Nematic-isotropic phase transition: A review

Prabir K. Mukherjee*

Saha Institute of Nuclear Physics, 1/AF Bidhan Nagar, Calcutta 700 064, India
*Present address: Department of Physics, Bar-Ilan University, Ramat-Gan 52900, Israel

The phase transition from isotropic liquid to nematic liquid crystals is a weak first-order one. The low value of $(T_{NI} - T^*)/T_{NI}$, where T_{NI} is the nematic–isotropic phase transition temperature and T^* denotes the virtual transition temperature, has been a long standing puzzle in the physics of liquid crystals. We calculate in a unified approach the value of $(T_{NI} - T^*)/T_{NI}$, both at critical and tricritical points. We investigate the possibility of the critical region near T_{NI}. The possibility of the tricritical behaviour at the nematic–isotropic transition is also discussed by means of Landau theory. The various predictions are compared with the available experimental results.

LIQUID crystals (LC) constitute a state of matter which is characterized by some degree of order that is intermediate between that of a molecular crystal where the mobility of the individual molecule is restricted, and a normal molecular liquid that has no long-range translational and orientational order. Due to the destruction of the lattice structure, the system possesses some of the mechanical properties of the liquid, e.g. fluidity, inability to support shear, formation of droplets, etc. Whereas long-range orientational ordering gives rise to the anisotropy in its optical, electrical and magnetic properties.

There are basically two types of LC, viz. thermotropic and lyotropic. In thermotropic LC, phase transitions are induced primarily by temperature. Thermotropic LC usually have a single component. They can also appear in mixture. Lyotropic LC are mixtures or solutions of unlike molecules in which one is a mesogenic liquid. They are generally mixtures of amphiphilic compounds and a polar solvent, most frequently water. The lyotropic LC phase transitions are primarily induced by concentration changes.

From the stand point of the shape molecules exhibiting LC, phases can be classified into two distinct groups: (i) rod-like and (ii) disc-like. Rod-like molecules are more or less elongated and lath-like[1,2]. It was found by Chandrasekhar *et al.*[3,4] that disc-shaped molecules can also form liquid crystalline phases.

An ordinary isotropic liquid (Figure 1) has full rotational and translational symmetry. The centers and orientations of the molecules are randomly distributed. The corresponding symmetry group is: $S = R^3 \Lambda O(3)$, which represents the semi-direct product of the group R^3 of continuous translations in 3-d space, by the full orthogonal group, i.e. the invariance group of the sphere which contains the three-dimensional rotational group $SO(3)$ and its multiplication by the inversion 1. In the simplest structure the group $O(3)$ is replaced by one of the uniaxial symmetry group $D_{\infty h}$. Thus the uniaxial nematic phase has the symmetry: $S = R^3 \Lambda D_{\infty h}$. In nematic liquid crystals (NLC) (Figure 1) the molecules are, on average, aligned with their long axes parallel to each other. Macroscopically, a preferred direction is thus defined. In many cases where there exists rotational symmetry around this direction, then the phase is uniaxial. It is convenient to describe the local direction of alignment by a unit vector $\hat{n}(\vec{r})$, the director, giving at each point the direction of the preferred axis. In nematic one always finds that $\hat{n}$ and $-\hat{n}$ are equivalent, even though the molecules may be polar. For example, no ferroelectricity has been observed. Microscopically, this means that an equal number of molecules points 'up' and 'down'. The equivalence of $\hat{n}$ and $-\hat{n}$ is crucial for the construction of the theory of the nematic phase. This will lead to (i) a first-order nematic isotropic (NI) phase

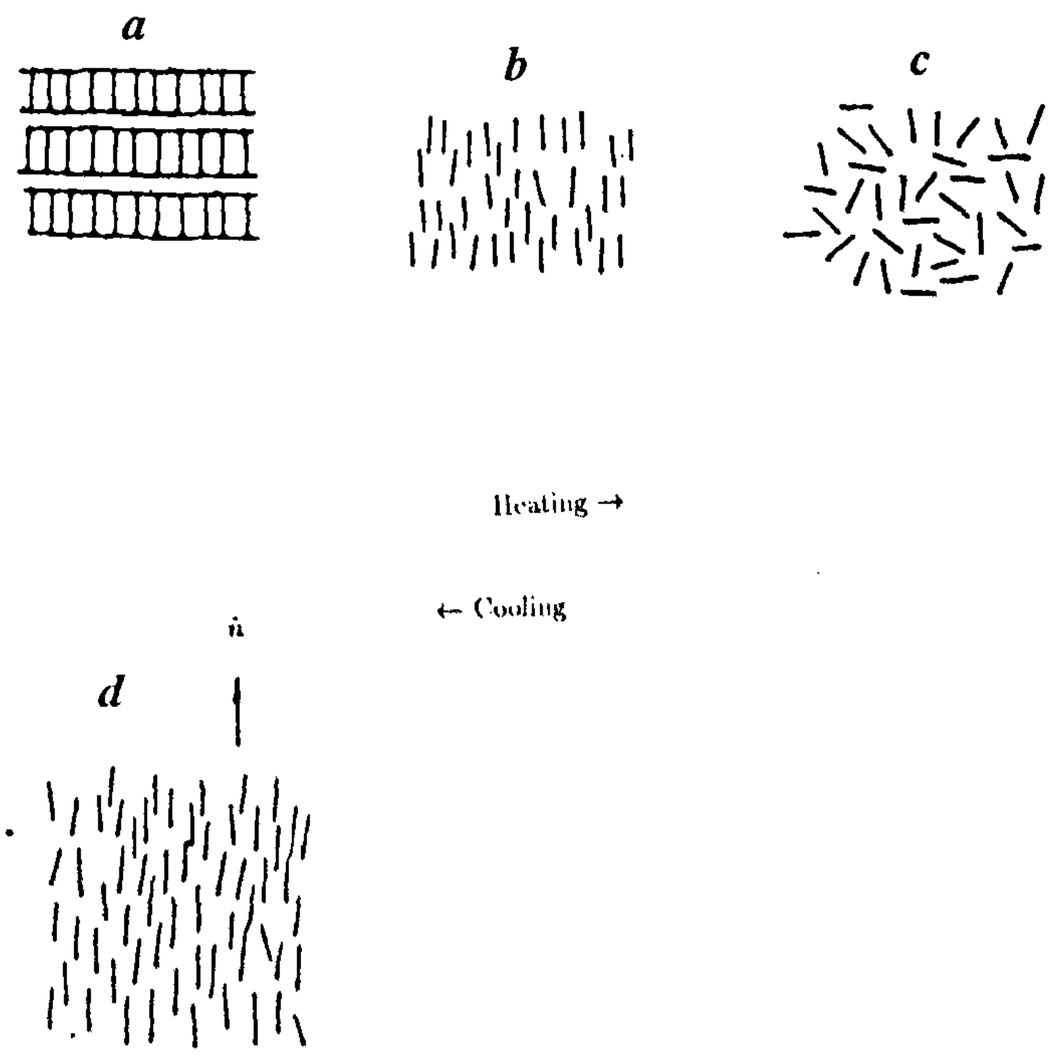

Figure 1. *a*, Crystal; *b*, liquid crystal, *c*, isotropic liquid and *d*, uniaxialnematic.

transition; (ii) the possibility of a biaxial phase; and (iii) a non-trivial Gaussian fluctuation spectrum in the isotropic phase.

The nematic order parameter

The identification of the appropriate order parameter (OP) for NLC is added by a consideration of the observed structure and symmetry of the phase. It is assumed[5] that the corresponding primary OP has the symmetry of a second-rank traceless tensor[6], the components of which can be written as

$$Q_{ij}(\vec{r}) = l_i l_j - \tfrac{1}{3}(l_i l_k)\,\delta_{ij} = Q(\vec{r})\,[n_i(\vec{r})\,n_j(\vec{r}) - \tfrac{1}{3}\delta_{ij}]. \quad (1)$$

It represents the local averages of bilinear combinations formed by projections of the unit vector **l** of the long-molecular axis, or analogous combinations of the director components $\hat{n}_i$ which determine the local orientation of the molecules. The quantity $Q(\vec{r})$ defines the fraction of molecular axes pointing along $\hat{n}$ at a given point. $Q = \langle 3\cos^2(\theta) - 1\rangle/2$, θ is the angle made by the long molecular axis with $\hat{n}$ and the bracket $\langle \ldots \rangle$ denotes the ensemble average. Thus in the isotropic phase $Q(\vec{r}) = 0$, and in the nematic phase $Q(\vec{r}) \neq 0$. Let us note that eq. (1) applies only for molecular subunits with symmetry $D_{\infty h}$ or D_{∞}, i.e. in which the two directions $\hat{n}$ and $-\hat{n}$ are equivalent.

Fluctuations and phase transitions

A unique feature of LC is that they are soft systems on a macroscopic scale. Another feature of LC is that they provide qualitative solutions to complicated, often unsolvable, equations on a large scale that can be observed using a polarizing microscope. Many LC phase transitions involve broken continuous symmetries in real space and their interactions on a molecular scale are short range. As a result, fluctuations have long been known to be important features of LC phase transitions – even weakly first-order (discontinuous) ones. Compared to major advances in our understanding of fluctuation-controlled second-order (continuous) phase transitions, relatively little is known about the fluctuation phenomenon (critical phenomenon) at a first-order phase transitions such as NI transitions. Critical phenomenon in LC has specific features due to the variety of symmetries of different phases and coupling of different OPs. These features complicate theoretical considerations and restrict methods which are well proved in other cases (e.g. renormalization group (RG) method). Despite the variety of their continuous broken symmetries, most LC phase transitions are expected to fall in the 3D-XY (helium) universality class with $\alpha \sim -0.01$, $\nu \sim 0.67$ and $\beta \sim 0.33$. A salient feature of LC materials is that they have generic long-range correlations even far from critical points or hydrodynamic instabilities[7] that could make it difficult to access critical regimes before being finessed by a first-order (FO) phase transition. At these high temperatures, externally supplied noise[8] can suppress the onset of macroscopic instabilities such as spatial turbulence far from any phase transition[9]. The richness implicit in what we have learned and can learn from fluctuations in LC seems endless.

NI phase transition

Density effects at the NI transition

Background. As one of the earliest findings which indicated the existence of the liquid crystalline phase, the NI transition has been a topic of active theoretical and experimental studies over the past few decades. Early theories include the phenomenological model of Landau–de Gennes (LdeG)[10] and the Hamiltonian approach of Maier–Saupe[11] (MS). Yet, in spite of these and many subsequent efforts, there remains a series of fascinating problems associated with the NI transition that are not completely settled. Although the NI transition is one of the most ubiquitous found in nature, it is also one of the least understood. First of all it is not quite clear what makes this transition so weakly first-order.

The phase transition from isotropic liquid to nematic liquid crystals is a weak first-order one. As a rule, it is characterized by a small latent heat and by large pretransitional anomalies in a relatively wide temperature region, similar to those observed near a second order transition. Light scattering and magnetic birefringence measurements in the isotropic phase of nematogens indicate strong pretransitional effects. The weakness of the first-order character of the NI transition is characterized by the low value of $(T_{NI} - T^*)/T_{NI} \sim 0.1\%$ (refs 12, 13), where T_{NI} is the NI transition temperature and T^* denotes the virtual transition temperature or the supercooling temperature. De Gennes has pointed out how MS theory implies $(T_{NI} - T^*)/T_{NI} \approx 8.0\%$. The difference of $(Q^* - Q_{NI})/Q_{NI}$ is experimentally found to be of the order of a few per cent instead of 50% as predicted theoretically. Thus the low values of $T_{NI} - T^*$ and that of $Q^* - Q_{NI}$ pose a long standing puzzle in spite of the numerous theories of the NI transition. In order to gain insight into this problem, several workers showed how the inclusion of fluctuations can give considerable improvement. This was done by special inhomogeneity in the order parameter in the LdeG theory. These calculations include Gaussian fluctuation only. For including higher order fluctuation, Priest[14] did a RG calculation to show that $T_{NI} - T^* = 12.8$ K. Zhang *et al.*[15] studied the nature of

the orientational phase transition in the 3D Lebwohl-Lasher model of LC by computer simulation. They obtained the impressive value of $(T_{NI}-T^*)/T_{NI}$. Again, Tao, Sheng and Lin[16] argued that fluctuation effects being higher order effects, a remedy for the MF calculation should be considered first. They have included a density-dependent term in the pseudo potential and have shown how only one adjustable parameter can give consistent 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. Naturally such discrepancies raise many questions regarding our understanding of the NI transition.

We looked into this particular problem in the context of LdeG theory with the inclusion of density variation[17–20].

Landau–de Gennes theory. For purely geometrical reasons, the NI transition is first-order as it was recognized by Landau. The LdeG model containing a cubic term in order parameter in the free-energy expansion was proposed and used to describe first-order transition in LC. We start from the expansion of LdeG free-energy density in powers of tensor order parameter Q_{ij}

$$F-F_0=\frac{3}{4}AQ_{ij}Q_{ij}-\frac{3}{2}BQ_{ij}Q_{jk}Q_{ki}+\frac{9}{16}C(Q_{ij}Q_{ij})^2, \quad (2)$$

which contains a cubic invariant as the states where Q_{ij} and $-Q_{ij}$ are energetically non-equivalent. Here F_0 is the free-energy density of the isotropic phase. The coefficient A is assumed to have the form $A=a(T-T^*)$. Here a, B and C are positive constant and T^* is a temperature close to the transition temperature T_{NI}.

For a uniform uniaxial LC substituting eq. (1) leads to the free-energy expansion

$$F=F_0+\frac{1}{2}AQ^2-\frac{1}{3}BQ^3+\frac{1}{4}CQ^4. \quad (3)$$

The presence of the cubic term in eq. (3), which does not disappear at the NI transition point, leads to the fact that the jump in entropy is small and the transition is close to a transition of second kind ($B=0$). The constant C also turns out to be unexpectedly small. This weakness of the NI transition can be characterized numerically by the parameter $\delta=(T_{NI}-T^*)/T_{NI}\propto B^2$. In most LC that have been studied $\delta\approx 10^{-2}-10^{-3}$, i.e. $\delta\ll 1$. But in any MF theory with a single interaction constant the parameter δ should be order 1. The fluctuations of the nematic order parameter can be quite high and provide a universal reason for the smallness of B. If B is absent, T^* would be the MF second-order transition temperature. But since in our model $B>0$, T^* is the temperature of the absolute stability limit of the isotropic phase.

In order to find out the density effect at NI transition, the free-energy density (3) can be written[19] as

$$F^*(\rho,Q,T)=\frac{1}{2}A^*Q^2-\frac{1}{3}B^*Q^3+\frac{1}{4}C^*Q^4+\frac{1}{2}E\rho^2+\lambda_1\rho Q^2+\lambda_2\rho Q^3. \quad (4)$$

The term $E\rho^2$ is the free-energy density of the isotropic phase. The coefficients λ_1 and λ_2 are coupling constant. A minimization of the free-energy results in the following renormalization[19] of the expansion coefficients

$$A=A^*+2\lambda_1 M/E, \quad (5)$$

$$B=B^*-3\lambda_2 M/E, \quad (6)$$

$$C=C^*-2\lambda_1^2/E. \quad (7)$$

Thus the coupling of the scalar parameters Q and ρ leads to the renormalization of the constant A, B and C. Here M is the quantity thermodynamically conjugate to density ρ. It is seen from eqs (5) and (6) that the interaction between Q and ρ leads to the decrease of B and the increase of T^*. Thus the influence of density may be another factor leading to the renormalization of the LdeG expansion coefficients. The shift of the transition temperature becomes

$$T_{NI}=T^*-2\lambda_1\rho/a_1. \quad (8)$$

Thus the coupling constant λ determines the shift of the transition temperature (8) and can be found easily from experiment as

$$\lambda_1=-\frac{a_1}{2}\frac{dT_{NI}}{d\rho}. \quad (9)$$

What transpires from the above analysis is that not only the director fluctuation, but also the density effects play an important role on the NI transition. The density fluctuation alters the character of the NI transition and make it very weakly first-order.

In the presence of density the modified form of temperature T^* in eq. (3) can be expressed[17] as

$$T^*(\rho)=T_0^*+\alpha(\rho-\rho_0)^2. \quad (10)$$

Here α is a positive constant and ρ_0 is the equilibrium density without order parameter–density coupling. T_0^* is the MF absolute stability limit of the isotropic phase in the absence of any density-order.

It was shown[17] that with the Landau expansion parameters once fixed utilizing some experimental data,

the calculated values of dT_{NI}/dP (= 41.50 K/kbar) and $d(\ln T_{NI})/d(\ln V)$ (= −0.3964) agree well with the experimental results (20–40 K/kbar and −0.39) and also with a low value of $T_{NI} - T^* = 1$ K. However, $Q^* - Q_{NI}$, instead of being very close (approximately 2% experimentally) remains about 50% obtained in the LdeG 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 of $(dQ/dT)_{T=T_{NI}}$ that we obtained is in disagreement with the observed value 0.008. This clearly shows that a complete resolution of $T_{NI} - T^*$ puzzle remains outside the realm of simple MF analysis where fluctuations are not taken into consideration. These results support the molecular MF results of Tao *et al.*[16] and also brings out the inadequacy in explaining the small value of $(Q^* - Q_{NI})/Q_{NI}$ and $(dQ/dT)_{T=T_{NI}}$ in LdeG framework.

As can be seen from eqs (5) and (7) that as the temperature decreases and ρ increases, the quantity $\partial M/\partial\rho$ decreases and the coefficient C tends to zero, i.e. a tricritical point (TCP) appears. On further variation of the temperature and density, the coefficient changes sign. In general, when two coefficients of the same symmetry in the Landau free-energy expansion vanish simultaneously, such a point is called tricritical. Since the coefficients C and A have the same symmetry and $C = A = 0$ gives a TCP. In that case a positive stabilizing sixth order term has to be included in the free-energy expansion[18–21].

As we have to consider a situation with $C = 0$, a stabilizing sixth order term is added with $E \gg 0$. The alternative free-energy expression is thus

$$F = \frac{A}{2} Q^2 - \frac{B}{3} Q^3 + \frac{C}{4} Q^4 + \frac{E}{6} Q^6, \qquad (11)$$

with the expression (11) one can have TCP $B = 0$, $C = 0$. One way of studying the weakly first-order NI transition occurring near a TCP would be to have a B with a small non-zero value. This was done in references 19 and 20. Then the free-energy (11) takes the form[19–21]

$$F = \frac{A}{2} Q^2 - \frac{B}{3} Q^3 + \frac{E}{6} Q^6. \qquad (12)$$

The value of $T_{NI} - T^*$ obtained[20] from the model (12) was 7.68 K (without density variation). The model (12) also gives the value of $(Q^* - Q_{NI})/Q_{NI} \approx 26\%$, which shows an improvement of 50% over the previous model (3). These results are encouraging but the value of $(Q^* - Q_{NI})/Q_{NI}$ left ample scope for improvement. Again taking into account the density variation[19] in the model (12), one obtains $T_{NI} - T^* \approx 0.9999$ K but the value of $(Q^* - Q_{NI})/Q_{NI} \approx 26\%$ hardly improves. However, we can present yet another approach[18] to study the NI transition occurring near a TCP. We can do that by taking $B = 0$ in eq. (11). The first-order nature of the NI transition and the neighbourhood of the TCP both can be achieved if we take a small negative value of C. It should be mentioned that by taking $B = 0$ we do not mean to imply that the cubic term is to be altogether discarded in the free-energy expression of the nematic phase. It only implies that as the critical point is approached, the already small entity becomes even smaller to be neglected. This only points to the inadequacy in the Landau scheme of keeping all the coefficients except A to be constant. In this case the free-energy density in the vicinity of TCP takes[18] the form as

$$F = \frac{A}{2} Q^2 - \frac{C}{4} Q^4 + \frac{E}{6} Q^6. \qquad (13)$$

The value of $T_{NI} - T^*$, calculated from the scaling equation of state[18], is 2.55 K. The model (13) gives the value of $(Q^* - Q_{NI})/Q_{NI} \approx 15.47\%$, which shows an improvement of 70% over the previous results. The critical exponents obtained from the model (13) are $\beta = 0.25$ and $\Delta = 1.25$, whereas experiment shows the values to be $\beta = 0.247 \pm 0.01$ and $\Delta = 1.26 \pm 1.0$. Thus the consistent values of $(T_{NI} - T^*)/T_{NI}$ and $(Q^* - Q_{NI})/Q_{NI}$ along with the β and Δ value suggest the model (13) better and favours its tricritical nature. However, the low value of $(T_{NI} - T^*)$ with the high value of $(Q^* - Q_{NI})$ or an equivalent high value of $(dQ/dT)_{T=T_{NI}}$ seems to be glaringly inconsistent which support the molecular MF results.

Influence of nonmesogenic impurities on a NI transition. Generally all real nematic contain impurities. It is well known that solute impurities which are not sufficiently rod-like and rigid in molecular structure depress the NI transition temperature. Hence, the addition of nonmesogenic impurities to the pure nematic leads to a broadening of the NI transition temperature and the appearance of a two-phase region (see Figure 2). We studied[22] the formation of this two-phase region in the context of LdeG theory. It was shown[22] that this two-phase region indicates the first-order character of the NI transition.The depression of the NI transition temperature is connected with the width of the two-phase region and the entropy of the transition[22]

$$T_{NI} - T_{NI}^0 = \Delta x/\Delta S_{NI}, \qquad (14)$$

where Δx and ΔS_{NI} are the width of the two-phase region and entropy of the pure nematic solvent. Hence for $\Delta S_{NI} \neq 0$, a two-phase region must exist at a fixed temperature. For second-order transition $\Delta S_{NI} = 0$, i.e. two-phase region disappears. The form of the two-phase region (see Figure 2) is determined by two factors: (i)

anomaly small values of the coefficients B and C in expansion (11). (ii) nonideality of the mixture. The smallness of B means that the transition is close to second order. In the case of $B=0$, nonideality of the solution may lead to the appearence of a TCP due to the coupling between the order parameter and concentration[22]. If the transition in a mesogenic solvent is very near to TCP ($C \ll 1$), the phase diagram for a dilute solution has the form presented in Figure 3.

Hence from the above analysis it is clear that the two-phase region of Figure 3 indicates the tricritical behaviour of the NI transition.

Critical behaviour at the NI phase transition

Background. Though the singular-like behaviour of various quantities at the NI transition is still a puzzle, the solution could well be obtained within the LdeG theory and the prediction of this theory should be compared with the experimental data. Owing to the first-order nature of the NI phase transition, the part of the critical region, closest to the critical point, is not accessible to experiment. Therefore the critical exponents, being defined in this very region, cannot be determined without the use of some extrapolation. Poggi *et al.*[23], for example, obtained a critical exponent $\beta = 1/2$ (classical) for the order parameter versus temperature in methoxybenzylidene butylaniline (MBBA). Keyes, however, has shown[24] that $\beta = 1/4$ (tricritical) can also fit the data quite well in demonstrating the potential ambiguity in obtaining the critical exponents at a first-order transition. Others have also found tricritical-like exponents[25] although these measurements are by no means unambiguous. Keyes suggested[26] that the critical exponents for quantities diverging toward temperature T^*, before being cut off by a first-order transition at T_{NI}, should be the characteristic of TCP. The difference between critical and tricritical behaviour of the NI transition is difficult to verify. The main reason to suspect the tricritical behaviour is the value of β. For the exponent β, a best value $\beta = 0.247 \pm 0.01$ was obtained for 8CB. This value strongly supports the suggestion of tricritical character of the NI phase transition. On the other hand, high precision measurements of specific heat near the NI phase transition of MBBA show that the behaviour of this transition is near tricritical and does not appear to agree with the LdeG model (3). Concerning the specific heat phenomena, Anisimov *et al.*[27] made a strong plea for tricritical hypothesis fitting their data of very precise specific heat measurements of MBBA and other compounds.

In the nematic phase the '*director*' fluctuations are critical. Nelson and Pelcovits[28] pointed out that strongly developed director fluctuations could alter the character of the NI transition and make it very weakly first order. Vigman, Larkin and Filev[29] applied the RG approach to the description of fluctuation behaviour near the isolated critical point on the NI transition line. At this point the cubic invariant in the effective Hamiltonian is equal to zero. With quadratic (A) and cubic (B) variables (in the laboratory one could adjust the temperature and pressure of which A and B are smooth functions) we would get a first-order transition except at an isolated critical point $A = B = 0$, where the jump in the order parameter vanishes. Several workers investigated the Landau point with fluctuation by means of Landau theory[30] and epsilon expansion method[31,32]. The values of the critical exponents for the five components of the order parameter ($n = 5$) at $d = 3$, $\varepsilon = 1$, in the vicinity of this point are obtained as $\beta \approx 0.38$, $\nu \approx 0.64$, $\gamma \approx 1.27$, $\eta \approx 0$ and $\alpha \approx 0.04$. However, these results are far from the experimental results. Trimper[33] studied the NI transition in $2+\varepsilon$ dimensions. Applying the procedure in $2+\varepsilon$ dimensions, he showed that the

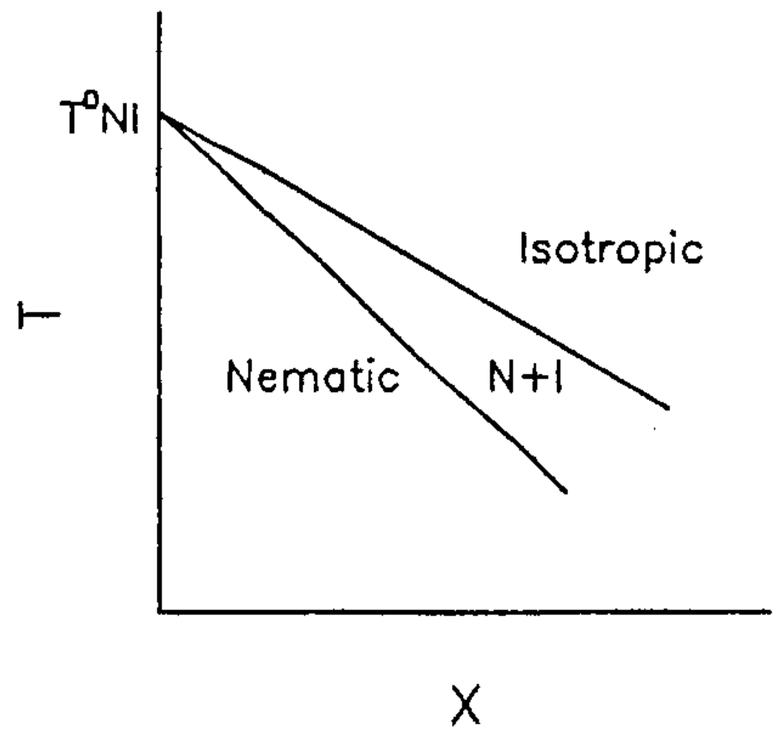

Figure 2. Typical temperature (T) versus concentration (x) diagram at a low solute mole fraction.

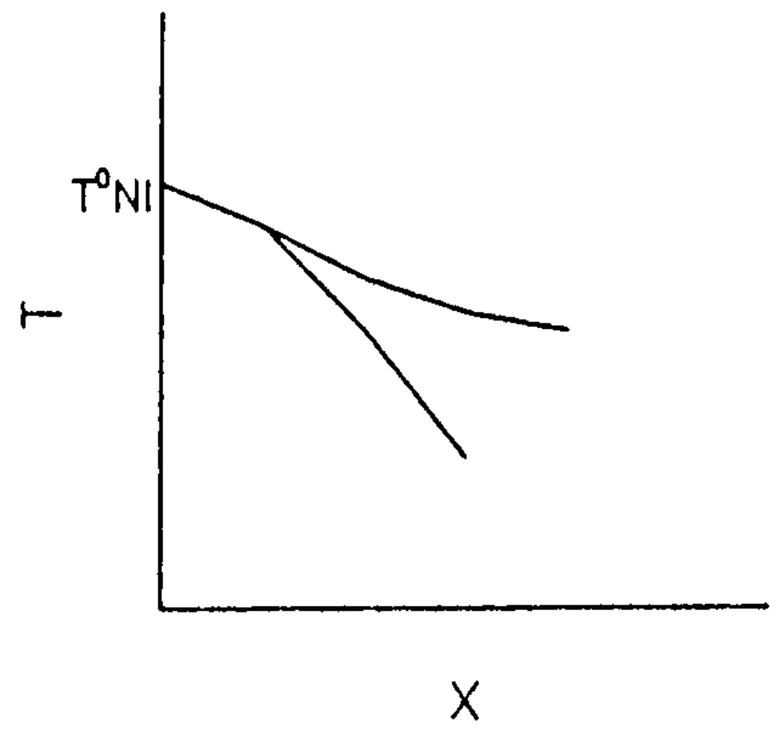

Figure 3. Phase diagram of a dilute solution in the case of tricritical behaviour of the pure solvent

phase transition remains second-order with a 'transition temperature' proportional to ε. Recently, Wang and Keyes[34] calculated the fluctuations of all five components of the orientational order parameter of a NLC in a wide variety of circumstances involving several types of critical and multicritical points. Rzoska *et al.*[35] discussed the critical behaviour of dielectric permitivity in the isotropic phase of nematogens. Their analysis shows an adequate description of the pretransitional behaviour of dielectric permitivity in the isotropic phase of nematogens.

Therefore the study of the pretransition (fluctuation) phenomenon near the first-order phase transition can reveal the physical reasons for their closeness to the second order.

Landau–de Gennes theory. When there are no external magnetic or electric fields, the nematic and isotropic liquid do not have the same symmetry. The character of the NI phase transition can be changed by applying an electric or magnetic field. The effect of an applied field is to induce orientational order in the isotropic phase that grows with increasing field intensity. For the case of positive dielectric anisotropy, the first-order phase boundary in the temperature-applied field plane terminates in a field-induced critical point. This phase diagram is thus analogous to that of a liquid–gas system in the temperature–pressure plane. Eventually, with increasing the external fields, the jump at the transition vanishes at the field-induced critical point. The increase in orientational order in the isotropic liquid results in an enhancement of the NI transition temperature, δT_{NI}. As an analogy to paramagnetism, the isotropic liquid with field-induced orientational order is called paranematic. As a result, it is now possible to pass through the field-induced critical point and observe the state beyond where nematic and paranematic states are indistinguishable.

The physical consequences of the LdeG theory will be investigated when an external field is induced. The LdeG free-energy in the presence of an external magnetic field is obtained[10] by

$$F = F_0 + \frac{A}{2} Q^2 - \frac{B}{3} Q^3 + \frac{C}{4} Q^4 + D(\nabla Q)^2 - HQ. \quad (15)$$

Near an isolated critical point on the NI transition line, we find[36–38] a critical region at $H = 0$ if the first-order transition is near enough to the isolated critical point. If the transition point is remote enough, we have a critical region if $H \neq 0$. We also investigated the possibility[37] of the critical region at the first-order transition line of the NI transition in the context of epsilon expansion. We see[37] that a model (2) with tensorial order parameter, which has a BQ^3 interaction in addition to CQ^4, has a critical value $B = B_c(C, \Lambda)$ below which there is no transition. At the critical value the system undergoes a second-order transition with no symmetry break. Above the critical value of B the transition is of first order. This is contrary to the prediction of Landau's theory. This result holds also for $d > 4$, since it depends only on the fact that $A_c = 0$. Thus if at T_{NI} the behaviour is critical, assuming that in the scaling law[37] the nonanalycity appears at the critical point (fluid-like critical point) and also on the spinodal curve, the critical indices of the absolute stability limit of the nematic phase (metastable) are $\beta_1 = \beta$ and $\alpha_1 = \gamma_1 = 1 - \beta_1$. Thus we see that there is a possibility of critical behaviour with $d = 3$ for the NI phase transition. This argument has recently been verified experimentally by Rzoska *et al.*[35].

We have calculated[39] the anomalous parts of the specific heat capacity of NLC above the transition point on the basis of continuum theory of de Gennes. The excess specific heat capacity at constant pressure (per volume) due to fluctuation is given[39] by

$$\Delta C_p(T) = 2.54 \times 10^{-4}\, T^2\, [T - 318.7]^{-1/2}\ \text{J/mol/K}. \quad (16)$$

The experimental and theoretical heat capacities are shown in Figure 4. For the case of MBBA the experimental points of Anisimov *et al.*[27] are found to be well reproduced by the empirical formula (16). We also observe that the amplitude of the order parameter fluctuation increases abnormally near T_{NI} and it brings about the anomalous increments in heat capacity. This may be caused by either a very weak first-order character of this transition which is driven by the fluctuations of the nearby NI transition or more likely a macroscopically inhomogeneous distribution of impurities. This analysis

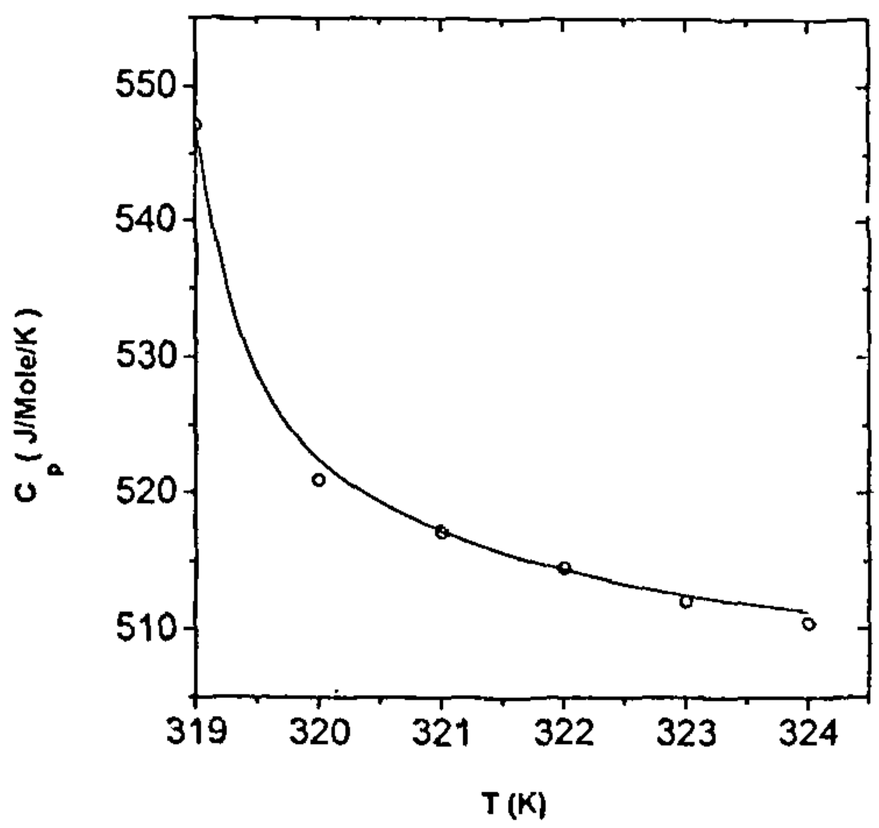

Figure 4. The specific heat capacity (C_p) versus temperature (T) of MBBA. Solid line, theoretical data; open circle, experimental data of reference 27.

clearly indicates the pretransitional phenomenon of NLC. This pretransitional phenomenon indicates that the NI transition is close to being second-order.

Renormalization-group theory. In recent works[40,41], we have used the RG technique to calculate the $T_{NI} - T^*$ of the NI transition. The model free-energy of the LdeG form can be written as

$$F = \int d^d x \left[\tfrac{1}{4} (A Q_{ij}^2 + \nabla_k Q_{ij} \nabla_k Q_{ij}) - B Q_{ij} Q_{jk} Q_{ki} + C(Q_{ij} Q_{ij})^2 - H_{ij} Q_{ij}. \right. \quad (17)$$

Here $d^d x$ indicates à functional integral in d dimension over the tensor field $Q = Q(\mathbf{x})$. The external field H_{ij} is set to the uniaxial form $H_{11} = H$, $H_{22} = H_{33} = -H/2$.

The model (17) was studied extensively by ε $(= 4 - d)$ expansion technique[42]. This method relies on the fact that the MF approximation is exact for $d > 4$. It is a perturbation expansion about the solution for $d = 4$. The fixed point of the RG corresponds to a second-order phase transition with $B = 0$. The cubic coupling was found to be a 'relevant' term so B was treated as a perturbation. The scaling form of the equation of state in the second order of epsilon expansion is obtained[36,40] as follows:

$$\frac{H}{Q^\delta} + \frac{B}{Q^\omega} = f(x). \quad (18)$$

The result for

$$f(x) = 1 + x + \varepsilon f_1(x) + \varepsilon^2 f_2(x), \quad (19)$$

where $x = t/Q^{1/\beta}$

$$\delta = 3 + \varepsilon, \ \omega = 1 + \frac{7\varepsilon}{13}, \ \beta = \frac{1}{2} - \frac{3\varepsilon}{26}. \quad (20)$$

The quantity t is the reduced temperature $t = (T - T^*)/T^*$. The quantity t is the temperature at which the second-order phase transition would take place if B were zero. Therefore, T^* is the temperature that retains its original significance as the temperature at which the light scattering intensity would diverge if there were no cubic coupling and hence no first-order transition.

From general thermodynamic arguments we know that $H = -\partial F/\partial Q$. The free-energy may therefore be found by integrating the equation of state with respect to Q. The conditions that the free energies of the isotropic and nematic states be equal and that the free-energy be a local minimum with respect to Q can be expressed as

$$\int_0^Q H(Q')\, dQ' = 0, \quad (21)$$

$$H(Q) = 0. \quad (22)$$

For fixed B these equations are to be solved for $Q = Q_{NI}$ and $t = t_{NI}$. The resulting value of T_{NI} is then expressed as $t_{NI} = (T_{NI} - T^*)/T^*$. This requires a numerical solution of eqs (21) and (22) as a function of B by putting the experimental value $Q_{NI} = 0.4$. One obtains the value of $T_{NI} - T^* = 7.4699$ K. The strong point of this method over the earlier methods described above is that this method needs only one experimental datum input namely the jump in order parameter at T_{NI}. Although this result is more encouraging than the previous work[14], it is far away from the experimental finding. In order to improve this result we then extend this calculation near the coexistence curve[41]. Here coexistence curve is defined as the region of small external field and below the critical temperature. NLC are arrangements of approximately parallel molecules whose centre of mass have no long-range order, similar to ordinary liquids. Interaction between the molecules is invariant under simultaneous rotation of the axis of the molecules of their centre of mass. The total angular momentum is conserved and the components of their molecular quadrupole moment, the director are the 'symmetry breaking' and 'symmetry restoring' variables. Therefore the director fluctuations correspond to the dynamical mode which is critical for all temperatures in the nematic phase. The role of symmetries is a new topic of considerable current interest. It is observed that scale invariance is a natural property for systems in which infinitesimal symmetries lead to Goldstone modes in many-body degenerate states. This has been tested both experimentally and numerically for NLC. Fluctuations in NLC are unique in that they vary from microscopic to macroscopic length scales.

Considering the uniaxial system with a continuous symmetry, there exists massless modes, Goldstone bosons at all temperature $T < T_C$ (critical temperature) when the external field H is taken to zero, leaving a spontaneously broken symmetry. Because of these Goldstone modes, the limit $H \to 0$ can be thought of as a critical point for all $T < T_c$. In other words, the transverse susceptibility becomes infinite when $H \to 0$. The improved value of $(T_{NI} - T^*)$ was obtained[41] near the coexistence curve as $T_{NI} - T^* = 3$ K. The closeness of this result with the observed $T_{NI} - T^* = 1$ K supports the idea that a RG calculation can lead to the resolution of the $T_{NI} - T^*$ puzzle. This supports the view that the discrepancies between the usual analysis of the model and the experimental results are due to the MF calculation and not due to the model itself.

We also calculated[43] the critical exponents numerically for the $d = 3$ LdeG model near the isolated critical point on the NI transition line from the recursion relations obtained by Wilson[44] in the $\eta = 0$ approximation from RG theory. We find that the critical exponents, namely

$\gamma = 1.277$ and $\nu = 0.638$ are in fair agreement with the best epsilon expansion results $\gamma = 1.277$ and $\nu = 0.64$.

Conclusion

The low values of $(T_{NI} - T^*)/T_{NI}$ and $(Q^* - Q_{NI})/Q_{NI}$ pose a long standing puzzle in spite of the numerous theories of the NI transition. Further, the very nature of the critical behaviour near T_{NI} is not properly understood. We have consistently and semi-quantitatively succeeded in explaining these puzzling aspects. The consistent values of $T_{NI} - T^*$ and $(Q^* - Q_{NI})/Q_{NI}$ along with β and Δ value suggest the tricritical nature of the NI transition. We also find that not only the director fluctuations but also the density fluctuation alter the character of the NI transition and make it very weakly first order. Although we have made some progress in explaining different phenomena related to the critical properties of the NI transition, in no case have we found complete numerical agreement between theory and experiments. Realistic results are expected to come from more realistic Hamiltonian or, maybe better approximations than used here are also needed. In short, for the NI transition one does not have the final word as yet.

1. Gray, G. W., *Advances in Liquid Crystals* (ed. Brown, G. H.), Academic Press, New York, 1976, vol. 2.
2. Priestly, E. B., Wojtowicz, P. J. and Sheng, P., *Introduction to Liquid Crystals*, Plenum, New York, 1975.
3. Chandrasekhar, S., Sadashiva, B. K. and Suresh, K. A., *Pramana*, 1977, **9**, 471; Chandrasekhar, S., Sadashiva, B. K., Suresh, K. A., Madhusudana, N. V., Kamar, S., Sashidhar, R. and Venkatesh, G., *J. Phys. (France) Colloq.*, 1979, C3, Suppl. 4., **40**, C3-120–124.
4. Chandrasekhar, S., *Liquid Crystals*, Cambridge Univ. Press, Cambridge, 1992.
5. de Gennes, P. G. and Prost, J., *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1993.
6. Indenbom, V. L. and Loginov, E. B., *Sov. Phys. Crystallogr.*, 1981, **26**, 526–531.
7. Dorfman, J. R., Kirkpatrick, T. R. and Sengers, J. V., *Ann. Phys. Chem.*, 1994, **45**, 213–217.
8. Schenzle, A. and Brand, H. R., *Phys. Rev. A*, 1979, **20**, 1628–1647.
9. Brand, H. R., Kai, S. and Wakabayashi, S., *Phys. Rev. Lett.*, 1985, **54**, 555–557.
10. de Gennes, P. G., *Phys. Lett. A*, 1969, **30**, 454–456; *Mol. Cryst. Liq. Cryst.*, 1971, **12**, 193–214.
11. Maier, W. and Saupe, A., *Z. Naturfosch. A*, 1958, **13**, 564–570.
12. Shih, Y. M., Huang, H. M. and Woo, C. W., *Mol. Cryst. Liq. Cryst.*, 1976, **34**, 7–12.
13. Fan, C. and Stephen, M. J., *Phys. Rev. Lett.*, 1970, **25**, 500–502; Stinson, T. W. and Litster, J. D., *Phys. Rev. Lett.*, 1970, **25**, 503–506.
14. Priest, R. G., *Mol. Cryst. Liq. Cryst.*, 1978, **41**, 223–227.
15. Zhang, Z., Mouritsen, O. G. and Zuckerman, M. J., *Phys. Rev. Lett.*, 1992, **69**, 2803–2806.
16. Tao, R., Sheng, P. and Lin, Z. F., *Phys. Rev. Lett.*, 1993, **70**, 1271–1274.
17. Mukherjee, P. K., Bose, T. R., Ghose, D. and Saha, M., *Phys. Rev. E*, 1995, **51**, 4570–4573.
18. Nandi, B., Mukherjee, P. K. and Saha, B., *Mod. Phys. Lett. B*, 1996, **10**, 777–781; Mukherjee, P. K., *Int. J. Mod. Phys. B*, (in press).
19. Mukhopadhyay, K. and Mukherjee, P. K., *Int. J. Mod. Phys. B*, 1997, **11**, 3479–3489.
20. Mukherjee, P. K., *Mod. Phys. Lett. B*, 1997, **11**, 107–114.
21. Gramsbergen, E. F., Longa, L. and de Jeu, W. H., *Phys. Rep.*, 1986, **135**, 195–257.
22. Mukherjee, P. K., *Liq. Cryst.*, 1997, **22**, 239–243.
23. Poggi, Y., Allen, P. and Filippini, J. C., *Mol. Cryst. Liq. Cryst.*, 1976, **37**, 1–7.
24. Keyes, P. H., *Phys. Lett. A*, 1978, **67**, 132–134 ; Priest, R. G., *Phys. Lett. A*, 1974, **41**, 475–476.
25. Frankel, D. and Eppanga, R., *Phys. Rev. Lett.*, 1982, **49**, 1089–1092.
26. Keyes, P. H. and Shane, J. R., *Phys. Rev. Lett.*, 1979, **22**, 722–725.
27. Anisimov, M. A., Garber, S. R., Esipov, V. S., Mamnitskii, V. M., Ovodov, G. I., Smolenko, L. A. and Sorkin, *Sov. Phys. JETP*, 1977, **45**, 1042–1047; Anisimov, M. A., Zaprudskii, V. M., Mamnitskii, V. M. and Sorkin, E. L., *JETP Lett.*, 1979, **30**, 491–494; Anisimov, M. A., *Mol. Cryst. Liq. Cryst.*, 1986, **162**, 1.
28. Nelson, D. R. and Pelcovits, R. A., *Phys. Rev. B*, 1977, **16**, 2191–2199.
29. Vigman, P. B., Larkin, A. I. and Filev, V. M., *Sov. Phys. JETP*, 1976, **41**, 944–948.
30. Mukherjee, P. K., *Liq. Cryst.*, 1998, **24**, 519–523.
31. Vause, C. and Sak, J., *Phys. Rev. B*, 1978, **18**, 1455–1463.
32. Mukherjee, P. K., *J. Chem. Phys.*, (in press).
33. Trimper, S., *Phys. Stat. Sol.(b)*, 1987, **141**, 369–375.
34. Wang, Z. H. and Keyes, P. H., *Phys. Rev. E*, 1996, **54**, 5249–5262.
35. Rzoska, A. D., Rzoska, S. J. and Ziolo, J., *Phys. Rev. E*, 1996, **54**, 6452–6456; ibid, 1997, **55**, 2888–2891.
36. Mukherjee, P. K., Ph D thesis, Calcutta University, 1996.
37. Mukherjee, P. K. and Mukherjee, T. B., *Phys. Rev. B*, 1995, **52**, 9964–9969.
38. Mukherjee, P. K., *Mod. Phys. Lett. B*, 1996, **10**, 771–775.
39. Mukherjee, P. K., *J. Chem. Phys.*, (in press).
40. Mukherjee, P. K., Saha, J., Nandi, B. and Saha, M., *Phys. Rev. B*, 1994, **50**, 9778–9780.
41. Mukherjee, P. K. and Saha, M., *Phys. Rev. E*, 1995, **51**, 5745–5747.
42. Priest, R. G. and Lubensky, T. C., *Phys. Rev. B*, 1976, **13**, 4159–4171.
43. Mukherjee, P. K. and Saha, M., *Mol. Cryst. Liq. Cryst.*, 1997, **307**, 103–110.
44. Wilson, K. G., *Phys. Rev. B*, 1971, **4**, 3174–3183; 3184–3205.

ACKNOWLEDGEMENTS. I thank Prof. Y. Singh for useful discussions and comments during my TPSC visit at BHU. Special thanks go to Dr C. D. Mukherjee for critical reading of the manuscript.

Received 19 January 1998; revised accepted 29 April 1998