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Effects of three-body intermolecular interactions on the nematic–paranematic phase diagram

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An extension of the Maier–Saupe theory of the nematic–isotropic transition in liquid crystals, which incorporates three-body intermolecular interactions into the effective single-particle pseudopotential, is presented. Numerical calculations based on this theory are performed to investigate the effect of these three-body interactions on the nematic–isotropic transition in zero field, on the nematic–paranematic coexistence curve in the presence of an applied field, and on the mean field nematic–paranematic critical point. The zero field results are in good agreement with experimental measurements.

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1. Introduction

The nematic–isotropic transition in liquid crystals has been extensively studied in the context of mean field theory, beginning with the well-known Maier–Saupe (MS) theory [1]. The MS theory and its generalizations [2–4] are typically constructed by writing down an expression for the attractive part of the intermolecular pair potential and converting it to an effective single-particle pseudopotential by performing the appropriate averages. These theories predict a first-order nematic–isotropic (N–I) phase transition, as is observed experimentally.

The effects of an externally applied field can be incorporated into a MS-type single-particle pseudopotential in a straightforward way. This has been done by Wojtowicz and Sheng [5] (WS) and Hanus [6], who showed that in the presence of a field, the N–I transition becomes a nematic–paranematic (N–pN) transition. The N–pN transition temperature and the degree of ordering at the transition vary as a function of the field and the resulting coexistence curve ends at a critical point at a certain critical value of the field. The N–pN phase diagram has also been discussed in the framework of Landau theory [7–10].

In this paper we investigate the effects on the N–pN coexistence curve of incorporating into an MS-type single-particle pseudopotential a term which represents three-body intermolecular interactions. The effects of these interactions on the zero field N–I transition, on the shape and range of the N–pN coexistence curve, and on the behaviour of the system near the N–pN critical point are studied. This work was motivated in part by a recent paper by Vause [11], who discussed the N–pN critical point in terms of the theory of critical phenomena and thermodynamic scaling, and by the recent work of Goldstein *et al.* [12, 13], who discussed the effects of triplet interactions on the critical behaviour of liquid–vapour systems.

Vause [11] pointed out that the N–pN critical point probably belongs to the universality class of the three dimensional Ising model [14], as do liquid–vapour critical points, the Curie points of three dimensional uniaxial ferromagnets, and critical points in other real systems. He then discussed the scaling behaviour [14] of the free

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energy near the N–pN critical point. Due to the invariance of the molecular susceptibility under end-for-end rotations of the molecules, an external field h couples to the order parameter S like h^2 rather than linearly. This implies that the two relevant scaling fields are not simply proportional to h and the reduced temperature $t=(T_c-T)/T_c$, where T_c is the critical temperature, but are instead linear combinations of h and t. This field mixing is known [15] to affect the shape of the coexistence curve, and, in particular, to lead to a breakdown in the classical law of rectilinear diameter [16].

The diameter of the coexistence curve is the normalized average of the order parameters of the two coexisting phases

$$S_d=(S_N+S_{pN})/2S_c, \tag{1}$$

where S_N and S_{pN} are the order parameters in the nematic and paranematic phases, and S_c is the order parameter at the critical point. Classically, S_d is linear in t. In the presence of field mixing, however, it displays a weak singularity near T_c, where to leading order $S_d \sim t^{1-\alpha}$. Here α is the critical exponent characterizing the divergence of the specific heat at the critical point. This anomaly is not expected to appear in mean field calculations, however, since then $\alpha=0$.

Goldstein *et al.* [12, 13] argued that, at least in the case of liquid–vapour systems, the microscopic origin of this field mixing is many-body intermolecular interactions. By extending the (mean field) van der Waals model of the liquid–vapour critical point to include three-body interactions, they made predictions concerning the shape of the coexistence curve and the behaviour of the coexistence curve diameter, as functions of the importance of triplet interactions relative to pairwise interactions. These predictions were in agreement with experimental data [12, 13].

In the following the effects of triplet interactions on the mean-field N–pN coexistence curve are studied. The theory is developed in the next section. Results of numerical calculations are presented in § 3 and discussed in § 4, particularly with regard to the relevance of these calculations to the experimental situation. Section 5 is a brief conclusion.

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2. Theory

The MS theory of the N–I transition is well known and is discussed in the standard texts [17–19]. Here we take a rather phenomenological approach. We start by assuming that the pairwise interactions of a single molecule with its neighbours can be represented in the mean field approximation by a single-particle pseudopotential,

$$V(\cos\theta)=-uSP_2(\cos\theta), \tag{2}$$

where θ is the angle the long axis of the molecule makes with the direction of average orientation, or director. $P_2(\cos\theta)=\frac{1}{2}(3\cos^2\theta-1)$ is the second Legendre polynomial in $\cos\theta$ and models the anisotropic nature of the interactions. The order parameter S is given by the average of $P_2(\cos\theta)$

$$S=\langle P_2(\cos\theta)\rangle=\frac{1}{Z}\int_0^1 P_2(x)\exp\left[-\beta V(x)\right]dx, \tag{3}$$

where $\beta=1/k_BT$ and the single-particle partition function Z is

$$Z=\int_0^1 \exp\left[-\beta V(x)\right]dx. \tag{4}$$

The coefficient u represents the strength of the two-body interactions, and is assumed to be positive, so that the interactions are attractive. Its precise form depends on the nature of the interactions; it is often simply used as a fitting parameter when comparing theoretical predictions with experimental data. If, as was done originally by MS [1] we take the two-body forces to be due to induced-dipole–induced-dipole interactions, then $u \sim v^{-2}$, where v is the average molecular volume. This pseudopotential, given in equation (2), models the *two-body* interactions between a given molecule and all other molecules by an effective *one-body* interaction between that molecule and a field S due to the average orientation of the other molecules.

The free energy F of this system can be derived from thermodynamics [19].

$$F = U - T\mathscr{S}, \tag{5}$$

where U is the internal energy and $\mathscr{S}$ the entropy. $\mathscr{S}$ is given by

$$\begin{aligned}\mathscr{S} &= -Nk_B\langle \ln\{\exp[-\beta V]/Z\}\rangle \\ &= N\left(k_B \ln Z + \frac{1}{T}\langle V\rangle\right) \\ &= N\left(k_B \ln Z - \frac{1}{T}uS^2\right),\end{aligned} \tag{6}$$

and the internal energy by

$$U = \frac{N}{2}\langle V\rangle = -N\frac{uS^2}{2}. \tag{7}$$

The factor of 1/2 in equation (7) is necessary to avoid double-counting of interactions when averaging the pseudopotential. Finally, using equation (5) we get for the free energy per molecule

$$\mathscr{F} = F/N = -k_B T \ln Z + \frac{uS^2}{2}. \tag{8}$$

It is instructive to work backwards from this expression for the free energy to calculate the form of $V(\cos\theta)$. We start from equation (8), with Z defined as in equation (4), and note that a stable state of the system must correspond to an extremum (actually a minimum) of $\mathscr{F}$ with respect to the order parameter. Thus we must have

$$\frac{\partial \mathscr{F}}{\partial S} = -\frac{k_B T}{Z}\frac{\partial Z}{\partial S} + uS = 0, \tag{9}$$

or

$$S = \frac{k_B T}{uZ}\frac{\partial Z}{\partial S} = -\frac{k_B T}{uZ}\int_0^1 \beta\frac{\partial V}{\partial S}\exp[-\beta V]\,dx, \tag{10}$$

where we explicitly treat the pseudopotential V as a function of both S and $\cos\theta$. If we now substitute equation (3), the definition of S, into the left-hand side of equation (10), we get

$$\frac{1}{Z}\int_0^1 P_2(x)\exp[-\beta V]\,dx = -\frac{1}{uZ}\int_0^1 \frac{\partial V}{\partial S}\exp[-\beta V]\,dx. \tag{11}$$

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For this to be true in general we must have

$$\frac{\partial V}{\partial S} = -uP_2(\cos\theta), \tag{12}$$

so

$$V(\cos\theta) = -uSP_2(\cos\theta) + g(\cos\theta). \tag{13}$$

If $g=0$, this is the MS pseudopotential we started with, equation (1). The additional term $g(\cos\theta)$ represents the one-body interactions of a molecule with, for example, an externally applied field. The presence of such terms does not change the form of $\mathscr{F}$, although of course the partition function Z will depend on g.

With $g=0$ the physical states of the system are found by solving equation (3) self-consistently for S, with the true solution being that which minimizes $\mathscr{F}$. The results are well known: for $k_BT/u > k_BT_K(0)/u = 0{\cdot}22019$, $S=0$ and the system is isotropic. $T_K(0)$ is the nematic–isotropic transition temperature, at which there is a first-order transition to a nematic state which persists as the temperature is further lowered. At the transition, $S=S_K(0)=0{\cdot}42903$, and S increases monotonically to 1 as T is decreased to 0.

To incorporate the effect of an externally applied field, we consider a magnetic field here but an electric field would be treated in exactly the same way, we follow [5] and set

$$g = -u\gamma P_2(\cos\theta), \tag{14}$$

where $\gamma = \Delta\chi H^2/3u$. Here H is the strength of the applied field, which we assume is oriented parallel to the director. $\Delta\chi = \chi_\parallel - \chi_\perp$ is the molecular diamagnetic anisotropy, here assumed to be positive; $\chi_\parallel$ and $\chi_\perp$ are the diamagnetic susceptibilities parallel and perpendicular to the director.

This model was studied by Wojtowicz and Sheng [5] and from a somewhat different perspective by Hanus [6]. Solution of it is exactly analogous to the case where $g=0$, except that the model now has a slightly larger parameter space to be explored. These workers [5, 6] found that with an applied field the system had a nematic–paranematic coexistence curve. The point at the $\gamma=0$ end of the coexistence curve is the usual MS N–I transition. At $\gamma=\gamma_c(0)=0{\cdot}010454$ the coexistence curve ends at a critical point with a critical temperature $k_BT/u = k_BT_c(0)/u = 0{\cdot}23094$ and an order parameter $S=S_c(0)=0{\cdot}21408$ [20].

The primary purpose of this paper is to study the effect of incorporating into the single-particle pseudopotential a term which models three-body interactions. We do this by adding a term proportional to S^3 to the internal energy, giving a free energy equal to

$$\mathscr{F} = -k_BT\ln Z + \frac{uS^2}{2} + \frac{qS^3}{3}, \tag{15}$$

where q parametrizes the strength of the three-body forces. If we take the two-body interactions to be induced-dipole–induced-dipole interactions, for which $u \sim v^{-2}$, then it is reasonable to take the three-body forces to be due to Axilrod–Teller triple-induced-dipole interactions, in which case $q \sim v^{-3}$. This identification is not, however, in any way important to the calculations in this paper. The dimensionless ratio q/u is a measure of the relative importance of these two types of interactions.

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We can now derive the appropriate form of $V(\cos\theta)$ as before. We have

$$\frac{\partial \mathscr{F}}{\partial S}=-\frac{k_B T}{Z}\frac{\partial Z}{\partial S}+uS+qS^2, \tag{16}$$

so

$$S(1+qS/u)=-\frac{1}{uZ}\int_0^1 \frac{\partial V}{\partial S}\exp[-\beta V]\,dx. \tag{17}$$

Now, using the definition of S (equation (3)), we can write

$$(1+qS/u)\int_0^1 P_2(x)\exp[-\beta V]\,dx=-\frac{1}{u}\int_0^1 \frac{\partial V}{\partial S}\exp[-\beta V]\,dx. \tag{18}$$

For this to be true in general we must have

$$-\frac{1}{u}\frac{\partial V}{\partial S}=(1+qS/u)P_2(\cos\theta), \tag{19}$$

which gives

$$V(\cos\theta)=-uSP_2(\cos\theta)-\frac{q}{2}S^2P_2(\cos\theta)-u\gamma P_2(\cos\theta), \tag{20}$$

where we have used equation (14) for the external field term. We have thus introduced into the single-particle pseudopotential a term quadratic in S, which models three-body interactions. This term can be thought of in the following way. The term *linear* in S models pairwise interactions by having a single molecule interact with a field due to the average effect of all the other molecules. The average interaction energy due to these two-body interactions is proportional to $\langle SP_2(\cos\theta)\rangle = S^2$. Our new term treats triplet interactions as interactions of a single molecule with a field due to the average effect of all other *pairs* of molecules, which is therefore also proportional to S^2.

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This model was solved in the same way as the MS and WS models: equation (3) was solved self-consistently for S, using equation (20) for $V(\cos\theta)$. Equation (15) was used to calculate the free energies of the various solutions found, with the stable physical state being that which minimized $\mathscr{F}$. The calculations were performed using a standard numerical software package [21]. Integrals were calculated to an accuracy of at least 10 figures. First order phase transitions were located by the following procedure: At low temperatures, the most stable solution to equation (3) is that with the highest value of S. The temperature was increased in steps from some appropriately low value, and S and $\mathscr{F}$ were calculated for each solution at each temperature. The computer program noted when the solution with the lowest free energy changed from being that with the highest value of S to one with a lower value of S. An interpolation procedure was then used to find the N–pN transition temperature accurately; it was taken to be the temperature at which the free energies of the two phases coexisting at the transition were equal to within 10^{-12}. Values of the transition temperatures and order parameters were retained to 6 or 7 figures precision. The results of these calculations are presented in the next section.

3. Results

3.1. *The nematic–isotropic transition*

At zero applied field ($\gamma=0$ in equation (20)), this model undergoes a first-order N–I transition, just as in the MS case. The transition temperature, $T_K(q/u)$, and the size of the jump in the order parameter at the transition, $S_K(q/u)$, both increase with increasing

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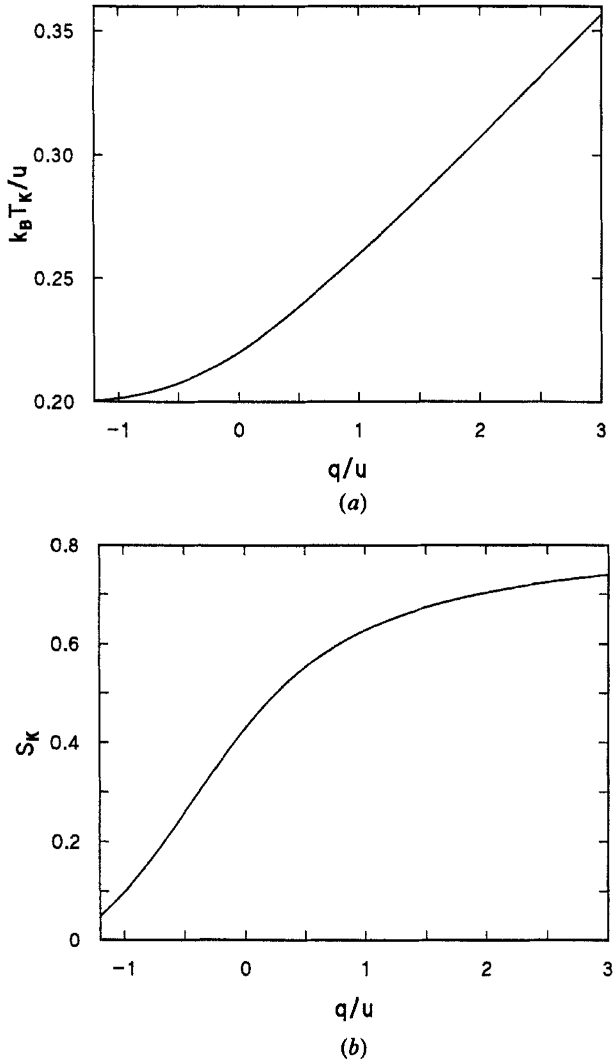

Figure 1. (*a*) The N–I transition temperature T_K as a function of the relative importance of triplet interactions, given by the ratio q/u. (*b*) The nematic order parameter at the N–I transition, S_K, as a function of q/u.

importance of attractive triplet interactions, i.e. with increasing q/u. These results are shown in figure 1 (*a*) and (*b*). A positive value of q/u, since we assume u to be positive, means that the triplet interactions are attractive and tend to increase the molecular alignment. Thus the nematic phase persists to higher temperatures, and the degree of ordering at the transition is larger for larger q/u.

Figure 2 shows the locus of zero-field N–I transition points as q/u is varied over the range $-1{\cdot}2 \leqslant q/u \leqslant 3$. Also shown are some representative $S(T)$ curves, showing the degree of ordering as a function of temperature in the nematic phase. Figure 2 also shows some experimental $S(T)$ data for the liquid crystal *p*-azoxyanisole (PAA) [22], and a corresponding curve calculated using this theoretical model. These experimental

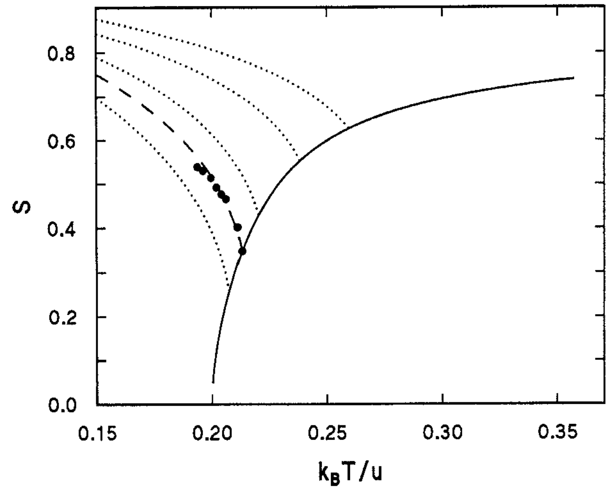

Figure 2. The solid curve is the line of zero-field N–I transitions for q/u between $-1{\cdot}2$ (low S_K) and 3 (high S_K). The dotted curves show the order parameter $S(T)$ in the nematic phase for $q/u = -0{\cdot}5$ (lowest S_K), 0, 0·5, and 1. The circles are experimental measurements of $S(T)$ at constant volume for PAA, from [22], and the dashed line through them is the theoretical curve for $q/u = -0{\cdot}24543$.

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data were measured at constant volume, so the volume dependence of the coefficients q and u is not a factor in this comparison. The theoretical curve was calculated using $q/u = -0{\cdot}24543$, for which S_K is equal to the experimental value obtained from [22]. From the experimental N–I transition temperature of $T_K = 437{\cdot}5$ K, and the value of $k_B T_K/u = 0{\cdot}213186$ from the theoretical curve, we get for this material $u/k_B = 2052$ K and $q/k_B = -504$ K. The negative value of q indicates that the triplet interactions for this particular liquid crystal are repulsive, i.e., they tend to decrease the alignment of the molecules. The theoretical curve describes the experimentally observed behaviour very well, with the degree of agreement between experiment and theory being similar to that found from other theoretical treatments [4, 23]. It should be pointed out that while this model in zero field has two undetermined constants, q and u, only one quantity, the *ratio* q/u, was used as an adjustable parameter to match theory and experiment.

As q/u becomes large and negative, S_K appears to approach zero as $k_B T_K/u$ approaches a limit near 0·2. The validity of this model is most likely limited to the regime $|q/u| \ll 1$; outside of this regime one would expect still higher-order terms in $V(\cos\theta)$, representing higher-order interactions, to become important as well. We therefore do not study this large $|q/u|$ behaviour further, and restrict our attention below to $|q/u| \leqslant 1$.

3.2. *The nematic–paranematic coexistence curve*

When $\gamma > 0$ this model has a N–pN coexistence curve which terminates at a critical point, as found in [5] and [6] for the case of the simple MS model with a field. Calculated coexistence curves for several values of q/u are shown in figure 3. The critical point itself was located by fitting the coexistence curve data to an expression for the expected critical behaviour, as discussed below. Figure 3 also shows $S(T)$ along lines of constant field for $q/u = 0{\cdot}5$. Three values of γ are shown, two subcritical and one supercritical.

As q/u increases, the temperature range covered by the N–pN coexistence curve becomes larger. This range is given by the maximum reduced temperature, i.e. the reduced temperature at the zero-field N–I transition,

$$t_{\max}(q/u)=\frac{T_c(q/u)-T_K(q/u)}{T_c(q/u)}, \tag{21}$$

which is plotted as a function of q/u in figure 4.

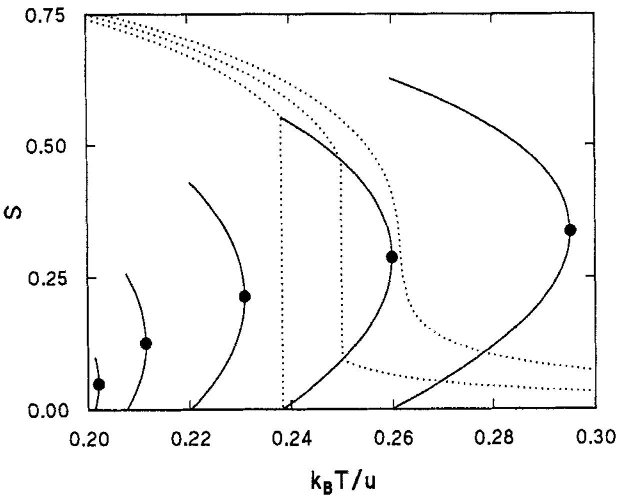

Figure 3. N–pN coexistence curves for $q/u=-1$ (leftmost curve), −0·5, 0, 0·5 and 1. The solid circles show the critical points in each case. The dotted curves are lines of constant γ (i.e. lines of constant applied field) for $q/u=0{\cdot}5$; they correspond to $\gamma=0$ (leftmost curve), 0·015, and 0·030. $\gamma_c=0{\cdot}027672$ for this value of q/u.

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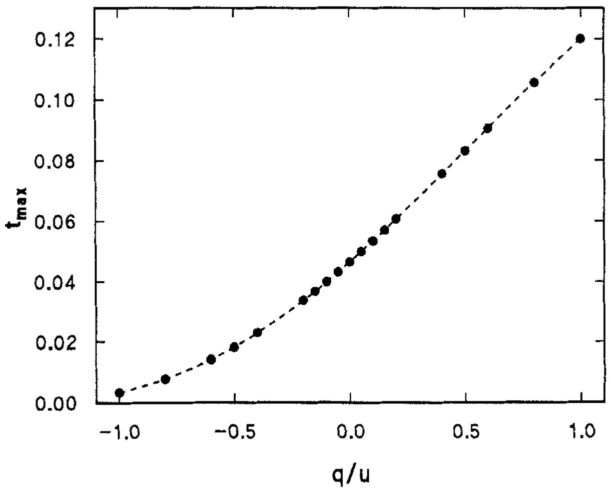

Figure 4. The N–pN coexistence range, $t_{\max}(q/u)$. The dashed line is a smooth curve through the data.

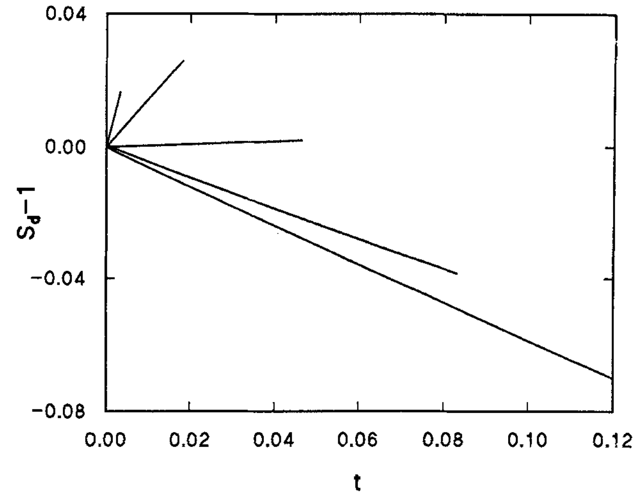

Figure 5. The diameter of the N–pN coexistence curve plotted as a function of reduced temperature t for $q/u=-1$ (shortest line), $-0{\cdot}5$, 0, $0{\cdot}5$ and 1 (longest line).

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The coexistence curve diameter, defined in equation (1), is the average of the order parameters in the two coexisting phases. The diameter is plotted in figure 5 for five values of q/u. The slope of the diameter is a function of q/u, as expected from the work of Goldstein *et al.* [12, 13], and changes sign at a value of q/u slightly greater than zero. The diameter slope is small and positive if the three-body interaction term is zero.

3.3. *The critical point and critical behaviour*

From the theory of critical phenomena [14], it is well known that close to the critical point the order parameter behaves like a power law in the reduced temperature t. Specifically, if we define ΔS^* to be the normalized difference between the order parameters of the coexisting nematic and paranematic phases

$$\Delta S^*=\frac{S_N-S_{pN}}{2S_c}, \tag{22}$$

then

$$\Delta S^*=B_0t^{\beta} \tag{23}$$

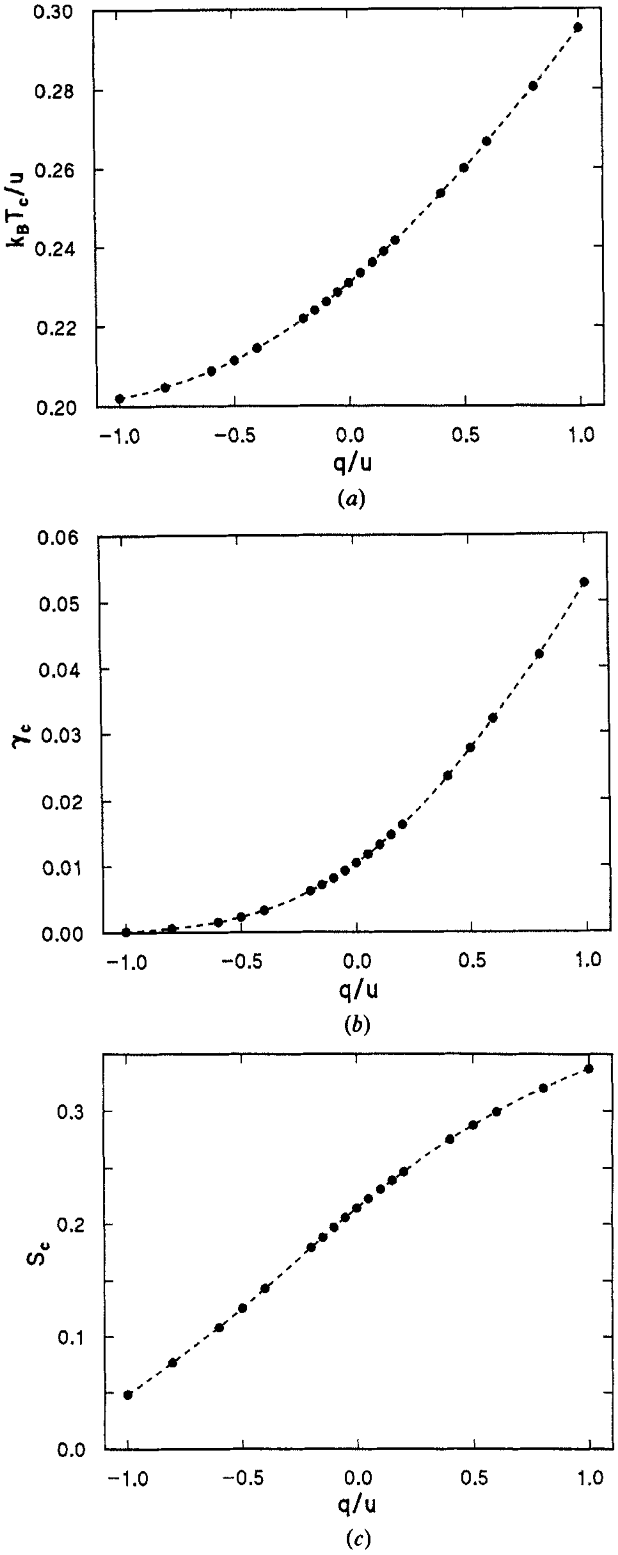
close enough to the critical point. How close is close enough depends on the particular system under study, but in general higher order correction terms [24] must be added to equation (23) to allow a comparison with experimental data over a reasonable range of t.

In mean field theory, the critical exponent $\beta=1/2$ and the expected corrections to equation (23) would be terms behaving like t^n and $t^{n+\beta}=t^{n+1/2}$, where n is an integer. T_c was therefore found by fitting the data for the N–pN coexistence curve to the function

$$\Delta S^*=B_0t^{1/2}+B_1t+B_2t^{3/2}, \tag{24}$$

using T_c and the amplitudes B_i as fitting parameters. The resulting values of $T_c(q/u)$ are plotted in figure 6 (*a*).

Equation (24) fitted the calculated coexistence curves essentially perfectly for $q/u \lesssim 0{\cdot}2$. For larger q/u, relatively small but systematic deviations from the fitting



(*a*)

(*b*)

(*c*)

Figure 6. The N–pN critical temperature $T_c(q/u)$ (*a*), field $\gamma_c(q/u)$ (*b*), and order parameter $S_c(q/u)$ (*c*). The dashed lines are smooth curves through the data.

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function were present when the fit was performed over the entire coexistence range. These deviations disappeared when the fits were done over a smaller range of t, excluding the data furthest from T_c. The values of T_c and B_0 were insensitive to the range of t used in the fits, but the higher order amplitudes B_1 and B_2 changed significantly with the range of t.

The critical field γ_c is plotted in figure 6 (*b*). For each value of q/u, γ_c was found by fitting the N–pN transition temperature to a polynomial in γ and extrapolating the fit to the appropriate value of T_c, determined as described above. The variation of the transition temperature with γ was described to within the precision of the data by a quadratic in γ for all values of q/u studied, but not by the linear expression used in [5].

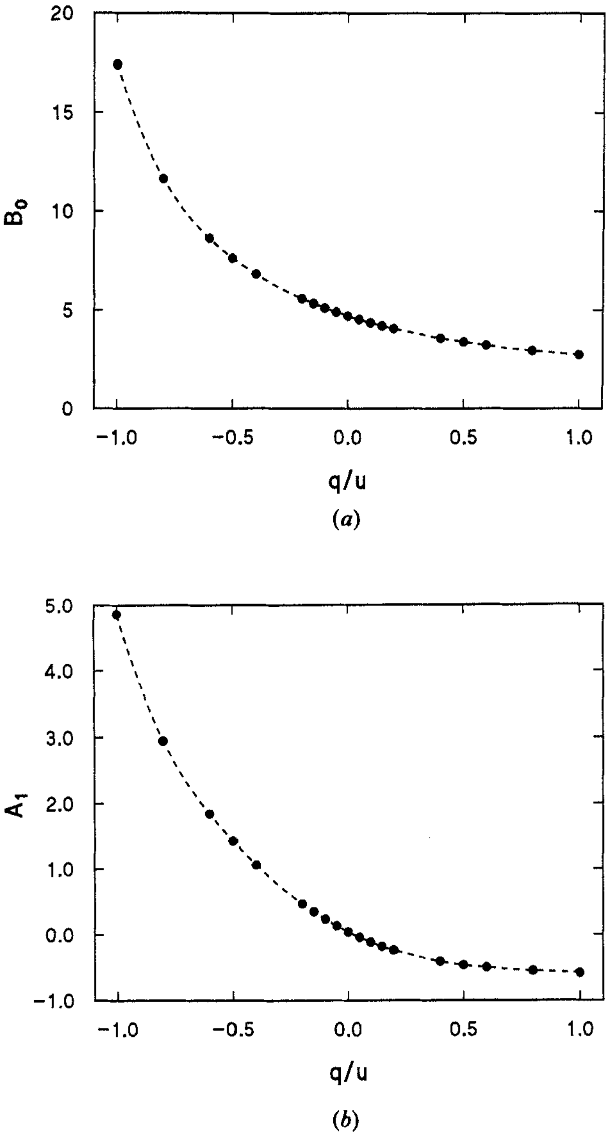

Figure 7. (*a*) The leading coexistence curve amplitude B_0 and (*b*) the slope of the coexistence curve diameter A_1 plotted versus q/u. The dashed lines are smooth curves through the data.

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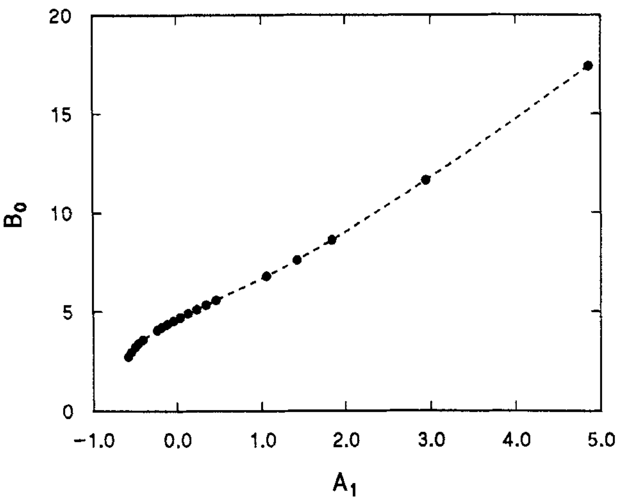

Figure 8. The coexistence curve amplitude B_0 versus the diameter slope A_1 for $-1 \leqslant q/u \leqslant 1$. The dashed line is a smooth curve through the data.

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The diameter of the coexistence curve, S_d, is expected to be linear in t close to the critical point, since the $t^{1-\alpha}$ singularity discussed in the introduction does not contribute in mean field theory. The diameter data were therefore fitted to the expression

$$\frac{S_N + S_{pN}}{2} = S_c(1 + A_1 t), \tag{25}$$

with S_c and A_1 free parameters, and using the values of T_c determined from the coexistence curve fits discussed above. Small systematic deviations from linearity were always observed, although these were almost at the level of the numerical precision for $q/u \lesssim -0{\cdot}8$. Even at higher q/u these deviations were typically plus or minus a few in the sixth decimal place and at worst represented about 0·5 per cent of $|S_K - S_c|$. The diameters are virtually indistinguishable from straight lines when plotted as in figure 5. In some cases small systematic deviations reminiscent of a critical anomaly were observed near T_c. These seemed to be associated with increasing error in the numerical calculations as T_c was approached, not with any true critical behaviour, and so were disregarded. The values of S_c obtained from fits to equation (25) are plotted in figure 6 (*c*).

The leading coexistence curve amplitude, B_0, and the slope of the diameter, A_1, both decreased smoothly as q/u increased, as shown in figures 7 (*a*) and (*b*). Goldstein *et al.* [12, 13] predicted theoretically and confirmed from experimental data for liquid-vapour systems that B_0 and A_1 were linearly related at small values of the variable corresponding in their work to q/u. As can be seen in figure 8, the relationship between these two amplitudes is quite accurately linear for small q/u and is fairly close to linear over the range $-1 \leqslant q/u \leqslant 1$.

4. Discussion

The above results show that, within this mean field approach, many-body interactions can have a significant effect on the N–I transition, on the N–pN coexistence curve, and on the N–pN critical point. In particular, for three-body interactions which tend to enhance the molecular alignment, the range of existence of the N–pN coexistence curve is extended and, at a given applied field, the degree of ordering in the nematic phase is greater than that found if many-body interactions are not included in the pseudopotential.

Goldstein *et al.* calculated the effects of three-body interactions on a mean field model of the liquid-vapour phase transition. Their model, an extension of the van der Waals model, was sufficiently simple that analytic expressions for many quantities could be derived. Unfortunately such is not the case for our model of the N–pN system, and we are limited to numerical calculations. Nonetheless we can draw some qualitative comparisons with the results of [12, 13]. Certainly our results show that the slope of the coexistence curve diameter varies as a function of the relative importance the three-body term in the pseudopotential, increasing for more strongly repulsive triplet interactions (i.e., for more negative q/u) [25]. Similarly the critical amplitudes B_0 and A_1 increase for more strongly repulsive many-body interactions. We also find that B_0 and A_1 are linearly related, albeit with a different slope from that found in [12, 13], for small q/u. All of these results are in qualitative agreement with the results of Goldstein *et al.* [12, 13]. Thus although the quantitative aspects may be different for the two systems, many of the qualitative features of the effects of many-body interactions on the coexistence curve carry over from one system to the other.

It is possible to make contact with experimental results only in the case of the zero-field N–I transition. As shown in figure 2, the predictions of this model agree well with experimental measurements of the nematic order parameter, at constant volume, of PAA [22]. We emphasize that the single parameter q/u was used to match the experimental and theoretical values of S_K. The value of u was then determined by the experimental N–I transition temperature. No adjustments were made to fit to the experimental data away from the transition temperature.

At non-zero field the experimental situation is less satisfactory. Some experiments have been done on the liquid crystal 4-cyano-4′-(*n*-heptyl)biphenyl (7CB) in an electric field by Nicastro and Keyes [26]. They observed paranematic ordering and a first order nematic–paranematic transition in applied fields of order $10^5\,\mathrm{V\,cm^{-1}}$. They also reported indirect evidence for the existence of an endpoint of the N–pN coexistence curve, but were unable to approach this point closely due to dielectric breakdown of their samples at high fields. They estimated the critical electric field to be about $2{\cdot}5 \times 10^5\,\mathrm{V\,cm^{-1}}$, which is not difficult to attain in the laboratory. The equivalent critical magnetic field, however, would be about $2{\cdot}5 \times 10^6$ Oe, which is very high. Similar estimates of the critical field have been made by others [5–7, 9]. It thus seems that experiments to study the N–pN critical point in an electric field should not be impossible. Nonetheless, substantial technical difficulties, related mostly to dielectric breakdown and the response of charged species in the sample to the necessary high electric fields, must first be overcome.

5. Conclusions

We have presented an extension to the Maier–Saupe theory of the nematic–isotropic transition that incorporates three-body interactions into the effective single-particle pseudopotential. The effects of these interactions on the N–I transition, the N–pN coexistence curve, and the N–pN critical point have been studied. At zero field, this model is in good agreement with experimental data for PAA [22]. The dependence of the critical coexistence curve amplitude, and of the slope of the coexistence curve

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diameter, on the relative importance of triplet interactions is in qualitative agreement with calculations and experimental data for liquid-vapour systems [12, 13], but at present no data from the N–pN critical region are available for comparison.

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