

## Inclusion of density variation in the Landau–de Gennes theory of the nematic-isotropic phase transition

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The Landau–de Gennes model of the nematic-isotropic phase transition with the inclusion of the density change is examined in a simple way. We show how a density dependent term gives various thermodynamic quantities consistent with both experimental results and with an assumed low value of  $T_{NI} - T^* = 1$  K, where the temperature  $T_{NI}$  is the nematic-isotropic transition temperature and  $T^*$  is the absolute limit of stability of the isotropic phase. We also note that this density dependence does not improve with a high value of  $(Q^* - Q_{NI})/Q_{NI}$  (where  $Q^*$  and  $Q_{NI}$  are the values of the uniaxial nematic order parameter at  $T^*$  and  $T_{NI}$ , respectively), obtained in the usual Landau–de Gennes theory of the nematic-isotropic phase transition.

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### INTRODUCTION

It is generally believed that the Landau mean-field theory for nematic liquid crystal does quite well in predicting qualitative features such as order parameter changes and phase diagrams. When it comes to understanding thermodynamics quantitatively near phase transition regions, this is found to be wanting [1]. Early theories on the nematic-isotropic ( $N$ - $I$ ) phase transition include the phenomenological model of Landau–de Gennes [2] and the Hamiltonian approach of Maier-Saupe [3], and these give us the basic understanding of the phenomenon. Yet, in spite of these and many subsequent efforts [4], there remains a series of fascinating problems associated with the  $N$ - $I$  transition that are not completely settled. The most conspicuous shortcoming concerns the ratio  $(T_{NI} - T^*)/T_{NI}$  [5], where the temperature  $T_{NI}$  is the nematic-isotropic transition temperature and  $T^*$  is the absolute limit of stability of the isotropic phase. It is known experimentally that  $T_{NI} - T^* = 1$  K. In an earlier work [6] it was shown how a renormalization group calculation, even when done up to second order in epsilon ( $\epsilon$ ), gives at best  $T_{NI} - T^* = 7.46$  K. In a recent paper Tao, Sheng, and Lin [7] argued that fluctuation effects being higher order effects, the remedy should be first looked into the mean-field calculation. They have included a density dependent term in the pseudopotential results in  $(T_{NI} - T^*)/T_{NI}$  and also in specific volume change at  $T_{NI}$ . In support of their contention, they have shown how some other thermodynamic results [namely,  $dT_{NI}/dP$  and  $d(\ln T_{NI})/d(\ln V)$ ] could be reasonably reproduced with the already adjusted value of the aforementioned parameter. In the present work we have endeavored to ascertain the validity of their ideas in the context of Landau–de Gennes theory with the inclusion of density dependence. The conclusion we reached is quite interesting. It is seen that with the Landau expansion parameters, once fixed utilizing some experimental data, the calculated values of  $dT_{NI}/dP$  and

$d(\ln T_{NI})/d(\ln V)$  tally well with experimental results and also with a low value of  $T_{NI} - T^* = 1$  K as in the work of Tao, Sheng, and Lin [7]. However,  $Q^* - Q_{NI}$  (where  $Q^*$  and  $Q_{NI}$  are the values of the uniaxial nematic order parameter at  $T^*$  and  $T_{NI}$ , respectively), instead of being very close (approximately 2% experimentally) remains near about 50% obtained in the Landau–de Gennes theory without incorporating any effect of density variation. This  $Q^* - Q_{NI}$  discrepancy implies that the change in the value of the calculated order parameter over a small temperature interval of 1 K (as  $T_{NI} - T^* = 1$  K) would be much higher than that observed in experiments. In fact, the value of 0.3998 for  $(dQ/dT)_{T=T_{NI}}$  that we obtain is in disagreement with the observed value of 0.008. This clearly shows that a complete resolution of the  $T_{NI} - T^*$  puzzle remains outside the realm of simple mean-field analysis where fluctuations are not taken into consideration.

### THEORY

For purely geometrical reasons, the nematic-isotropic transition is first order, as it was recognized by Landau [8]. The Landau–de Gennes model [2] containing a cubic term in order parameter in the free energy expansion was proposed and used to describe first order transition in liquid crystals. Retaining only terms which have rotational invariance, the free energy per unit volume,  $F$  is given by

$$F = F_0 + \frac{3}{4} A Q_{ij} Q_{ji} - \frac{3}{2} B Q_{ij} Q_{jk} Q_{ki} + \frac{9}{16} C (Q_{ij} Q_{ji})^2. \quad (1)$$

Here  $F_0$  is the free energy density of the isotropic phase,  $Q_{ij}$  is the tensor order parameter which describes the degree of order in a nematic liquid crystal, and a summation over repeated indices is implied. The coefficient  $A$  is assumed to have the form  $A = a(T - T^*)$ , while  $B$  and  $C$  are regarded as constants independent of the temperature. All coefficients are assumed independent of the

volume. For a liquid crystal of uniaxial symmetry the single preferred direction of the molecules is along the direction  $\hat{n}$ , and  $Q_{ij}$  takes the form

$$Q_{ij}(\mathbf{r}) = Q(\mathbf{r})[\hat{n}_i(\mathbf{r})\hat{n}_j(\mathbf{r}) - \frac{1}{3}\delta_{ij}], \quad (2)$$

where  $\hat{n}_i$ 's are the components of  $\hat{n}$  and  $Q(\mathbf{r})$  denotes the fraction of molecules at  $\mathbf{r}$  aligned parallel to  $\hat{n}$ .

For a uniform uniaxial crystal substituting Eq. (2) into Eq. (1) leads to the free energy expansion

$$\begin{aligned} F &= F_0 + F_1(Q) \\ &= F_0(\rho) + \frac{1}{2}AQ^2 - \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4. \end{aligned} \quad (3)$$

Landau theory has been widely applied to a number of different phase transitions and examples where the order parameter couples to some other variables are also common [9,10]. In the present case we want to describe the coupling of  $Q$  and the density  $\rho$ . The simplest assumption is to add a term to Eq. (3) of the form  $g(\rho)Q^2$ . In expression (3) if  $B$  were absent,  $T^*$  would be the mean-field second order transition temperature. Since  $B > 0$ ,  $T^*$  is the (mean-field) absolute stability limit of the isotropic phase. The temperature  $T^*$  in Eq. (3) can be expressed as

$$T^*(\rho) = T_0^* + \alpha(\rho - \rho_0)^2. \quad (4)$$

Here  $\alpha$  is a positive constant and  $\rho_0$  is the equilibrium density without the order parameter-density coupling.

The free energy can then be expressed as

$$\begin{aligned} F(\rho, Q, T) &= F_0(\rho) + \frac{a}{2}(T - T_0^*)Q^2 - \frac{B}{3}Q^3 + \frac{C}{4}Q^4 \\ &\quad + \frac{\lambda}{2}(\rho - \rho_0)^2Q^2, \end{aligned} \quad (5)$$

where  $\lambda = -\alpha a$  and  $T_0^*$  is the (mean-field) absolute stability limit of the isotropic phase in the absence of any density-order parameter coupling.

The value of the order parameter  $Q_{NI}$  at the transition temperature is given by

$$Q_{NI} = \frac{2B}{3C}. \quad (6)$$

The transition temperature  $T_{NI}$  is given by

$$T_{NI} = T_0^* + \frac{2B^2}{9aC} - \lambda(\rho_N^i - \rho_I^i)^2/a, \quad (7)$$

where  $\rho_N^i$  and  $\rho_I^i$  are the nematic and isotropic density at  $T_{NI}$ , respectively.

The minimization of Eq. (5) yields the following solutions:

$Q = 0$  (isotropic phase),

$$\begin{aligned} Q &= \frac{B}{2C} \{1 + [1 - (4C/B^2)[a(T - T_0^*) + \lambda(\rho - \rho_0)^2]]^{1/2}\} \\ &\quad \text{(nematic phase)}. \end{aligned} \quad (8)$$

The variation of the order parameter with the transition temperature  $T_{NI}$  is given by

$$\begin{aligned} \left. \frac{dQ}{dT} \right|_{T=T_{NI}} &= -\frac{a}{B} [1 - (4C/B^2)\{a(T_{NI} - T_0^*) \\ &\quad + \lambda(\rho_N^i - \rho_I^i)^2\}]^{-1/2}. \end{aligned} \quad (9)$$

The absolute limit of stability of the isotropic phase ( $T = T^*$ ) the order parameter is

$$Q^* = \frac{B}{2C} \{1 + [1 - (4\lambda C/B^2)(\rho - \rho_0)^2]^{1/2}\}. \quad (10)$$

In the same way, the entropy, molar volume, and enthalpy discontinuities are

$$S_I - S_N = \frac{1}{2}aQ_{NI}^2 = 2aB^2/9C^2, \quad (11)$$

$$\begin{aligned} V_I - V_N &= (S_I - S_N) / \left[ \frac{dP}{dT} \right]_{NI} \\ &= (2aB^2/9C^2) / \left[ \frac{dP}{dT} \right]_{NI}, \end{aligned} \quad (12)$$

$$H_I - H_N = T_{NI}(S_I - S_N) = (2aB^2/9C^2)T_{NI}. \quad (13)$$

Let us now consider a nematic to isotropic ( $N-I$ ) phase transition at constant pressure.

Then  $P_N = P_I$  and assuming  $(\partial F_0/\partial \rho)_{NI} = (\partial F_N/\partial \rho)_{NI} = a_1$  at  $T_{NI}$ , we get

$$a_1 = -\lambda[\rho_N Q_{NI}^2 / (1 + \rho_I^i/\rho_N^i)], \quad (14)$$

where  $\rho_I^i$  and  $\rho_N^i$  are the densities of the isotropic and nematic phase at  $T_{NI}$ , respectively.

The pressure at the nematic phase can be expressed as

$$P_N = -\lambda\rho_N^3 Q_{NI}^2 E \quad (15)$$

with

$$E = \{(\rho_I^i/\rho_N^i)^2 / [1 + (\rho_I^i/\rho_N^i)]\}, \quad (16)$$

where we have used the expression for pressure as  $P = \rho^2(\partial F/\partial \rho)$ .

Substituting the value of  $\rho_N^i$  from Eq. (15) into Eq. (7) we obtain the transition temperature as

$$\begin{aligned} T_{NI} &= T_0^* + \frac{2B^2}{9aC} - \frac{\lambda}{a} [(-P_N/\lambda E Q_{NI}^2)^{2/3} \\ &\quad - 2\rho_I^i(-P_N/\lambda E Q_{NI}^2)^{1/3} + \rho_I^i{}^2]. \end{aligned} \quad (17)$$

The variation of  $T_{NI}$  with the pressure and volume can be expressed as

$$\begin{aligned} dT_{NI}/dP &= -\frac{2\lambda}{3a} [(-1/E\lambda Q_{NI}^2)^{2/3} P_N^{-1/3} \\ &\quad - \rho_I^i(-1/E\lambda Q_{NI}^2)^{1/3} P_N^{-2/3}], \end{aligned} \quad (18)$$

$$d(\ln T_{NI})/d(\ln V) = 2\lambda\rho_N^i(\rho_N^i - \rho_I^i)/aT_{NI}. \quad (19)$$

#### COMPARISON WITH EXPERIMENT

Equations (6), (7), (13), and (15) have been used for evaluating the phenomenological parameters  $a$ ,  $B$ ,  $C$ , and

$\lambda$  for 4-methoxybenzylidene-4'-butylaniline (MBBA); these are determined from the experimental values of  $Q_{NI}$ ,  $\Delta H$ ,  $\Delta V/V$ ,  $T_{NI}$ , and  $P_N$ . As input to our theory we take the measured values of the transition temperature  $T_{NI}$  ( $T_{NI}=318.2$  K) [11], the latent heat  $\Delta H$  ( $\Delta H=0.82$  J cm<sup>-3</sup>) [11], the discontinuity of the order parameter  $Q_{NI}$  at  $T_{NI}$  ( $Q_{NI}=0.4$ ) [3], the pressure at the nematic phase  $P_N$  ( $P_N=1$  atm) [12], the density  $\rho_N^l$  ( $\rho_N^l=1.049$  g/cm<sup>3</sup>) [12], and  $\Delta V/V=0.0016$  [12].

Using the relations (6), (13), and (15) and the measured values of  $Q_{NI}$ ,  $\Delta H$ ,  $T_{NI}$ ,  $P_N$ , and  $\rho_N$ , we obtain  $a=0.0322$  J cm<sup>-3</sup> K<sup>-1</sup> and  $\lambda=-1.09959$  J cm<sup>6</sup> g<sup>-3</sup>. Then using relation (7) and taking the input as  $T_{NI}-T_0^*=1$  K, we obtain  $B=0.2415$  J cm<sup>-3</sup> and  $C=0.4025$  J cm<sup>-3</sup>. From relation (18) we find the variation of temperature  $T_{NI}$  with pressure ( $dT_{NI}/dP$ )=41.50 K/kbar which is of the same order as the experimental value of 20–40 K/kbar [11,13,14]. The experimental data on MBBA show [15]  $d \ln T_{NI} / d \ln V = -3.9$ . Using relation (19) we also obtain  $d \ln T_{NI} / d \ln V = -3.964$  in fairly good agreement with experimental value. Using relation (12) we obtain the volume change  $\Delta V=0.2726$  cm<sup>3</sup>/mol which also fairly agrees with the experimental result  $\Delta V=0.40$  cm<sup>3</sup>/mol [12]. We had  $T_{NI}-T_0^*=1$  K as an input. In order to calculate the temperature difference of  $T_{NI}-T^*$  (as mentioned earlier  $T^*$  is the modified value of  $T_0^*$  due to the density-order parameter coupling), we use relation (4). Taking  $\rho=\rho_N^l$  and  $\rho_0=\rho_I^l$  and utilizing the value of  $\alpha$  ( $\alpha=-\lambda/a=34.1490$  cm<sup>9</sup> K g<sup>-3</sup>) we get  $T_{NI}-T^*=0.9998$  K. What transpires out of the above analysis is that if one takes into account the variation of density in the Landau–de Gennes expansion,  $T_{NI}-T^*=1$  K is consistent with observed values of  $Q_{NI}$ ,  $\Delta H$ ,  $\Delta V/V$ ,  $T_{NI}$ , and  $P_N$  for MBBA. Further, calculated values of  $dT_{NI}/dP$  and  $d(\ln T_{NI})/d(\ln V)$  have fairly good agreement with experimental observations. These findings corroborate the claims of Tao, Sheng, and Lin. However, the problem of inordinately large values of  $Q^*-Q_{NI}$  remains totally unresolved. Using Eqs. (6) and (10) and assuming that  $\rho_N$  at  $T^* \sim \rho_N^l$  (as  $T_{NI}-T^*$  is small) we get  $(Q^*-Q_{NI})/Q_{NI}=1.49$  in place of 1.5 obtained without the inclusion of density dependence. Now using relation (9) (putting in the values of  $a$ ,  $B$ ,  $C$ ,  $\lambda$ ,  $\rho_N^l$ , and  $\rho_I^l$ ), we ob-

tain  $(dQ/dT)_{T=T_{NI}}=0.3998$ /K which becomes very large in comparison to the experimental result  $(dQ/dT)_{T=T_{NI}}=0.008$ /K. Hence the density dependence does not resolve the low value of  $dQ/dT$  at the transition point.

## DISCUSSION

Table I shows the fitted values of the Landau expansion parameters, the calculated and experimental values of  $dT_{NI}/dP$  and  $d(\ln T_{NI})/d(\ln V)$ . In order to obtain the values of  $B$  and  $C$ , we have taken as input  $T_{NI}-T_0^*=1$  K instead of  $T_{NI}-T^*=1$  K. Since we have  $T^*=T_0^*+\alpha(\rho-\rho_0)^2$ , and the value of  $\alpha=34.1490$  cm<sup>9</sup> K g<sup>-3</sup>, the effect of  $\alpha(\rho-\rho_0)^2$  is negligibly small. Using relations (4) and (7) we obtain  $T_{NI}-T^*=0.9998$  K. But the most puzzling aspect is that  $Q^*-Q_{NI}$  hardly improves if we take the input  $T_{NI}-T_0^*=5$  K or 10 K instead of 1 K;  $Q^*-Q_{NI}$  shows only minor improvements. Further, this discrepancy shows up glaringly in the calculated value of  $dQ/dT$  at  $T_{NI}$ . From Eq. (9) we get a value of  $(dQ/dT)_{T=T_{NI}}=0.3998$ /K, which is too high compared to the experimental value of 0.008/K. These results support the molecular mean-field results of Tao, Sheng, and Lin and also bring out the inadequacy in explaining the small value of  $Q^*-Q_{NI}$  and  $(dQ/dT)_{T=T_{NI}}$  in a Landau–de Gennes framework. A low value of  $T_{NI}-T^*$  with a high value of  $Q^*-Q_{NI}$  or an equivalently high value of  $(dQ/dT)_{T=T_{NI}}$  seems to be glaringly inconsistent. One of the possible reasons may well be the fact that in Landau expansion no change of the values of  $B$  and  $C$  are allowed as one approaches the temperature  $T^*$ . In other words, renormalization of  $B$  and  $C$  are called for as one approaches  $T^*$ . It would also be of interest to have an estimate of  $Q^*-Q_{NI}$  and  $(dQ/dT)_{T=T_{NI}}$  in the model of Tao, Sheng, and Lin.

In this context we should mention the works of Alben [16,17], who analyzed the same issue in the molecular mean-field approximation and came to similar conclusions as we have here. He considered some lattice models and continuum models of a hard rod liquid with and without attractive energies. At given pressures and

TABLE I. Calculated values of the different parameters.

Parameters	Our results	Experimental results
$a$ (J cm <sup>-3</sup> K)	0.0322	
$\lambda$ (J cm <sup>6</sup> g <sup>-3</sup> )	-1.09959	
$B$ (J cm <sup>-3</sup> )	0.2415	
$C$ (J cm <sup>-3</sup> )	0.4025	
$dT_{NI}/dP$ (K/kbar)	41.50	20–40
$d(\ln T_{NI})/d(\ln V)$	-3.964	-3.9
$\frac{dQ}{dT} \Big _{T=T_{NI}}$ (/K)	0.3998	0.008
$T_{NI}-T^*$ (K)	0.9998	1.0
$T_{NI}-T_\xi$ (K)	1.2684	1.0

temperatures he obtained the state of minimum Gibbs free energy by varying the long range order parameter and density and hence showed that isobaric expansivity, isothermal compressibility, and specific heat at constant pressure display pretransition behavior qualitatively similar to the effects seen below but near the transition point. The results, however, showed important discrepancies quantitatively. A thorough and careful analysis led him to conclude that the discrepancies were due to the approximations inherent in the mean-field calculations and not due to the idealized nature of the models. His assertion that the near critical nature of liquid crystal phase transitions cannot be well reproduced in terms of a long range order parameter alone is supported by this work utilizing the Landau-de Gennes theory.

Further, an experimental determination of  $T^*$  rests on the large fluctuations leading to divergence of light scattering intensity. In order to calculate the correlation length we followed the method of Ref. [18]. The free energy density associated with the long wavelength part of

the order parameter fluctuation for uniaxial liquid crystal is

$$F(\mathbf{r}) = F_0 + \frac{1}{2} \{ a(T - T^*) Q^2(\mathbf{r}) + L [\nabla Q(\mathbf{r})]^2 \} - \frac{1}{3} B Q^3(\mathbf{r}) + \frac{1}{4} C Q^4(\mathbf{r}). \quad (20)$$

In our model the local free energy gets modified as

$$F(\mathbf{r}, \rho) = F_0(\rho) + \frac{1}{2} \{ a(T - T_0^*) Q^2(\mathbf{r}) + L [\nabla Q(\mathbf{r})]^2 \} - \frac{1}{3} B Q^3(\mathbf{r}) + \frac{1}{4} C Q^4(\mathbf{r}) + \frac{1}{2} \lambda (\rho - \rho_0)^2 Q^2(\mathbf{r}). \quad (21)$$

The total free energy  $F = \int F(\mathbf{r}) dV$  can then be expressed in terms of  $Q_q$ , the Fourier terms of  $Q(\mathbf{r})$ . Here  $L$  is the elastic constant.

The expression for the correlation length can be obtained by a simple modification of the results of Ref. [18] as

$$\xi^2(T) = \frac{L + kT(B/L)^2 \xi_0^3 g_B}{a(T - T_0^*) + \lambda(\rho - \rho_0)^2 + kT(C/L)(f_c/\xi_0) - (B/L)^2 kT \xi_0 f_B}, \quad (22)$$

where

$$\xi_0 = (L/A)^{1/2}$$

and

$$g_B \equiv (1/16\pi^2) \left[ \tan^{-1}(\phi) + \frac{\phi(\phi^2 - 1)}{(1 + \phi^2)^2} \right], \quad (23)$$

$$f_B \equiv (1/4\pi^2) \left[ \tan^{-1}(\phi) - \frac{\phi}{(1 + \phi^2)} \right], \quad (24)$$

$$f_C \equiv (3/2\pi^2) [\phi - \tan^{-1}(\phi)], \quad (25)$$

where  $\phi = \xi_0 q_m$  and  $q_m$  is the cut-off wave number ap-

proximately related to the reciprocal of the interparticle separation. Defining  $T_\xi$  to be the temperature at which the correlation length  $\xi$  diverges and taking the value of  $q_m = 25 \times 10^{-8}$  cm [18], we obtain  $T_{NI} - T_\xi = 1.2684$  K, which is quite close to the value of  $T_{NI} - T^* = 0.9998$  K obtained earlier. This indicates  $T_\xi \approx T^*$  and  $T^*$  has the desired significance. Lastly, this simple extension of the Landau-de Gennes theory gives some results not obtainable with the standard Landau-de Gennes expansion.

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