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Influence of non-mesogenic impurities on a nematic to isotropic phase transition

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Non-mesomorphic solutes depress the normal nematic–isotropic transition temperature in liquid crystals. When non-mesomorphic solutes are added to a nematic liquid crystal, the nematic–isotropic transition temperature is depressed and a two phase region is formed due to the presence of impurities of the solutes. The present paper explains the formation of this two phase region by the Landau–de Gennes phenomenological theory, which agrees fairly well with the experimental observations. We also note that this two phase region indicates the tricritical behaviour of the nematic–isotropic phase transition and the phase diagram near the tricritical point is also obtained.

1. Introduction

As one of the earliest findings which indicate the existence of the liquid crystalline phase, the nematic–isotropic (N–I) transition has been a topic of active theoretical and experimental studies over the past few decades [1]. Although the N–I phase transition is one of the most ubiquitous found in nature, it is also one of the least understood. Although the N–I phase transition is weakly first order, Keyes [2] suggested that the critical exponents for quantities diverging toward temperature T^* (T^* is defined as the temperature of the absolute stability limit of the isotropic phase), before being cut-off by a first order transition at T_{NI}, should be characteristic of a tricritical point. According to Keyes and Shane [3], the N–I transition does, in fact, exhibit tricritical exponents and a magnetically induced critical point (the termination of the N–I coexistence line in a field versus temperature diagram).

Generally all real nematics contain impurities. It is well known [4] that solute impurities which are not sufficiently rod-like and rigid in molecular structure depress the N–I transition temperature. Hence, the addition of non-mesogenic impurities to the pure nematic leads to a broadening of the N–I transition temperature and the appearance of a two phase region (see figure 1). It is clear [5] that the width of the two phase region is proportional to the entropy of the solvent. Normally, the N–I transition temperature decreases with the increase of concentration. This is entirely consistent with the laws of thermodynamics and the first order nature of the N–I transition (enthalpy change $\Delta H \neq 0$ [6, 7], volume change $\Delta V \neq 0$ [8], order parameter change $\Delta Q \neq 0$ [9, 10]. The general phase behaviour at low solute mole friction x is illustrated in figure 1. Several workers have explained the formation of this two phase region from a thermodynamic point of view. The possible existence of this two phase region has been examined theoretically using a variety of models, although they are all founded on a purely repulsive potential between the constituent particles [11–14]. As a consequence the majority of theories employ a lattice model in order to simplify the calculation of the configurational partition function. Indeed the calculation then reduces to a coupling problem which is solved using the scheme devised by Di Marzio [15] and extended by Alben [16]. All of the models predict the existence of a two phase region and there can be no doubt concerning the qualitative correctness of this conclusion. There is however considerable uncertainty as to the quantitative aspects of these calculations because of the inherent deficiencies of the lattice model [17]. The statistical theories of nematics based on such potentials, handled within the molecular

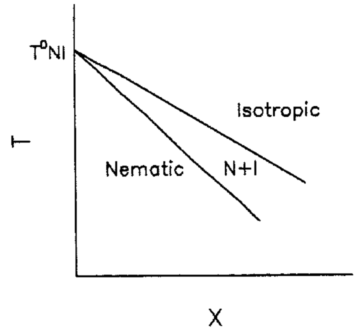

Figure 1. Typical temperature (T) versus concentration (x) diagram at a low solute mole fraction.

field approximation have met with considerable success in accounting for the orientational properties of the mesophase [18–23].

In the present paper, this behaviour has been studied in the context of the Landau–de Gennes phenomenological theory. I have explained the phase diagrams of dilute solution of a non-mesogenic substance in a nematic liquid crystal both for large and small impurity concentrations which agree fairly well with the experimental observations. It is also shown how the coupling of the concentration and also of the order parameter shift the N–I transition temperature. We also see that this two phase region indicates the tricritical behaviour of the N–I phase transition.

2. Theory and results

For purely geometrical reasons the N–I transition is first order, as was recognized by Landau [24]. Thus the Landau–de Gennes expansion of the order parameter Q can be written as

$$F = F_o + \frac{1}{2}AQ^2 - \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4, \tag{1}$$

where B and C are constants and $A = a(T - T^*/T_{NI})$. T^* is a temperature slightly below the N–I transition temperature T_{NI}, below which no stable isotropic phase can exist.

Landau theory has been widely applied to a number of different phase transitions; examples where the order parameter couples to some other variables are also common [25, 26]. In the present case we want to describe the coupling of the order parameter Q and the relative concentration x of the binary mixture. The simplest assumption is to add a term in equation (1) of the form $g(x)Q^2$, expand $g(x)$ as a power series in x and keep only the leading terms. The Landau–de Gennes free energy of the binary mixture can then be expressed as

$$F^*(T, P, Q, x) = F_o + \frac{1}{2}A_oQ^2 - \frac{1}{3}B_oQ^3 + \frac{1}{4}C_oQ^4 + \frac{1}{2}A_M x^2 + \frac{1}{2}\lambda Q^2 x, \tag{2}$$

where $A_o = a_o(T - T^*)/T^{\circ}_{NI}$. T°_{NI} is the temperature of the N–I transition in the absence of coupling between x and Q, and λ is the coupling constant. Here Q is the usual order parameter of the nematic phase and x is concentration of the non-mesogenic substance. The coefficients B and C are functions of temperature and concentration. Now,

$$\left(\frac{\partial F^*}{\partial x}\right)_{T,P} = \mu^* = A_M x + \lambda Q^2 \tag{3}$$

Hence,

$$A_M = \left(\frac{\partial^2 F^*}{\partial x^2}\right)_{T,P} = \left(\frac{\partial \mu^*}{\partial x}\right)_{T,P} \tag{4}$$

and

$$\mu^* = \left(\frac{\partial F^*}{\partial x}\right)_{T,P} = x\left(\frac{\partial \mu^*}{\partial x}\right) + \lambda Q^2 \tag{5}$$

is the difference of the chemical potentials of the non-mesogenic and mesogenic substance and μ^* is the quantity thermodynamically conjugate to x, the non-mesogenic concentration.

From equation (5), we get

$$x = (\mu^* - \lambda Q^2)\left(\frac{\partial x}{\partial \mu^*}\right) = x_{NI} + \delta x \tag{6}$$

where

$$x_{NI} = \left(\mu^* \frac{\partial x}{\partial \mu^*}\right) \quad \text{and} \quad \delta x = -\lambda Q^2\left(\frac{\partial x}{\partial \mu^*}\right). \tag{7}$$

In the isotropic phase $Q = 0$, then $x = x_{NI} = \mu^*(\partial x/\partial \mu^*)$. The term δx in the concentration is related to the order parameter Q. In the case of a second order transition, $Q = 0$ and $\delta x = 0$, and in the case of a first order transition δx is proportional to Q. The temperature of the N–I transition decreases when the concentration of the solutes increases. On transforming $F^*(Q, x)$ to a free energy depending on the field variables μ^*, one obtains

$$\begin{aligned} F^*(T, P, Q, \mu^*) &= F^*(T, P, Q, x) - \mu^* x \\ &= F_o + \left[\frac{A}{2}Q^2 - \frac{B}{3}Q^3 + \frac{C}{4}Q^4\right] \end{aligned} \tag{8}$$

with the renormalized coefficients

$$A = A_o + 2\lambda\mu^* \frac{\partial x}{\partial \mu^*}, \tag{9}$$

$$B = B_o, \tag{10}$$

and

$$C = C_o - 2\lambda^2 \frac{\partial x}{\partial \mu^*} \tag{11}$$

The transition temperature is given by the condition $F = 0$ and $\partial F/\partial Q = 0$:

$$T^{\circ}_{NI} = \frac{T^*}{(1 - 2B_o^2/9a_oC_o + \lambda x/a_o)} \tag{12}$$

which shows that the NI transition temperature decreases when the non-mesogenic substance is added.

The temperature of the absolute stability limit of the nematic phase is determined by the $Q \neq 0$ solution of equation (2):

$$T^{\mathrm{o}}_{\mathrm{NI}}=\frac{T^{**}}{(1+B_{\mathrm{o}}^{2}/36a_{\mathrm{o}}C_{\mathrm{o}})} \tag{13}$$

where B_{o} and C_{o} are given by equations (10) and (11). The values of B_{o} and C_{o} change with the change of temperature and concentration.

For particular values of B and C, with the increase of the concentration, the temperature decreases, the quantity $\partial\mu^{*}/\partial x$ decreases and the constant C tends to zero, i.e. a tricritical point appears. On further variation of the temperature and concentration, the coefficient C changes sign and the transition becomes first order. For low concentration of impurities the phase diagram takes the same form as figure 1. Using the relations (12) and (13) we obtain the same phase diagram as shown in figure 1. In figure 1 for any temperature of the fixed concentration on the lower line of the diagram, is the highest temperature at which the solution is entirely nematic and for any temperature of the fixed concentration on the upper line of the diagram, is the lowest temperature at which the solution is entirely isotropic. Any temperature on the lower line of the diagram is the temperature T^{*} of the absolute stability limit of the isotropic phase. Below this line the isotropic phase is completely unstable with respect to the nematic phase. Again any temperature on the upper line of the diagram is the temperature T^{**} of the absolute stability limit of the nematic phase. Above this line nematic phase is completely unstable with respect to the isotropic phase. Therefore T^{*} and T^{**} correspond to the spinodal of the first order transition. Hence the upper and lower lines of phase diagram 1 indicate the boundary of the metastable region. Within this boundary a two phase region is formed. This two phase region is formed due to the presence of δx in x of equation (6). As soon as δx vanishes the two phase region disappears. As δx vanishes only for second order transitions, this two phase region clearly indicates the first order character of the N–I transition. In the lower line the isotropic phase begins to appear at T_{N} and the nematic phase completely disappears at T_{I}.

The form of the phase diagram (see figure 1) is determined by the values of B and C and also the non-ideality of the mixture, which may sometimes lead to phase separation in the isotropic phase. Non-ideality of the mixture appears due to the small values of B and C. The smaller the values of B, the weaker the first order character of the N–I transition. This weakness is characterized by the factor

$$\Delta=\frac{T_{\mathrm{NI}}-T^{*}}{T_{\mathrm{NI}}}\sim B^{2}.$$

For $B=0$, the transition becomes second order. Thus when a second order transition occurs then $A=0$. Thus, $A_{1}=-2\lambda x$, i.e. the critical temperature becomes

$$T_{\mathrm{C}}(x)=T^{\mathrm{o}}_{\mathrm{NI}}-\frac{2\lambda x}{a_{\mathrm{o}}}. \tag{14}$$

Thus, the coupling constant λ shifts the transition temperature and

$$\lambda=-(a_{1}/2T_{\mathrm{NI}})(\mathrm{d}T_{\mathrm{NI}}/\mathrm{d}x)>0. \tag{15}$$

The depression of the N–I transition temperature is connected with the width of the two phase region and the entropy of the transition:

$$T_{\mathrm{NI}}-T^{\mathrm{o}}_{\mathrm{NI}}=\frac{\Delta x}{\Delta S_{\mathrm{NI}}} \tag{16}$$

where T_{NI} is the temperature of the N–I transition in a pure specimen. Again,

$$\Delta S_{\mathrm{NI}}=2aB^{2}/9C^{2} \tag{17}$$

is the N–I transition entropy for a pure nematic solvent. Hence, for $\Delta S_{\mathrm{NI}}\neq 0$, a two phase region must exist at a fixed temperature. From equation (16) it is clear that the lower the values of the entropy change, the larger the depression of the N–I transition temperature. When B and C change then ΔS_{NI} also changes. Thus, when second order phase transition occurs, i.e. when $B=0$, then the entropy change $\Delta S_{\mathrm{NI}}=0$, then the two phase region disappears.

From the relations (10) and (11) it is clear that with the increase in concentration, the temperature decreases, the quantity $\partial\mu^{*}/\partial x$ and the coefficient C also decrease. If the transition in a mesomorphic solvent is very near to the tricritical point ($C\ll 1$), the phase diagram has the form represented in figure 2. On the other hand, since the coupling between Q^{2} and x makes a negative contribution to C it also decreases (even for $B=0$) the tendency to first order behaviour. Also, since for dilute solutions $(\partial\mu^{*}/\partial x)^{-1}\propto x$ one can reasonably expect that

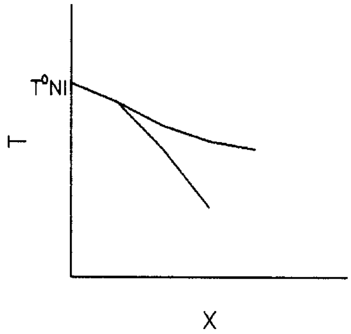

Figure 2. Phase diagram of a dilute solution in the case of tricritical behaviour for the pure solvent.

the effect of adding a second component to a pure material that exhibits a second order N–I transition may be to induce a tricritical point at some finite x. In general when two coefficients of the same symmetry in the Landau free energy vanish simultaneously such a point is called tricritical [24, 27]. Therefore, the experimental situation has led to the question whether the N–I transition is close to the tricritical point $A = C = 0$. This leads to an alternative formulation of the N–I phase transition by taking $C = 0$. In the paper of Mukherjee *et al.* [28, 29], the tricritical behaviour of the N–I transition was explained in detail. In that case a positive stabilizing E term must be added to the free energy:

$$F = F_o + \frac{1}{2}AQ^2 - \frac{1}{3}BQ^3 + \frac{1}{6}EQ^6 + \frac{1}{2}\lambda Q^2 x. \quad (18)$$

Then, the transition temperature is given by

$$T^{o}_{\mathrm{NI}} = T^* \bigg/ \left(1 - \frac{E}{a_o}(B/2E)^{1/3} + \lambda x/a_o\right). \quad (19)$$

In the case when the tricritical point appears, i.e. when $C = 0$, then the width of the two phase region [30] is given by $\Delta x \propto x^2$ and in the ordinary case $\Delta x \propto x$. The critical stratification of the mixtures occurs below the tricritical point. The heat capacity at a constant chemical potential and pressure near the critical point is given by

$$C_{\mathrm{P},\mu^*} = -T[\partial^2 F/\partial T^2]_{\mathrm{P},\mu^*} = \frac{1}{4}a^{3/2}E^{-1/2}(-t)^{-1/2} \quad (20)$$

where t, the reduced temperature, is given by $t = (T - T_{\mathrm{NI}})/T_{\mathrm{NI}}$. From equation (20) it is clear that the specific heat has a square root divergence in the two phase region. The tricritical point in ferromagnets, that appear on addition of an equilibrium non-magnetic impurity, can be described in the same way. Hence from the above analysis it is clear the two phase region of figure 1 indicates the tricritical behaviour of the N–I transition.

3. Discussion

What transpires from the above analysis is that the formation of a two phase region of a dilute solution of a non-mesogenic substance in a nematic liquid crystal depends on the small values of the coefficients B and C in expression (2). The different values of B and C indicate the depression of the N–I transition temperature and also the two phase region. The above analysis clearly indicates the tricritical behaviour of the N–I phase transition. Since the singular-like behaviour of the various quantities of the N–I phase transition is still a puzzle, the solution could well be obtained within the Landau–de Gennes theory, and the predictions of this theory should be compared with experimental findings. However, in reality, the critical stratification point of the nematic–non-mesogenic mixture is unattainable, as the temperature decreases and concentration increases, the quantities $\partial\mu^*/\partial x$ decrease and the quartic term C tends to zero, i.e. a tricritical point appears. This case also occurs in ^{3}He–^{4}He mixtures. Some puzzling questions persist, however, the present analysis is encouraging.

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