaction. The angular bracket $\langle \ldots \rangle$ denotes the ensemble average over the $N - 1$ particles of the system.

The Helmholtz free-energy in the first-order perturbation is written as

$$\frac{\beta A^{(1)}}{N} = \beta \int d\Omega_1 f(\Omega_1) \psi^{(1)}(\Omega) \qquad (8)$$

where

$$\psi^{(1)}(\Omega) = \tfrac{1}{2}\rho \int d\Omega_2 f(\Omega_2) \int d\bar{r}\, u_p(\bar{r}, \Omega_1, \Omega_2) g^{\circ}(\bar{r}, \Omega_1, \Omega_2) \qquad (9)$$

We approximate the perturbation potential by the relation

$$u_p(\bar{r}, \Omega_1, \Omega_2) = -r_{12}^{-6}(C_i + C_a P_2(\cos\theta_{12})) \qquad (10)$$

where C_i and C_a are constants related with the isotropic and anisotropic dispersion interactions and θ_{12} is the angle between the orientations of the two molecules.

Adopting the procedure of I, we get the following relation for the effective one-body orientational potential

$$\psi^{(1)}(\cos\theta_1) = -\phi_0 - \phi_2 S_s P_2(\cos\theta_1) - \phi_4 S_4 P_4(\cos\theta_1) + \cdots \qquad (11)$$

where

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

$$\phi_2 = \frac{1}{12}\pi\eta I_6(\eta)xC_i^*\left[A_2 + \left(A_0 + \frac{2}{7}A_2 + \frac{2}{7}A_4\right)\frac{C_a^*}{C_i^*}\right] \tag{12b}$$

$$\phi_4 = \frac{1}{12}\pi\eta I_6(\eta)xC_i^*\left[A_4 + \left(\frac{18}{35}A_2 + \frac{20}{27}A_4\right)\frac{C_a^*}{C_i^*}\right] \tag{12c}$$

$$S_n = \int f(\Omega)\,d\Omega\,P_n(\cos\theta) \tag{13}$$

A_0, A_2 and A_4 are the constants which are tabulated in I as a function of x, and

$$I_6(\eta) = 0.333334 + 0.429911\eta + 0.241818\eta^2 + 0.017573\eta^3 + 0.090841\eta^4 - 0.171067\eta^5$$

$$C_i^* = C_i/V_0^2, \qquad C_a^* = C_a/V_0^2$$

We found in I that the average contribution of ϕ_2 and ϕ_4 increases with x. The relative contribution of ϕ_4 with respect to ϕ_2 is about 17% for $x = 2$ and 38% for $x = 3$. Therefore for $x > 2$ the contribution of ϕ_4 is expected to be substantial and cannot be neglected. However, in the present work, which is valid only for $x \leq 2$, we approximate the effective one-body orientational potential $\psi(\Omega)$ by the first two terms of Eq. (11) and write the free energy as

$$\frac{\beta A^{(1)}}{N} = -\beta\phi_0 - \beta\phi_2 S^2 \tag{14}$$

With the help of Eqs. (5) and (14), the total configurational Helmholtz free-energy can be written as

$$\frac{\beta A}{N} = \langle \ln[4\pi f(\Omega)] \rangle + C_2 - B_2 S^2 \tag{15}$$

where

$$C_2 = \ln\rho - 1 + \frac{\eta(4-3\eta)}{(1-\eta)^2}F_1(\chi) - \beta\phi_0 \tag{16}$$

and

$$B_2 = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} F_2(\chi) + \beta\phi_2 \tag{17}$$

The one-particle orientational distribution at a specified temperature and presure is determined by minimizing the free-energy with respect to the variations of $f(\Omega)$ subject to constraint

$$\int f(\Omega)\, d\Omega = 1 \tag{18}$$

From Eqs. (15) and (18), $f(\Omega)$ can be written as

$$f(\Omega) = \frac{\exp[2B_2 S P_2(\cos\theta)]}{\int \exp[2B_2 S P_2(\cos\theta)]\, d\Omega} \tag{19}$$

which leads directly to a transcendental equation for the lowest order parameter $S(= \langle P_2(\cos\theta)\rangle)$:

$$S = \frac{\int P_2(\cos\theta)\exp[2B_2 S P_2(\cos\theta)]\, d\Omega}{\int \exp[2B_2 S P_2(\cos\theta)]\, d\Omega} \tag{20}$$

The NI transition at constant pressure is located by equating the pressure and chemical potentials of the two phases,

$$\begin{aligned} P_{\text{nem}}(\eta_{nc}, T_c, S_c) &= P_{\text{iso}}(\eta_{ic}, T_c) \\ \mu_{\text{nem}}(\eta_{nc}, T_c, S_c) &= \mu_{\text{iso}}(\eta_{ic}, T_c) \end{aligned} \tag{21}$$

S_c is determined from Eq. (20). If we keep the pressure fixed, we get four equations involving four unknowns η_{nc}, η_{ic}, T_c and S_c. These unknown parameters can be determined by solving simultaneously Eqs. (20) and (21).

3. RESULTS AND DISCUSSION

We first investigate the effects caused by the spherocylindrical hard-core length to width ratio x and the potential parameters C_i and C_a as defined by Eq. (10) on the thermodynamic properties close to NI phase transition as a function of pressure. The method of calculation is similar to that given in I. The NI transition parameters are determined from Eq. (21) at various constant values of pressure ranging from 1 bar to 500 bar.

The variation of transition temperature T_c with the interaction strength C_i^*/k corresponding to pressure 1 bar and 300 bar is plotted in Figure 1 for three values of x. Figure 2 is a plot of the variation of T_c with the ratio C_i^*/C_a^* for a fixed value of C_i^*/k. As physically

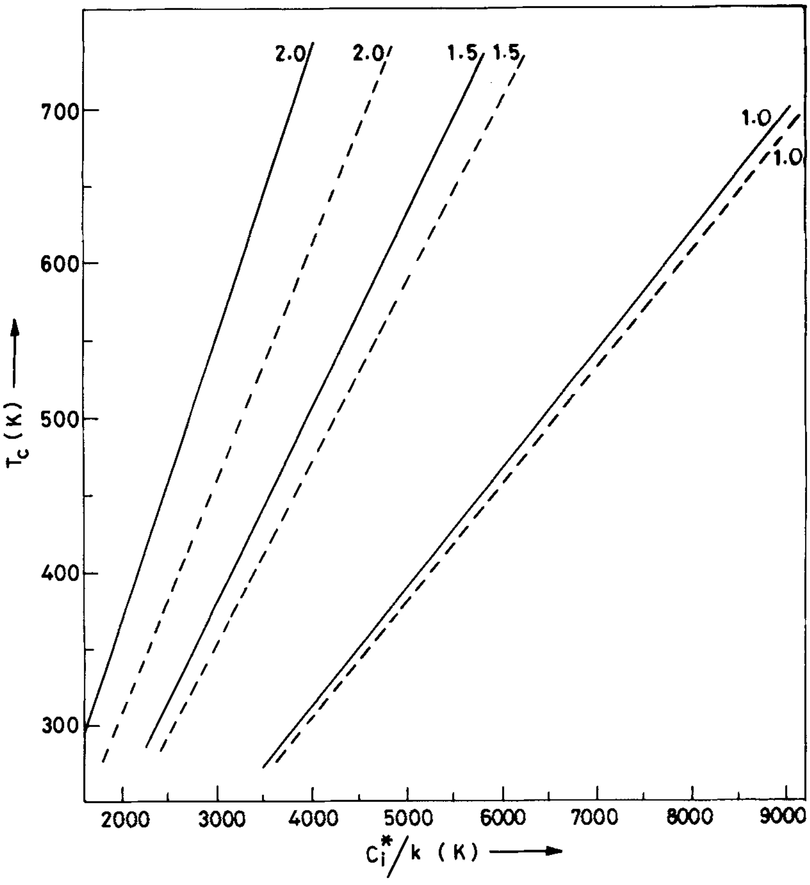

FIGURE 1 The variation of NI transition temperature T_c as a function of C_i^*/k (K) for a fixed value of $C_i^*/C_a^* = 8$. The number on the curves indicates the value of x. Dashed and solid lines correspond, respectively, to pressure 1 bar and 300 bar.

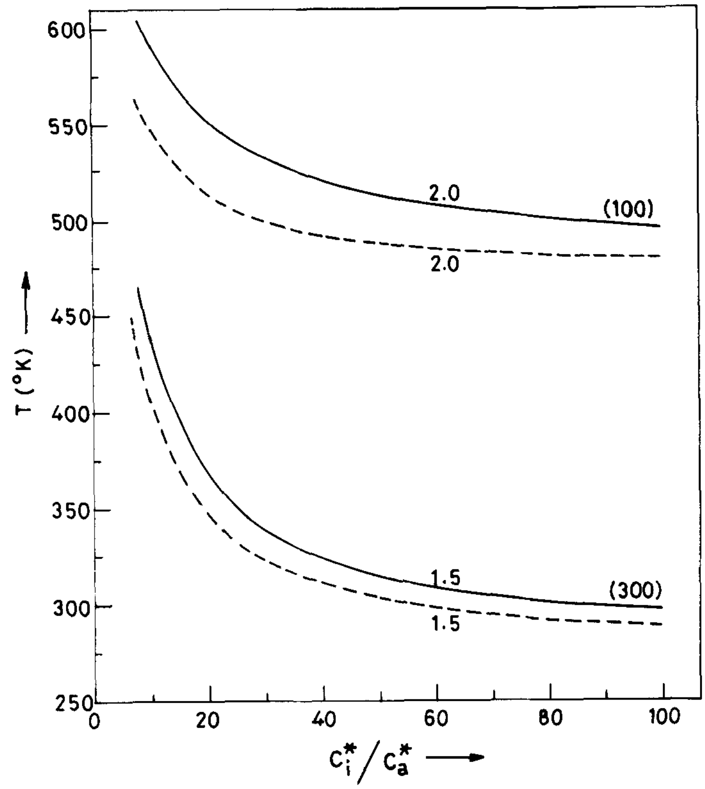

FIGURE 2 The variation of NI transition temperature T_c as a function of C_i^*/C_a^* for a fixed value of $C_i^*/k = 3647.56$ (K). The number on the curves indicates the value of x. Dashed lines correspond to pressure 1 bar and the number in small brackets on solid lines indicates the pressure in bars.

expected, from the calculation we find that at fixed value of pressure with increasing x the phase transition is shifted to higher temperature, lower density with increasing density change and jump of the order parameter. The interaction parameters C_i and C_a have a strong influence on the thermodynamic properties at the transition.

In Figure 3 we have shown the variation of the order parameter S at the NI transition as a function of C_i^*/C_a^*. The values plotted correspond to the transition temperature $T_c \simeq 409$ °K. From the numerical results we observe that the anisotropy of a pairwise intermolecular potential increases both the long-range orientational order and the nemtic-isotropic transition temperature. The change in density at the transition decreases as the ratio C_i^*/C_a^* increases for a given value of

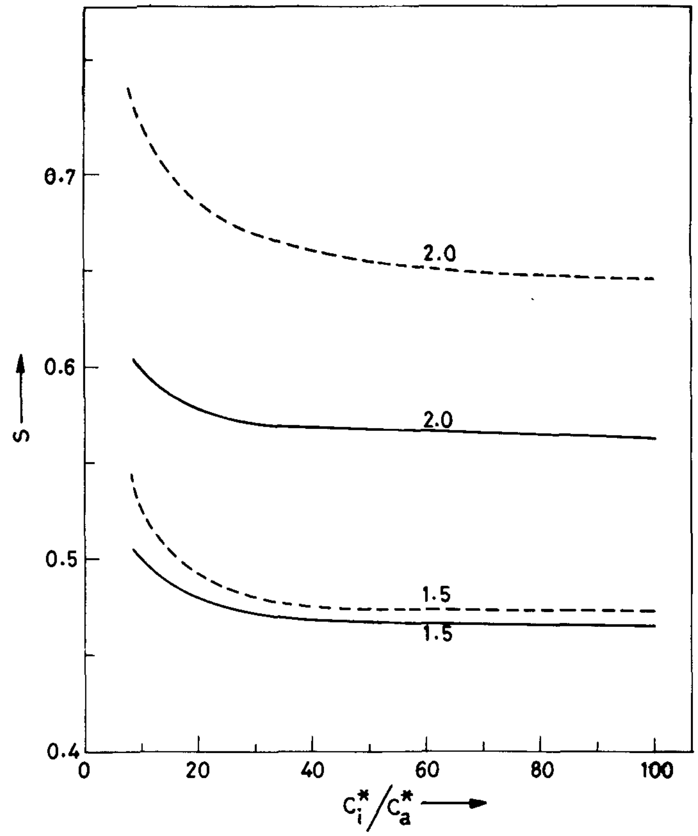

FIGURE 3 The variation of order parameter S at the NI transition as a function of C_i^*/C_a^*. C_i^*/k are chosen so as to reproduce $T_c \simeq 409$ (°K). The number on the curves indicates the value of x. The line symbols are the same as that of Figure 1.

C_i^*/k. A very slow increase in the value of packing fraction is found with C_i^*/C_a^*. For the higher values of C_i^*/C_a^* the phase transition quantities are not very sensitive to the value of C_a^*/k. This result is in accordance with the result of Baron and Gelbert[17].

Table I summarizes a number of thermodynamic properties at the NI transition. For a given x and C_i^*/C_a^* parameter C_i^*/k was chosen so as to reproduce quantitatively the transition temperature $T_c \simeq 409$°K at $P = 1$ bar. This corresponds to the NI transition temperature of the most common nematogen PAA. Figure 4 is a plot of the reduced volume $V^* = \pi/(V_0\rho)$ at the NI transition vs. the transition temperature T_c and the relative volume discontinuity $\Delta V/V$ at the NI

TABLE I

The nematic–isotropic transition parameters under high pressure; S_c is the order parameter, $\Delta\Sigma/Nk$ the transition entropy, $\Gamma(T_C)$ is defined in eq. (22). The model parameters are chosen so as to reproduce transition temperature $T_c \simeq 409\,^\circ$K at $P = 1$ bar. $V^* = \pi/6\eta$ and $\Delta V/V$ is the change in fractional volume.

x	C_i^*/K	C_i^*/C_a^*	P (bar)	T_c	V^*	$\Delta V/V$	S_c	$\frac{\Delta\Sigma}{Nk}$	$\Gamma(T_c)$	$\left(\frac{dT_c}{dP}\right)$
1.0	5361.9126	8	10	409.27	0.8524	0.0078	0.4538	0.6996	1.628	30.02
			100	411.95	0.8492	0.0072	0.4525	0.6888	1.629	28.70
			200	414.78	0.8458	0.0068	0.4513	0.6783	1.631	27.38
			300	417.50	0.8404	0.0064	0.4500	0.6680	1.632	26.18
1.5	3472.4767	8	10	410.16	1.0056	0.0446	0.5426	1.248	1.890	119.79
			100	420.52	0.99775	0.0364	0.5272	1.111	1.917	107.95
			200	430.93	0.9889	0.0303	0.5149	1.009	1.943	97.72
			300	440.41	0.9807	0.0262	0.5058	0.938	1.968	87.62
	4311.4154	20	10	409.64	0.92362	0.0191	0.4905	0.8657	2.13	66.27
			100	415.51	0.91859	0.0174	0.4860	0.8280	2.15	62.47
			200	421.65	0.91315	0.0158	0.4813	0.7949	2.18	58.80
			300	427.46	0.90900	0.0146	0.4782	0.7676	2.20	55.75
	4902.32	50	10	409.35	0.8840	0.0129	0.4747	0.7543	2.31	48.82
			100	413.67	0.8803	0.0121	0.4724	0.7345	2.33	46.80
			200	418.31	0.8765	0.0113	0.4702	0.7156	2.35	44.79
			300	422.75	0.8729	0.0107	0.4682	0.6993	2.37	43.00
2.0	2662.7206	8	300	491.12	1.138	0.0810	0.6046	1.465	2.20	216.70
			400	512.02	1.128	0.0649	0.5821	1.269	2.27	196.47
			500	531.11	1.119	0.0547	0.5650	1.139	2.33	180.68
	3048.3272	50	300	465.72	1.067	0.0540	0.5674	1.205	2.53	160.70
			400	495.99	1.054	0.0399	0.5420	1.000	2.67	139.34
			500	509.70	1.0442	0.0357	0.5331	0.935	2.73	131.41

transition with the transition temperature T_c is plotted in Figure 5. The parameter Γ listed in the table measures the relative sensitivity of the order parameter to volume change (at constant temperature) and the temperature change (at constant volume) and is defined by the relation,

$$\Gamma = \frac{V}{T}\left(\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V}\right) = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_S = \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S \tag{22}$$

The pressure dependence of the transition temperature (dT_c/dp) is determined by Clausius–Clapeyron's law. $\Delta\Sigma/Nk$ measures the change in entropies at the transition.

For the temperature dependence of the order parameter S at constant pressure and density we refer, respectively, to Figures 8 and 9

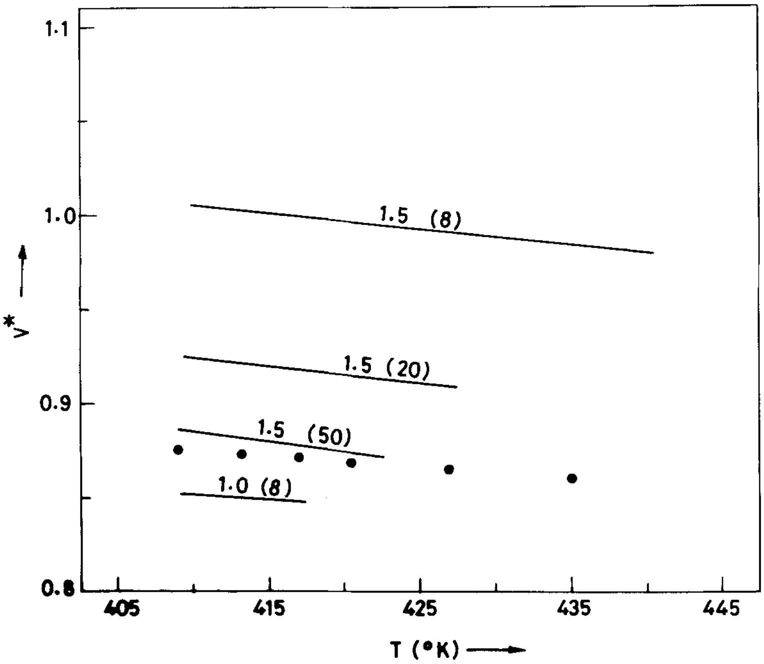

FIGURE 4 The variation of the reduced volume $V^*(=\pi/6V_0\rho)$ at the NI transition as a function of the transition temperature T_c. The numbers on the curves with and without small brackets indicate, respectively, the values of C_i^*/C_a^* and x. The parameter C_i^*/k is chosen so as to reproduce the transition temperature $T_c \simeq 409\,°\mathrm{K}$ at $p = 1$ bar. Experimental points for PAA are taken from Ref. 12.

given in I. The calculated values were obtained by starting at atmospheric pressure ($P = 1$ bar) and a temperature of about 390 °K, the temperature is raised while keeping the density fixed as in the experiment of McColl and Shih.[2] The values of temperature and pressure as obtained for NI transition are, respectively, 424.9 °K and 550.8 bar for $x = 1.0$, $\eta = 0.6143$, $C_i^*/k = 5361.9$ (K), $C_i^*/C_a^* = 8$; 419.0 °K and 706.9 bar for $x = 1.0$, $\eta = 0.6641$, $C_i^*/k = 7321.74$ (K), $C_i^*/C_a^* = 12$ and 472 °K and 659 bar for $x = 1.5$, $\eta = 0.5219$, $C_i^*/k = 3472.47$ (K), $C_i^*/C_a^* = 8$; 447.7 °K and 688 bar for $x = 1.5$, $\eta = 0.5664$, $C_i^*/k = 4311.41$ (K) $C_i^*/C_a^* = 20$. The variation of pressure with temperature is shown in Figure 6 for different values of x and C_i^*/C_a^*. Experimental values[12] for PAA are also given in the figure.

Due to the choice of the potential model we expect that our results may not quantitatively agree with the values for any real system. Therefore rather than try to compare our data with the experimental

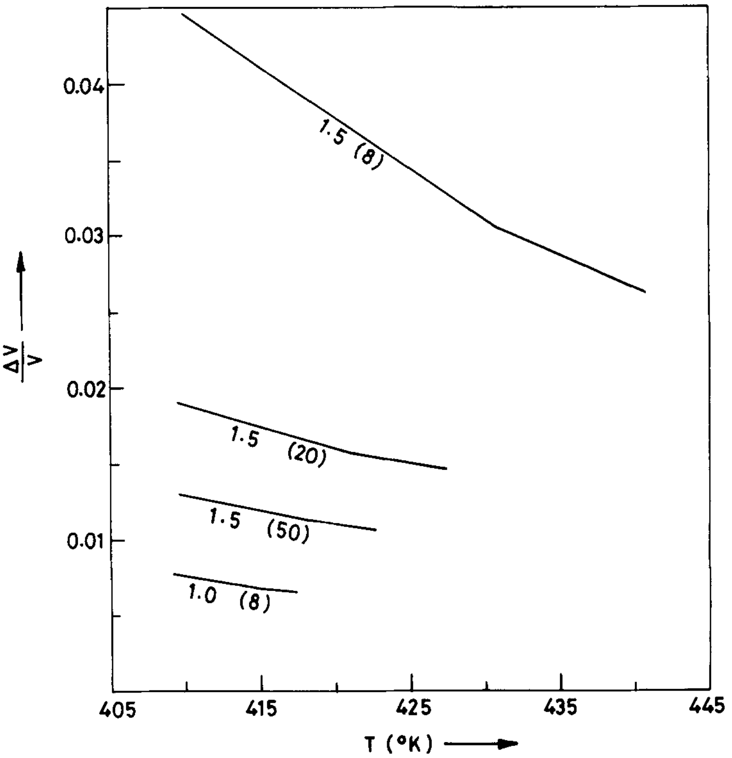

FIGURE 5 The variation of the fractional volume change $\Delta V/V$ at the NI transition as a function of the transition temperature T_c. The line symbols are the same as that of Figure 4.

results, we prefer to discuss general trends of the transition quantities as predicted by the theory. From the above figures and Table I the following general trends are evident about the variation of NI transition properties with pressure:

(i) The range of the stability of nematic phase is considerably larger at constant density as compared to its stability range at constant pressure, which is in agreement with the experimental observations.[2,9,12]

(ii) For the given x and interaction parameters as pressure increases the phase transition shifts to higher temperature and both the molar volume and the fractional volume change decrease. A decrease in the values of transition entropy, order parameter and dT_c/dP is found whereas the parameter Γ increases very slightly.

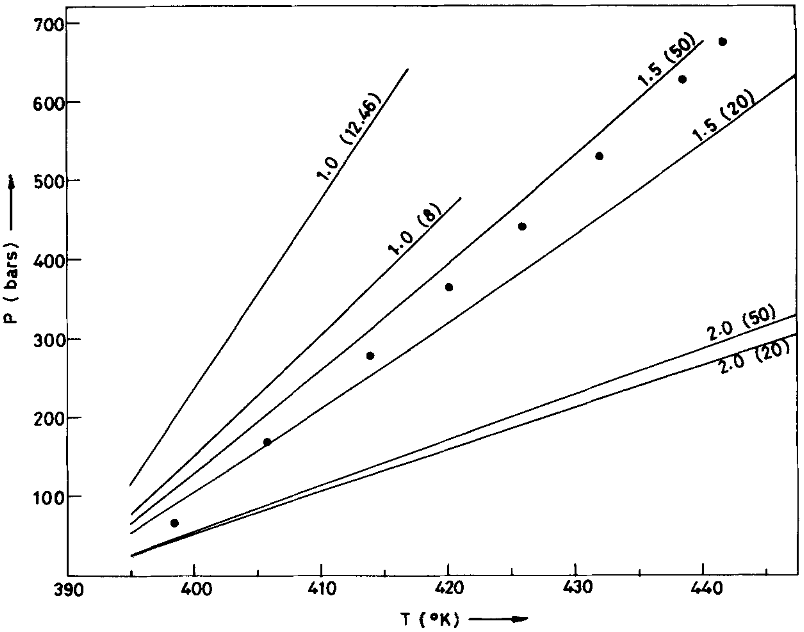

FIGURE 6 The variation of pressure with temperature for different values of x and C_i^*/C_a^* at constant density. The line symbols are the same as that of Figure 4.

The predicted qualitative trends in NI transition temperature, molar volume and fractional volume change is in accordance with the experimental observations.[12,18,19] Similar trends have also been observed in other compounds by Keyes and Daniels[9] and are predicted by Ågren and Martire[21] in their lattice model of rigid, rodlike central cores with semiflexible pendant tails. The predicted decrease in ratio dT_c/dP as T_c increases is in qualitative agreement with the experimental data on PAA[18-20], *N*-*p*-methoxybenzylidene-*p*′-butylaniline (MBBA)[22,23], *p*-*n*-pentyl-*p*′-cyanobiphenyl (5CB)[22] and *N*-*p*-ethoxybenzylidene-*p*′-butylaniline (EBBA).[19,23] Variation of transition entropy with pressure is in qualitative agreement with the experimental trends.[18,19]

McColl[24] observed that for PAA the order parameter S at T_c is constant along the NI transition line. Almost a similar behaviour has been predicted theoretically by Savithramma and Madhusudana.[13] However, the experiment on 5CB and MBBA by Horn and Faber[8] shows that S is not constant along the NI transition line. They observe a decrease in the value of order parameter at T_c with the increase of pressure which is in agreement with our predicted trend.

(iii) At a given pressure with the decreasing values of the ratio C_a^*/C_i^* the values of the transition temperature, molar volume, fractional volume change, transition entropy, order parameter and dT_c/dP decrease and the parameter Γ increases.

In conclusion, we see that the theory predicts the NI transition properties which are in broad agreement with the experimental results at high pressures. Quantitative agreement between the theory and experiment can not really be expected for the reasons discussed in I but this simple approach enables us to study the thermodynamic properties at the NI transition as a function of pressure and thus is hoped to provide a basis for the interpretation of the thermodynamics of nematic liquid crystals.

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References

1. S. Chandrasekhar and R. Shashidhar, In Adv. in Liquid Crystals, (ed. by G. H. Brown, Academic Press, N.Y.) Vol. **4**, p. 83 (1979).
2. J. R. McColl and C. S. Shih, *Phys. Rev. Lett.*, **29**, 85 (1972).
3. G. R. Luckhurst, In The Molecular Physics of Liquid Crystals, (ed. by G. R. Luckhurst and G. W. Gray, Academic Press, London) Chapt. 4 (1979).
4. P. E. Schoen, R. G. Priest, J. P. Sheridan and J. M. Schnur, *J. Chem. Phys*, **71**, 317 (1979).
5. P. E. Cladis, R. K. Bogardus, W. B. Daniels and G. N. Taylor, *Phys. Rev. Lett.*, **39**, 720 (1977).
6. T. J. McKee and J. R. McColl, *Phys. Rev. Lett.*, **34**, 1076 (1975).
7. R. Shashidhar, A. N. Kalkura and S. Chandrasekhar, *Mol. Cryst. Liq. Cryst. Lett.*, **64**, 101 (1980).
8. R. G. Horn and T. E. Faber, *Proc. R. Soc. London*, **368A**, 199 (1979).
9. P. H. Keyes and W. B. Daniels, *J. Phys. (Paris)*, **40**, C3-380 (1979).
10. J. W. Emsley, G. R. Luckhurst and B. A. Timimi, *Molec. Phys.*, **46**, 659 (1982).
11. P. Pollmann and G. Scherer, *Ber. Bunsenges. Phys. Chem.*, **84**, 571 (1980).
12. R. V. Tranfield and P. J. Collings, *Phys. Rev.*, **A25**, 2744 (1982).
13. K. L. Savithramma and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **97**, 407 (1983).
14. S. Singh and K. Singh, *Mol. Cryst. Liq. Cryst.*, **101**, 77 (1983).
15. S. Singh and Y. Singh, *Mol. Cryst. Liq. Cryst.*, **87**, 211 (1982); in the text is referred to as I.

16. J. D. Parson, *Phys. Rev.*, **A19**, 1225 (1979).
17. W. M. Gelbert and B. A. Baron, *J. Chem. Phys.*, **66**, 207, 5795 (1977).
18. S. M. Stishov, V. A. Ivanov and V. N. Kachinskii, *JEPT. Lett.*, **24**, 297 (1976).
19. V. N. Kachinskii, V. A. Ivanov, A. N. Zisman and S. M. Stishov, *JEPT.*, **48**, 273 (1979).
20. S. Chandrasekhar, S. Ramaseshan, A. S. Reshamwala, B. K. Sadashiva, R. Shashidhar and V. Surendranath, Proc. Int. Liq. Cryst. Conf., Bangalore, 1973, *Pramana Suppl.*, **1**, p. 117.
21. G. I. Ågren and D. E. Martire, *J. Chem. Phys.*, **61**, 3959 (1974).
22. R. G. Horn, *J. de Physique*, **39**, 167 (1978).
23. E. Kuss, *Mol. Cryst. Liq. Cryst.*, **47**, 71 (1978).
24. J. R. McColl, *Phys. Lett.*, **38A**, 55 (1972).