The $T_{NI} - T^*$ puzzle of the nematic-isotropic phase transition

REVIEW ARTICLE

The $T_{NI} - T^{\star}$ puzzle of the nematic–isotropic phase transition

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Abstract. The low value of $(T_{NI} - T^{\star})/T_{NI}$, where T_{NI} is the nematic–isotropic phase transition temperature and $T^{\star}$ denotes the virtual transition temperature, is a long-standing puzzle in the physics of liquid crystals. The present review presents experimental and theoretical results on this long-standing problem. New experimental and theoretical results for the critical behaviour in the isotropic phase of nematogens are reviewed. We calculate in a unified approach the low value of $(T_{NI} - T^{\star})/T_{NI}$, at both critical and tricritical points. The possibility of 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.

Contents

1. Introduction

Liquid crystals (LC) are among the most interesting condensed states of matter; they are interesting in their own right and we also expect that insights into their properties will help us to understand other condensed phases that exist in nature. A unique feature of LC is that they are soft systems on a macroscopic scale. Another unique 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. In all LC phases there are thermally excited fluctuations. Depending on the spatial dimensionality along with the symmetry and range of interparticle interactions, these fluctuations can play roles of varying significance in determining the properties of matter. The fluctuations also profoundly alter the character of the LC material properties in the vicinity of phase transitions. Sometimes the fluctuations are so important as to prevent the establishing of phases which the interactions between the molecules would otherwise favour.

The most studied phase transition in liquid crystals is the nematic–isotropic (NI) phase transition. Since research on the NI phase transition has been continuous over the past few decades (de Gennes and Prost 1993, Gray 1976, Chandrasekhar 1992, de Jeu 1980, Priestly *et al* 1975, Vertogen and de Jeu 1988, Anisimov 1991), it is surprising that there are still no clear answers to some key questions concerning the nature of this phenomenon. Early theories include the phenomenological model of de Gennes (1969, 1971) and the Hamiltonian approach of Maier and Saupe (1958). Yet, despite these and many subsequent efforts, there remain a series of fascinating problems associated with the NI transition that are not completely resolved. First of all, it is not quite clear what makes this transition so weakly first order. The low value of $(T_{NI} - T^{\star})/T_{NI}$, where T_{NI} is the nematic–isotropic phase transition temperature and $T^{\star}$ denotes the virtual transition temperature, is a long-standing puzzle in the physics of liquid crystals, despite numerous theories having been advanced. The very nature of the critical behaviour is not properly understood. Fluctuations have long been known to be an important feature of the NI transition, but so far relatively little is known about the fluctuation phenomena (critical phenomena) near the NI transition. The specific heat capacity of the NI transition is also contradictory. In order to gain insight into these problems, several workers (Anisimov *et al* 1977, 1979, Shih *et al* 1976, Gohin *et al* 1983, Fan and Stephen 1970, Stinson and Litster 1970a, b, Priest 1974, 1978, Keyes 1978, Keyes and Shane 1979, Poggi *et al* 1976a, b, c) showed how inclusion of fluctuations can yield considerable improvement. This was done by means of the special inhomogeneity in the order parameter in the Landau–de Gennes (LdeG) theory. Naturally such discrepancies raise many questions regarding our understanding of the NI transition.

The properties of the NI phase transition have attracted considerable attention recently both theoretically (Averyanov 1990, Mukherjee 1996a, b, 1997a, b, 1998a, b, c, d, e, Mukherjee *et al* 1994, 1995, Mukherjee and Mukherjee 1995, Mukherjee and Saha 1995, Nandi *et al* 1996, Mukhopadhyay and Mukherjee 1997, Sengupta and Fayer 1995, Tao *et al* 1993, Zhang *et al* 1992, 1993, Wang and Keyes 1996) and experimentally (Rzoska 1998, Rzoska *et al* 1996a, b, 1997, Lelides *et al* 1993, Rjumtsev *et al* 1995). In this review we shall present a summary of the current theoretical and experimental understanding of the NI transition. There are numbers of excellent reviews (Anisimov 1988, Gramsbergen *et al* 1986, Stephen and Straley 1974) on the NI transition. But our intention in giving this review is to focus just on the $T_{NI} - T^{\star}$ problem and also criticality near the NI transition.

In section 2 we review the previous and current experimental data available. In section 3 we review the $T_{NI} - T^{\star}$ calculation of the NI transition on the basis of Landau–de Gennes theory. In this section we try to describe most of the current theoretical approaches to the study of the $T_{NI} - T^{\star}$ problem and critical properties of the NI phase transition. In some cases considerable detail is presented, while in other cases just a basic outline is given. In section 4 we discuss the $T_{NI} - T^{\star}$ calculation on the basis of renormalization-group (RG) theory. We apologize in advance to any workers in this field of research to whose work we did not give references. In section 5 we summarize our current understanding of this subject.

2. Review of experimental data: critical properties

The experimental determination of the critical-like behaviour of the NI phase transition requires extensive studies of light scattering (Stinson and Litster 1970a, b, 1973), the Kerr effect (Rjumtsev *et al* 1995), the Cotton–Mouton effect and the non-linear dielectric effect (Rzoska and Zioło 1994, Rzoska *et al* 1996a, b, 1997, Rzoska 1998). All such studies exhibit the same classical pretransitional anomaly in the isotropic phase of nematogens.

A salient feature of nematic liquid crystals (NLC) is that they have generic long-range correlations even far from critical points or hydrodynamic instabilities (Dorfman *et al* 1994) that could make it difficult to access the critical regimes before being finessed by a first-order phase transition. Due 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* (1976a, b, c) for example obtained a critical exponent $\beta = 1/2$ (classical) for the order parameter versus temperature in methoxybenzylidene butylaniline (MBBA). Keyes, however, has shown (Keyes 1978) 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 (Frenkel and Eppenga 1982), although their measurements are by no means unambiguous. Keyes and Shane (1979) suggested that the critical exponents for quantities diverging toward temperature $T^\star$, before being cut off by a first-order transition at T_{NI}, should be the identifying characteristic of a tricritical point. The difference between critical and tricritical behaviour of the NI transition is difficult to verify. The main reason to suspect tricritical behaviour is the value of β. For the exponent β, a best value of

$$\beta = 0.247 \pm 0.01$$

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 the 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. The results of early investigations (Mayer *et al* 1972, Sorai *et al* 1974, Anisimov *et al* 1979) of the heat capacity anomaly near the NI transition were so contradictory that sometimes they did not allow even a qualitative interpretation. Anisimov *et al* (1977) measured the temperature dependence of the specific heat for MBBA near the NI transition. The analysis of the temperature dependence of the specific heat showed that the fluctuations of the order parameter are not small at the phase transition point. Concerning the specific heat phenomena, Anisimov *et al* (1977, 1979) gave a strong argument in favour of the tricritical hypothesis, fitting their data from very precise specific heat measurements on MBBA and other compounds.

Recently Rzoska *et al* (1996a, b) discussed the critical behaviour of the dielectric permittivity in the isotropic phase of nematogens. They showed that the dielectric permittivity towards the NI phase transition follows the same pattern as in critical binary solutions. They obtained the critical exponent

$$\phi = 0.5 \pm 0.03$$

of the dielectric permittivity versus temperature for HCPP. This value suggests fluid-like critical behaviour for $d = 3$ of the NI phase transition. Their analysis gives an adequate description of the pretransitional behaviour of dielectric permittivity in the isotropic phase of nematogens. Again, the experimental investigation (Rzoska *et al* 1997) of high-pressure studies of MBBA also shows pretransitional effects of the NI transition. Furthermore, their studies on the pressure dependence of the clearing temperature and the low-frequency non-linear dielectric effect in the isotropic phase of MBBA strongly support the above theoretical analysis. Their experimental results show the close relationship between the pretransitional behaviour in the isotropic phase of nematogens and that in the homogeneous phase of critical solutions. Therefore the study of the pretransition (fluctuation) phenomena near the first-order phase transitions can reveal the physical reasons for their closeness to the second order.

3. $T_{NI} - T^{\star}$ calculation from the Landau–de Gennes theory

3.1. The nematic order parameter

The identification of the appropriate order parameter (OP) for NLC is aided by a consideration of the observed structure and symmetry of the phase. An ordinary isotropic liquid has full rotational and translational symmetry. The centres 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 3D space with 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 groups $D_{\infty h}$. Thus the uniaxial nematic phase has the symmetry $S = R^3 \Lambda D_{\infty h}$. In NLC the molecules are, on average, aligned with their long axes parallel. Macroscopically, a preferred direction is thus defined. It is assumed (de Gennes and Prost 1993) that the corresponding primary OP has the symmetry of a second-rank traceless tensor (Indenbom and Loginov 1981), the components of which can be written as follows:

$$Q_{ij}(\boldsymbol{r}) = l_i l_j - \frac{1}{3}(l_i l_k)\delta_{ij} = Q(\boldsymbol{r})\left[n_i(\boldsymbol{r})n_j(\boldsymbol{r}) - \frac{1}{3}\delta_{ij}\right]. \tag{1}$$

It represents local averages of bilinear combinations formed by projections of the unit vector $\boldsymbol{l}$ 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 $Q(\boldsymbol{r})$ defines the fraction of molecular axes pointing along $\hat{n}$ at a given point. $Q = \langle 3\cos^2(\theta) - 1\rangle/2$, where θ is the angle made by the long molecular axis with $\hat{n}$ and the brackets $\langle \cdots \rangle$ denote the ensemble average. Thus in the isotropic phase $Q(\boldsymbol{r}) = 0$, and in the nematic phase $Q(\boldsymbol{r}) \neq 0$. Let us note that equation (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.

3.2. Density effects at the NI phase transition

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 over 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 $(T_{NI} - T^{\star})/T_{NI} \sim 0.1\%$ (Shih *et al* 1976, Fan and Stephen 1970, Stinson and Litster 1970a, b, 1973); here T_{NI} is the NI transition temperature and $T^{\star}$ denotes the virtual transition temperature or the supercooling temperature. The most successful theory of the NI phase transition is the LdeG theory. On the lower-temperature side, the LdeG theory of phase transitions can explain the abnormal change well, but the upper-temperature side does not yield any abnormality in the thermodynamic derivatives (Maier and Saupe 1958, 1959, 1960, Alben 1970). The statistical continuum theory of de Gennes has succeeded in explaining many experiments, e.g. ones based on light scattering (Stinson and Litster 1970a, b), shear-wave attenuation (Martinoty *et al* 1971), ^{14}N nuclear magnetic relaxation (Cabane and Clark 1970), anomalous heat capacities (Imura and Okano 1972, Mukherjee 1998c), turbidity (Lin *et al* 1980) and the non-linear dielectric effect (Rzoska and Zioło 1994, Rzoska *et al* 1996a, b).

For purely geometrical reasons, the NI transition is first order, as was recognized by Landau. The LdeG model containing a cubic term in the order parameter in the free-

energy expansion was proposed (de Gennes 1969, 1971) and used to describe the first-order transition in LC. We start from the expansion of the LdeG free-energy density in powers of the tensor order parameter Q_{ij}:

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

which contains a cubic invariant, as the states with parameters 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 $A = a(T - T^\star)$. Here a, B and C are positive constants and $T^\star$ is a temperature close to the transition temperature T_{NI}.

For a uniform uniaxial LC, substituting in equation (1) leads to the free-energy expansion

$$F = F_0 + \frac{1}{2} A Q^2 - \frac{1}{3} B Q^3 + \frac{1}{4} C Q^4. \qquad (3)$$

The presence of the cubic term in equation (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 the 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 $\delta = (T_{NI} - T^\star)/T_{NI}$. If B were absent, $T^\star$ would be the MF (mean-field) second-order transition temperature. But since in our model $B > 0$, $T^\star$ is the temperature of the absolute stability limit of the isotropic phase.

de Gennes and Prost (1993) have pointed out how MS theory implies that $(T_{NI} - T^\star)/T_{NI}) \approx 8.0\%$ from the model (3). The difference $(Q^\star - Q_{NI})/Q_{NI}$ is experimentally found to be of the order of a few per cent instead of 50% as predicted theoretically (Anisimov 1991). In order to gain insight into this problem, several workers showed how the inclusion of fluctuations can yield considerable improvement. This was done by means of the special inhomogeneity in the order parameter in LdeG theory. These calculations include Gaussian fluctuation only. To include higher-order fluctuation, Priest (1978) carried out a RG calculation to show that $T_{NI} - T^\star = 12.8$ K. Zhang *et al* (1992, 1993) studied the nature of the orientational phase transition in the 3D Lebwohl–Lasher model of LC by means of computer simulation. They obtained an impressive value of $(T_{NI} - T^\star)/T_{NI}$. Again, Tao *et al* (1993) argued that, since fluctuation effects are higher-order effects, a correction for the MF calculation should be considered first. They included a density-dependent term in the pseudopotential and have shown how just one adjustable parameter can give consistent results for $(T_{NI} - T^\star)/T_{NI}$ and also for the specific volume change at T_{NI}. In support of their contention, they have shown how some other thermodynamic results (namely values of dT_{NI}/dP and $d(\ln T_{NI})/d(\ln V)$) could be reasonably well reproduced using the already adjusted value of the aforementioned parameter. In some recent work (Mukherjee *et al* 1995, Nandi *et al* 1996, Mukhopadhyay and Mukherjee 1997) it has been shown how a density-dependent term in the LdeG free-energy expansion (3) gives consistent results for $T_{NI} - T^\star$ and $Q^\star - Q_{NI}$ as compared to the experimental findings.

In order to reveal the density effect at the NI transition, the free-energy density (3) can be written (Mukhopadhyay and Mukherjee 1997) as

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

The term $E\rho^2$ is the free-energy density of the isotropic phase. The coefficients λ_1 and λ_2 are coupling constants. A minimization of the free energy results in the following renormalization (Mukhopadhyay and Mukherjee 1997) of the expansion coefficients:

$$A = A^\star + \frac{2\lambda_1 M}{E} \qquad (5)$$

$$B = B^\star - \frac{3\lambda_2 M}{E} \tag{6}$$

$$C = C^\star - \frac{2\lambda_1^2}{E}. \tag{7}$$

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

$$T_{NI} = T^\star - \frac{2\lambda_1 \rho}{a_1}. \tag{8}$$

Thus the coupling constant λ_1 determines the shift of the transition temperature (8) and can be found easily from experiment:

$$\lambda_1 = -\frac{a_1}{2} \frac{\mathrm{d} T_{NI}}{\mathrm{d}\rho}. \tag{9}$$

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

In the presence of density, the modified form of the temperature $T^\star$ in equation (3) can be expressed as

$$T^\star(\rho) = T_0^\star + \alpha_1(\rho - \rho_0) + \alpha_2(\rho - \rho_0)^2. \tag{10}$$

Here α_1 and α_2 are positive constants and ρ_0 is the equilibrium density without order parameter–density coupling. $T_0^\star$ is the MF absolute stability limit of the isotropic phase in the absence of any density–order parameter coupling. In this case the free energy (3) takes the form

$$
\begin{aligned}
F(\rho, Q, T) = F_0(\rho) &+ \frac{a}{2}(T - T_0^\star)Q^2 - \frac{B}{3}Q^3 + \frac{C}{4}Q^4 \\
&+ \frac{\eta_1}{2}(\rho - \rho_0)Q^2 + \frac{\eta_2}{2}(\rho - \rho_0)^2 Q^2.
\end{aligned}
\tag{11}
$$

The transition temperature T_{NI} and the value of $Q^\star$ (at $T = T^\star$) are calculated as

$$T_{NI} = T_0^\star + \frac{2B^2}{9aC} - \frac{\eta_1(\rho_N^t - \rho_I^t)}{a} - \frac{\eta_2(\rho_N^t - \rho_I^t)^2}{a} \tag{12}$$

$$Q^\star = \frac{B}{2C}\left[1 + \left(1 - \frac{4\eta_1 C}{B^2}(\rho - \rho_0) - \frac{4\eta_2 C}{B^2}(\rho - \rho_0)^2\right]^{1/2} \tag{13}$$

where ρ_I^t and ρ_N^t are the nematic and isotropic densities at T_{NI}. It was shown (Mukherjee *et al* 1995) that with the Landau expansion parameters fixed, utilizing some experimental data, the calculated values of $\mathrm{d}T_{NI}/\mathrm{d}P$ ($=41.50$ K kbar^{-1}) and $\mathrm{d}(\ln T_{NI})/\mathrm{d}(\ln V)$ ($=-0.3964$) tally well with the experimental results (20–40 K kbar^{-1} and -0.3964) and also with a low value of $T_{NI} - T^\star = 0.9998$ K. However, $Q^\star - Q_{NI}$, instead of being very close (within approximately 2% experimentally), remains about 50% of the value obtained in the LdeG theory without incorporating any effect of density variation. This $Q^\star - Q_{NI}$ discrepancy implies that the change in the value of the calculated order parameter over a small temperature interval of 1 K (as $T_{NI} - T^\star = 1$ K) would be much higher than that observed in experiments. In fact, the value of 0.3998 of $(\mathrm{d}Q/\mathrm{d}T)_{T=T_{NI}}$ that we obtain is at

variance with the observed value of 0.008. Thus the pressure dependence shows strongly pretransitional effects at the NI transition. This clearly shows that a complete resolution of the $T_{NI} - T^\star$ 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* (1993) and also bring out the inadequacy as regards explaining the small value of $(Q^\star - Q_{NI})/Q_{NI}$ and $(dQ/dT)_{T=T_{NI}}$ in the LdeG framework.

As can be seen from equations (5) and (7), 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 vanish simultaneously, such a point is called tricritical. Since the coefficients C and A have the same symmetry, $C = A = 0$ gives a TCP. 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

$$F = \frac{A}{2}Q^2 - \frac{B}{3}Q^3 + \frac{C}{4}Q^4 + \frac{E}{6}Q^6. \tag{14}$$

With expression (14), one can have a TCP for $B = 0$, $C = 0$. One way of studying the weakly first-order NI transition occurring near a TCP would be to have B take a small non-zero value. Then the free-energy expression (14) would take the form (Gramsbergen *et al* 1986, Mukherjee 1997a, Mukherjee *et al* 1994, Mukhopadhyay and Mukherjee 1997)

$$F = \frac{A}{2}Q^2 - \frac{B}{3}Q^3 + \frac{E}{6}Q^6. \tag{15}$$

The calculated value of $T_{NI} - T^\star$ obtained from the scaling equation of state (Mukherjee 1997a) of the model (15) is 7.68 K (without density variation). The model (15) also gives the value $(Q^\star - Q_{NI})/Q_{NI} \approx 26\%$, which shows an improvement of 50% over the previous model (3). These results are quite encouraging, but the value of $(Q^\star - Q_{NI})/Q_{NI}$ leaves ample scope for improvement. Again taking into account the density variation (Mukhopadhyay and Mukherjee 1997) in the model (15), one obtains $T_{NI} - T^\star \approx 0.9999$ K, but the value of $(Q^\star - Q_{NI})/Q_{NI} \approx 26\%$ is hardly any improvement. However, we can present yet another approach for studying the NI transition occurring near a TCP. We can do this by taking $B = 0$ in equation (14). The first-order nature of the NI transition and the neighbourhood of the TCP can both 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 for the nematic phase. This only implies that as the critical point is approached, the already small entity becomes even smaller, and so can be neglected. This only points to the inadequacy in the Landau scheme of keeping all of the coefficients, except A, constant. In this case the free-energy density in the vicinity of TCP takes (Mukherjee 1998d) the following form:

$$F = \frac{A}{2}Q^2 - \frac{C}{4}Q^4 + \frac{E}{6}Q^6. \tag{16}$$

The value of $T_{NI} - T^\star$ calculated from the scaling equation of state is 2.55 K. The model (16) gives the value $(Q^\star - Q_{NI})/Q_{NI} \approx 15.47\%$, which shows an improvement of 70% over the previous results. However, the low value of $T_{NI} - T^\star$ with the high value of $Q^\star - Q_{NI}$ or an equivalent high value of $(dQ/dT)_{T=T_{NI}}$ seems to be glaringly inconsistent, which supports the molecular MF results.
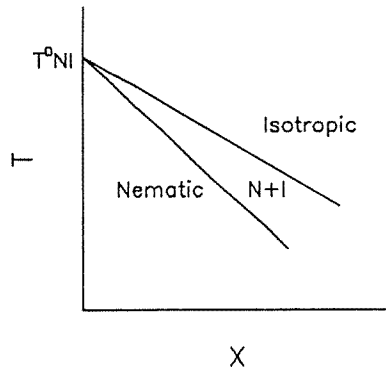
Figure 1. A typical temperature (T) versus concentration (x) diagram for a low solute mole fraction.

3.3. The influence of non-mesogenic impurities on the NI phase transition

Generally, all real nematics 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 non-mesogenic impurities to a pure nematic leads to a broadening of the NI transition temperature and the appearance of a two-phase region (see figure 1). It was shown (Luckhurst and Gray 1979, Mukherjee 1997b) 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 (Mukherjee 1997b):

$$T_{NI} - T_{NI}^0 = \frac{\Delta x}{\Delta S_{NI}} \tag{17}$$

where Δx and ΔS_{NI} are the width of the two-phase region and the entropy of the pure nematic solvent. Hence for $\Delta S_{NI} \neq 0$, a two-phase region must exist at a fixed temperature. For a second-order transition, $\Delta S_{NI} = 0$, i.e. the two-phase region disappears. The form of the two-phase region (see figure 1) is determined by two factors:

(1) anomalously small values of the coefficients B and C in expansion (14);
(2) non-ideality of the mixture.

The smallness of B means that the transition is close to being second order. In the case where $B = 0$, non-ideality of the solution may lead to the appearance of a TCP due to the coupling between the order parameter and the concentration. If the transition in a mesogenic solvent is very near to a TCP ($C \ll 1$), the phase diagram for a dilute solution has the form presented in figure 2. Hence from the above analysis it is clear that there is a possibility of tricritical behaviour in the presence of impurities at the NI transition.

3.4. Critical behaviour near the NI phase transition

The influence of electric and magnetic fields has been investigated extensively by many authors both theoretically (de Gennes 1969, Priestly *et al* 1975, Poggi *et al* 1976a, b, c, Dunmur and Tomes 1981, Palffy-Muhoray and Dunmur 1982, 1983, Savithramma and Madhusudana 1983) and experimentally (Nicastro and Keyes 1984, Helfrich 1970, Fan and Stephen 1970, Rosenblatt 1981, 1982, 1983). When there are no external magnetic
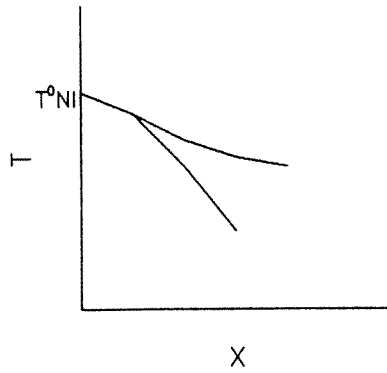
Figure 2. The phase diagram of a dilute solution in the case of tricritical behaviour of the pure solvent.

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 digram is thus analogous to that of a liquid–gas system in the temperature–pressure plane. The first experimental evidence of an electrically induced critical point was given by Nicastro and Keyes (1984).

The physical consequences of the LdeG theory will now be investigated for the case where an external field is induced. The LdeG free energy in the presence of an external magnetic field is obtained (de Gennes 1969, 1971) from

$$F = F_0 + \frac{A}{2} Q^2 - \frac{B}{3} Q^3 + \frac{C}{4} Q^4 + D(\nabla Q)^2 - HQ. \tag{18}$$

The value of Q in the para-nematic phase is small and therefore can be obtained (Gramsbergen *et al* 1986) from equation (18) while disregarding the terms containing B and C ($\nabla Q = 0$):

$$Q(H) = H/a(T - T^\star). \tag{19}$$

The jump of the order parameter at the NI phase transition is directly related to the value of the field. It decreases with the increasing field until the critical field H_C is reached where there is no longer any jump. At this point, the transition becomes second order. For fields higher than H_C, there is no phase transition and the nematic and para-nematic phases are indistinguishable. The location of the critical point is given (Gramsbergen *et al* 1986, Mukherjee 1996a, b) by ($\nabla Q = 0$)

$$H_C = \frac{B^3}{27C^2} \tag{20}$$

$$T_C = T^\star + \frac{B^2}{3aC} \tag{21}$$

$$Q_C = \frac{B}{3C}. \tag{22}$$

Near the critical point we find (Mukherjee 1996a, b)

$$\Delta T_{\text{critical}} \simeq \frac{1}{128\pi^2}\left(\frac{k_B^2 T_{NI}^2 C^2}{aD^3}\right). \tag{23}$$

In order to find T_{NI} outside this critical region, the following inequality has to be fulfilled:

$$T_C - T_{NI} > \Delta T_{\text{critical}} \tag{24}$$

or

$$D^3 > \frac{9}{128\pi^2}\left(\frac{k_B^2 T_{NI}^2 C^3}{aB^2}\right). \tag{25}$$

Since B varies strongly with T, and P may be zero, this inequality can be obeyed only if B is greater than B_1, which is the value of B for which (23) is an equality. Thus if $B^2 < B_1^2$, we may observe a critical region at $H = 0$. Hence near an isolated critical point on the NI transition line, we find 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 see (Mukherjee and Mukherjee 1995) that a model (2) with a 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 breaking. 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 the non-analyticity appears at the critical point (the 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 nicely agrees with recent experimental observations (Rzoska *et al* 1996a, Rzoska 1998).
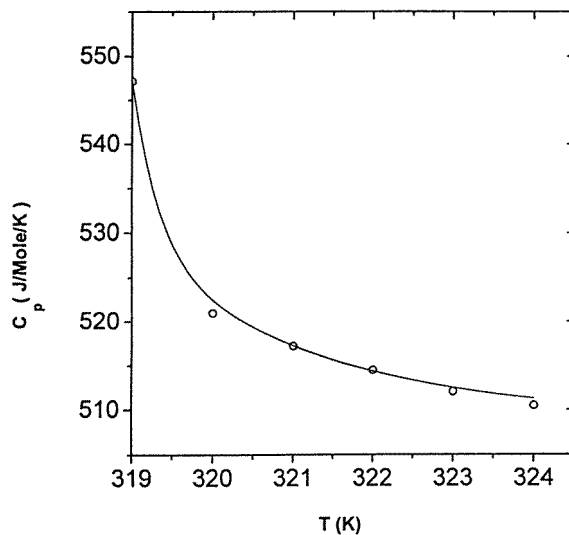
Figure 3. The specific heat capacity (C_P) versus temperature (T) for MBBA. The solid line shows theoretical data and the open circle shows the experimental data.

The anomalous parts of the specific heat capacity of NLC above the transition point were discussed by Imura and Okano (1972) and Mukherjee (1998c) on the basis of the continuum theory of de Gennes. The excess specific heat capacity at constant pressure (per volume) due to fluctuation is given (Mukherjee 1998c) by

$$\Delta C_P(T) = 2.54 \times 10^{-4} T^2 [T - 318.7]^{-1/2} \text{ J mol}^{-1} \text{ K}^{-1}. \tag{26}$$

The experimental and theoretical heat capacities are displayed in figure 3. For the case of MBBA the experimental points of Anisimov *et al* (1977) are found to be well reproduced by the empirical formula (26). The amplitude of the order parameter fluctuation increases abnormally near T_{NI} and it brings about anomalous increments in the 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 probably, a macroscopically inhomogeneous distribution of impurities. This analysis clearly indicates the pretransitional phenomena of NLC. This pretransitional phenomena indicate that the NI transition is close to being second order.

4. $T_{NI} - T^\star$ calculation from renormalization-group theory

The fluctuations near NI phase transitions were studied by several authors (Nelson and Pelcovits 1977, Mukherjee *et al* 1994, Mukherjee and Saha 1995, 1997, Mukherjee 1998b, Mukherjee and Mukherjee 1995, Priest and Lubensky 1976, Priest 1978, Sluckin and Shukla 1983, Trimper 1987, Vigman *et al* 1976) using the RG technique.

In the nematic phase the '*director*' fluctuations are critical. Nelson and Pelcovits (1977) pointed out that strongly developed director fluctuations could alter the character of the NI transition and make it very weakly first order. Recently, Wang and Keyes (1996) 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. Vigman *et al* (1976) 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 where $A = B = 0$, where the jump in the order parameter vanishes. Several workers investigated the Landau point with fluctuation by means of Landau theory (Mukherjee 1998a) and the epsilon expansion method (Vause and Sak 1978, Vigman *et al* 1976, Mukherjee 1998b). The values of the critical exponents for the five components of the order parameter ($n = 5$) at $d = 3$, $\epsilon = 1$, 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 (1987) studied the NI transition in $2 + \epsilon$ dimensions. Applying the procedure in $2 + \epsilon$ dimensions he showed that the phase transition remains second order with a 'transition temperature' proportional to ϵ. The numerical calculation (Mukherjee and Saha 1997) of the critical exponents of the NI transition also agrees well with the best epsilon expansion results.

In some very recent work (Mukherjee *et al* 1994, Mukherjee and Saha 1995) we used the RG technique to calculate $T_{NI} - T^\star$ for the NI transition. The model free energy of the LdeG form can be written as

$$F = \int d^d x \left[\frac{1}{4} (A Q_{ij}^2 + \nabla_k Q_{ij} \nabla_k Q_{ij}) - B Q_{ij} Q_{jk} Q_{ki} + C (Q_{ij} Q_{ij})^2 - H_{ij} Q_{ij} \right]. \tag{27}$$

Here $d^d x$ indicates a functional integral in d dimensions over the tensor field $Q = Q(x)$. The external field H_{ij} is set to the uniaxial form

$$H_{11} = H \qquad H_{22} = H_{33} = -\frac{H}{2}.$$

The model (27) was studied extensively by Priest and Lubensky (1976) using the ϵ ($=4-d$) expansion method. 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 the epsilon expansion is obtained (Mukherjee *et al* 1994) as

$$\frac{H}{Q^\delta} + \frac{B}{Q^\omega} = f(x). \tag{28}$$

The result for

$$f(x) = 1 + x + \epsilon f_1(x) + \epsilon^2 f_2(x) \tag{29}$$

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

$$\delta = 3 + \epsilon \qquad \omega = 1 + \frac{7\epsilon}{13} \qquad \beta = \frac{1}{2} - \frac{3\epsilon}{26}. \tag{30}$$

The quantity t is the reduced temperature $t = (T - T^\star)/T^\star$. The quantity t is also the temperature at which the second-order phase transition would take place if B were zero. Therefore, $T^\star$ 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 must be equal and that the free energy must be a local minimum with respect to Q can be expressed as

$$\int_0^Q H(Q') \, dQ' = 0 \tag{31}$$

$$H(Q) = 0. \tag{32}$$

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 $t_{NI} = (T_{NI} - T^\star)/T^\star$. This requires a numerical solution of equations (31) and (32) as a function of B by putting in the experimental value $Q_{NI} = 0.4$. One obtains the value $T_{NI} - T^\star = 7.4699$ K. The major advantage of this method over the earlier methods described above is that this method needs only one experimental datum input—namely the jump in the order parameter at T_{NI}. Although this result is more encouraging than those from previous work (Priest 1978), it is still far away from the experimental finding. In order to improve this result we now extend this calculation near the coexistence curve (Mukherjee and Saha 1995). Here, the coexistence curve is defined as the region of small external field and below the critical temperature. NLC are arrangements of approximately parallel molecules whose centres of mass have no long-range order, like ordinary liquids. Interactions between the molecules are invariant under simultaneous rotation of the axis of the molecules about their centre of mass. The director fluctuations correspond to the dynamical mode which is critical for all temperatures in the nematic phase. This has been tested both experimentally and theoretically.

Considering the uniaxial system with a continuous symmetry, there exist massless modes: Goldstone bosons at all temperatures $T < T_C$ (the 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 scaling form of the equation of state near the coexistence curve is obtained (Mukherjee and Saha 1995) as

$$\frac{H}{Q^\delta} + \frac{B}{Q^\omega} = x + 1 + \frac{\epsilon}{26}[4\ln(x+1) + 3 + 9\ln 2 - 9\ln 3](x+1)$$
$$+ \frac{\epsilon^2}{676}\left[-10\ln^2(x+1) + \left(72\ln 2 - 36\ln 3 + \frac{1424}{13}\right)\ln(x+1)\right](x+1). \tag{33}$$

Again applying the same thermodynamic conditions (31) and (32), the improved value of $T_{NI} - T^\star$ is obtained near the coexistence curve (Mukherjee and Saha 1995) as $T_{NI} - T^\star = 3$ K. The closeness of this result to the observed value $T_{NI} - T^\star = 1$ K supports the idea that a RG calculation can lead to the resolution of the $T_{NI} - T^\star$ 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.

5. Conclusions

The low values of $(T_{NI} - T^\star)/T_{NI}$ and $(Q^\star - Q_{NI})/Q_{NI}$ pose a long-standing puzzle, despite numerous theories of the NI transition having been advanced. Furthermore, 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 low value of $T_{NI} - T^\star$ near the hypothetical coexistence curve along with exponents $\phi = 0.5 \pm 0.03$ of the dielectric permittivity suggest fluid-like critical behaviour for $d = 3$ of the NI phase transition. The consistent values of $T_{NI} - T^\star$ and $(Q^\star - Q_{NI})/Q_{NI}$ along with β- and Δ-values suggest a 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 Hamiltonians, or perhaps better approximations than those used here are also needed. In short, for the NI transition we do not have the final word as yet. We hope that the present analysis will encourage researchers to take a fresh look at this old but still unsolved problem.

Acknowledgments

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