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Pretransitional behaviour in nematogenic mixtures

A molecular field theory†

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The isotropic phase of nematogenic liquid crystals exhibits strong pretransitional behaviour which diverges rapidly as the transition to the nematic phase is approached. Similarly nematogenic mixtures also show pronounced pretransitional effects although these can be dramatically reversed on the formation of the biphasic regime when isotropic and nematic phases coexist. Here we develop a theory for such effects using approximations taken from previous molecular field theories of nematogenic mixtures. In particular we consider the composition dependence of the divergence temperature for binary nematogenic mixtures and its relation to those of the pure components. A variety of mixtures with particles of different shape are treated, namely rods and spheres, laths and spheres, rods and rods, as well as rods and laths. We also predict the temperature dependence of the field-induced order parameters, often used to monitor pretransitional behaviour, for certain mixtures in both the homogeneous isotropic phase and the subsequent biphasic regime. The predictions of the theory are found to be in good accord with those investigations of pretransitional behaviour which are available for nematogenic mixtures.

1. Introduction

The nematic–isotropic transition is associated with strong pretransitional effects which are particularly manifest in the isotropic phase as the transition to the nematic is approached [1]. Thus in the isotropic phase the extent of the angular correlations, characteristic of the nematic phase, grows rapidly with decreasing temperature. The range of the angular correlations can be monitored by a variety of experiments which includes the Cotton–Mouton effect. In this, the orientational order induced in the isotropic phase by an applied magnetic field is measured by the field-induced birefringence, $\Delta n(\equiv n_{\parallel} - n_{\perp})$. The Cotton–Mouton constant $\Delta n/B^2$, where B is the magnetic flux density, is proportional to the second-rank orientational order parameter; this is found to diverge in the vicinity of the nematic–isotropic transition. To a reasonable approximation the inverse of the Cotton–Mouton constant is observed to vary linearly with temperature and to vanish at a temperature T^*, slightly below T_{NI}.

Comparable pretransitional behaviour has been found for nematogenic mixtures [2] although for such systems there is an additional factor which must be taken into

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account. Because the nematic–isotropic transition is first order the addition of a solute creates a biphasic regime in which both isotropic and nematic phases coexist [3]. It is of some interest therefore to explore how the pretransitional behaviour changes when the coexisting nematic phase is formed. Such an investigation is extremely difficult using conventional techniques for the study of pretransitional effects because the response from the isotropic phase is not readily separated from that of the coexisting nematic. This difficulty can be overcome by using deuterium N.M.R. spectroscopy to determine the magnetic field-induced order because the spectra from both the isotropic and nematic phases are completely separate [4]. These studies have revealed that as soon as the biphasic regime is reached the divergence of the field-induced order is quenched. Indeed careful inspection of the results reveals that the order apparently decreases with decreasing temperature when the two phases coexist. To understand this intriguing behaviour we have developed a theory for pretransitional effects in nematogenic mixtures; this is based on approximations used in previous molecular field theories of liquid-crystalline mixtures. The theory is also of value in quite a different context. It is virtually impossible to determine much of the phase diagram exhibited by a mixture of a nematogen with a solute whose molecules deviate only slightly from spherical symmetry. This situation obtains because the nematic–isotropic transition is depressed below the freezing point for even small solute concentrations [3]. However, as Rosenblatt [5] has shown, it is possible to measure the divergence temperature T^* for the mixture over a much wider concentration range. Of course, T^* cannot be equated with the transition temperature, even for a pure nematogen and for a mixture the difference is expected to be even greater, as we shall see. It is important for the interpretation of such experiments to understand those factors which influence the pretransitional divergence temperature of a nematogenic mixture. The theory which we present here provides this understanding as well as predicting how T^* varies with the anisotropic molecular interactions and the composition.

The outline of the paper is as follows. The general theory for the pretransitional behaviour of a binary mixture composed of uniaxial and biaxial particles is developed in §3. The predictions of the theory are then specialized to particular systems, such as mixtures of rods and spheres as well as that of two rod-like species. In §4 the field-induced order is determined within the biphasic regime both for the uniaxial solvent as well as a biaxial solute. Where possible we shall make contact with experiment. However experimental studies of the pretransitional behaviour of nematogenic mixtures are rare, indeed we hope that the theoretical predictions given here will stimulate further investigations. We begin, in the following section, not with mixtures but with pure nematogens composed of uniaxial and biaxial molecules. This allows us to establish the formalism, which we shall need for mixtures, with systems that, of necessity, are somwhat simpler.

2. Pure nematogens

2.1. *Uniaxial molecules*

As we have seen the magnetic field in a Cotton–Mouton or an N.M.R. experiment can induce orientational order in an isotropic phase, provided the molecular magnetic susceptibility is anisotropic. This order is characterized by a set of orientational order parameters but of these only the second-rank quantities are determined in these two experiments. For a pure nematogen composed of cylindrically symmetric particles the second-rank order parameter, $\bar{P}_2$, is defined by the ensemble average of the second Legendre polynomial, $P_2(\cos\beta)$, where β is the angle between the magnetic field and the molecular symmetry axis. This average can be written in terms of the singlet orientational distribution function, $f(\beta)$, as

$$\bar{P}_2 = \int_0^{\pi} P_2(\cos\beta) f(\beta) \sin\beta d\beta. \tag{1}$$

The distribution function can be taken to define the potential of mean torque, $U(\beta)$, responsible for the orientational order, via

$$f(\beta) = Z^{-1}\exp\{-U(\beta)/kT\}, \tag{2}$$

where the normalization is provided by

$$Z = \int_0^{\pi} \exp\{-U(\beta)/kT\} \sin\beta d\beta. \tag{3}$$

The potential of mean torque contains two contributions, one resulting from the anisotropy in the magnetic susceptibility, $\Delta\chi(\equiv \chi_{\parallel} - \chi_{\perp})$, which couples to the magnetic flux density

$$U_{\text{mag}}(\beta) = -(1/3)\Delta\chi\, B^2 P_2(\cos\beta), \tag{4}$$

and the other comes from the anisotropic molecular interactions. The form of this second contribution is not known but it may be expanded, quite generally, as

$$U_{\text{mol}}(\beta) = -\sum_{L(\text{even})} u_L P_L(\cos\beta), \tag{5}$$

although, as we shall discover, only one of the terms in this summation is required.

The orientational order induced in the isotropic phase is small, $\bar{P}_2$ is typically about 10^{-4} even for the largest fields available for pretransitional studies, and so $U(\beta)/kT$ in the Boltzmann factor must also be small. In consequence the expansion of the exponential functions may be truncated after the first non-trivial term. This gives the orientational distribution function, in the limit of low order, as

$$f(\beta) = (1/2)\left\{1 + (\Delta\chi B^2/3kT)P_2(\cos\beta) + \sum_{L(\text{even})} (u_L/kT)P_L(\cos\beta)\right\}. \tag{6}$$

The second-rank field-induced order parameter is then simply

$$\bar{P}_2 = (1/5kT)(\Delta\chi B^2/3 + u_2), \tag{7}$$

because the other terms in the molecular contribution to the potential of mean torque vanish as a consequence of the orthogonality of the Legendre polynomials. The expansion coefficient, u_2, is dependent on the orientational order and according to the Maier–Saupe theory [6]

$$u_2 = \bar{u}_2 \bar{P}_2. \tag{8}$$

With this result, obtained through the molecular field approximation, the field-induced second-rank order parameter is given by

$$\bar{P}_2 = (\Delta\chi B^2/15k)/(T - T^*), \tag{9}$$

where the divergence temperature is predicted to be

$$T^* = \bar{u}_2/5k; \tag{10}$$

here T^* may also be identified as the temperature at which the isotropic phase would have undergone a second-order transition to the nematic if the first-order nematic–isotropic transition had not intervened. The nematic–isotropic transition temperature is predicted by the Maier–Saupe theory [6] to be

$$T_{\mathrm{NI}} = \bar{u}_2/4{\cdot}541k, \tag{11}$$

and so the ratio, T^*/T_{NI}, is found to be 0·908. This is in reasonable agreement with a typical experimental value of about 0·998 [1] although for our purposes the comparison may be misleading. This situation obtains because the prediction of the nematic–isotropic transition temperature requires the molecular field approximation to evaluate the orientational entropy whereas this is not needed to determine the divergence temperature. In consequence the two temperatures may well be predicted with differing accuracy, since our primary concern is with T^* alone we need to estimate the accuracy with which the divergence temperature can be predicted independently of how well T_{NI} can be calculated. It is possible to obtain such an independent test for T^* by using the results of two computer simulation studies of the Lebwohl–Lasher model nematogen [7]. Both investigations are consistent with a scaled divergence temperature, kT^*/ε, of 1·12 where ε determines the strength of the anisotropic pair potential. For this model nematogen the Maier–Saupe parameter $\bar{u}_2$ is just 6ε because the particles are confined to the sites of a simple cubic lattice whose coordination number is 6. The scaled divergence temperature is therefore predicted to be 1·200 which is in good agreement with the simulation experiments given the relatively simple form of the theory. In contrast, the scaled nematic–isotropic transition temperature is found from the simulations to be 1·127 whereas the Maier–Saupe theory predicts the considerably higher value of 1·321. The predictions for both temperatures can be improved by using cluster theories which take better account of the short range angular correlations. Thus for a two-site cluster Ypma and Vertogen, using the Bethe method, have calculated kT^*/ε to be 1·098 for a six-coordinate lattice [8]. The agreement with the observed value is clearly enhanced; however the simpler approach offered by the single-site cluster or molecular field approximation is sufficiently accurate for our treatment of binary mixtures.

2.2. *Biaxial molecules*

The molecules which constitute real nematogens rarely conform to the cylindrical symmetry assumed in the Maier–Saupe theory. Provided the molecular flexibility is ignored the molecules may be taken to be biaxial and so their orientational order must be characterized by a set of ordering tensors [9]. The second-rank member of this set, related to the pretransitional experiments, is the ensemble average of the second modified spherical harmonic, $C_{2m}(\omega)$, where ω denotes the spherical polar angles made by the magnetic field with a molecular frame. If this is the principal axis system for the ordering tensor then the $\bar{C}_{2\pm1}$ vanish and $\bar{C}_{22}$ is equal to $\bar{C}_{2-2}$. The non-zero components of this spherical tensor are related to the principal elements of the Saupe ordering matrix, which is its cartesian equivalent, by

$$\left.\begin{aligned} \bar{C}_{20} &= S_{zz} \\ \text{and} \qquad \bar{C}_{22}(\equiv \bar{C}_{2-2}) &= (S_{xx} - S_{yy})/\sqrt{6}, \end{aligned}\right\} \tag{12}$$

where *xyz* is the principal axis system [9]. We see therefore that to characterize the field-induced orientational order we require an experiment which yields at least two independent pieces of information. This is not possible for conventional techniques, such as the Cotton–Mouton effect, but can be achieved with an N.M.R. experiment [10].

The calculation of the two principal order parameters proceeds as for a system of uniaxial particles but now the singlet orientational distribution function, $f(\omega)$, and the potential of mean torque, $U(\omega)$, depend on the two spherical polar angles. The magnetic contribution to the potential of mean torque can be written, in irreducible spherical tensor notation, as

$$U_{\max}(\omega) = -(1/2)\sum_{k}\chi^{2k}C^{*}_{2k}(\omega), \tag{13}$$

where the magnetic susceptibility tensor is defined to include the magnetic field term $(2/3)^{1/2}B^2$ when the field is parallel to the laboratory z axis. The molecular field contribution to $U(\omega)$ could be expanded in a basis of modified spherical harmonics but only the second-rank term of this expansion is needed to evaluate the second-rank ordering tensors in the low order limit, as we have seen for uniaxial molecules. According to the molecular field theory for nematogens of biaxial molecules proposed by Luckhurst *et al.* [6, 11], the second-rank molecular field contribution to the potential of mean torque is

$$U_{\text{mol}}(\omega) = -\sum_{k,k'}\bar{u}_{2kk'}\bar{C}^{*}_{2k'}C_{2k}(\omega). \tag{14}$$

The orientational distribution function, in the low order limit, is then

$$f(\omega) = (1/4\pi)\{1 + (1/kT)\sum_{k,k'}(\chi^{2k} + \bar{u}_{2kk'}\bar{C}^{*}_{2k'})\,C_{2k}(\omega)\} \tag{15}$$

and the field-induced order parameters are predicted to be

$$\bar{C}_{20} = (1/5kT)(\chi^{20} + \sum_{k'}\bar{u}_{20k'}\bar{C}^{*}_{2k'})$$

and (16)

$$\bar{C}_{22} = (1/5kT)(\chi^{22} + \sum_{k'}\bar{u}_{22k'}\bar{C}^{*}_{2k'}).$$

The summations in these equations can be restricted to $k' = 0, \pm 2$, by using the principal molecular axis system which we take to be the same as that for the magnetic susceptibility tensor. This is consistent with D_{2h} or C_{2v} molecular symmetry which then constrains the expansion coefficients according to [6, 11]

$$\bar{u}_{2kk'} = \bar{u}_{2k-k'} = \bar{u}_{2-kk'} = \bar{u}_{2-k-k'}. \tag{17}$$

With these restrictions the two field-induced order parameters are given by the solutions to the simultaneous equations

$$\left.\begin{aligned}(5kT - \bar{u}_{200})\bar{C}_{20} - 2\bar{u}_{202}\bar{C}_{22} &= \chi^{20}\\ \text{and}\qquad & \\ -\bar{u}_{220}\bar{C}_{20} + (5kT - 2\bar{u}_{222})\bar{C}_{22} &= \chi^{22}.\end{aligned}\right\} \tag{18}$$

In determinental form the order parameters are

$$\left.\begin{aligned}\bar{C}_{20} &= \begin{vmatrix} \chi^{20} & -2\bar{u}_{202} \\ \chi^{22} & (5kT - 2\bar{u}_{222}) \end{vmatrix} \Bigg/ \begin{vmatrix} (5kT - \bar{u}_{200}) & -2\bar{u}_{202} \\ -\bar{u}_{220} & (5kT - 2\bar{u}_{222}) \end{vmatrix} \\ \text{and} \\ \bar{C}_{22} &= \begin{vmatrix} (5kT - \bar{u}_{200}) & \chi^{20} \\ -\bar{u}_{220} & \chi^{22} \end{vmatrix} \Bigg/ \begin{vmatrix} (5kT - \bar{u}_{200}) & -2\bar{u}_{202} \\ -\bar{u}_{220} & (5kT - 2\bar{u}_{222}) \end{vmatrix} .\end{aligned}\right\} \quad (19)$$

For both order parameters the numerators are non-zero and have a relatively weak temperature dependence in the vicinity of the nematic–isotropic transition; in consequence the divergence of the order parameters is determined by the temperature variation of the denominator. This is common to both order parameters and so, as we expect, the two order parameters are predicted to diverge at the same temperature which is obtained by setting the determinant in the denominator equal to zero; this gives

$$(5kT^* - \bar{u}_{200})(5kT^* - 2\bar{u}_{222}) - 2\bar{u}_{202}\bar{u}_{220} = 0. \quad (20)$$

We can simplify this result by noting that $\bar{u}_{202}$ is equal to $\bar{u}_{220}$ and by invoking the geometric mean approximation to relate the interaction parameters [6, 11]

$$\bar{u}_{202}^2 = \bar{u}_{200}\bar{u}_{222}, \quad (21)$$

which is valid when the anisotropic pair potential is determined by individual molecular properties, as for dispersion and quadrupolar interactions. With this approximation the divergence temperature for a nematogen of biaxial particles is predicted to be

$$T^* = (\bar{u}_{200}/5k)(1 + 2\bar{u}_{222}/\bar{u}_{200}). \quad (22)$$

The extent of the molecular biaxiality is defined via the ratio $\bar{u}_{202}/\bar{u}_{200}$ which is denoted by λ, and so within the geometric mean approximation $\bar{u}_{222}/\bar{u}_{200}$ is simply λ^2 [11]. In the limit of molecular uniaxiality λ vanishes and the divergence temperature becomes $\bar{u}_{200}/5k$ which we write as T_u^*. Accordingly the divergence temperature T_b^* for biaxial particles is

$$T_b^* = T_u^*(1 + 2\lambda^2). \quad (23)$$

The increase in T_b^* with the molecular biaxiality is shown in the table which also lists the nematic–isotropic transition temperature. We find that their ratio T_b^*/T_{NI} tends to unity as the molecular biaxiality increases which is in accord with the reduction in

The dependence of the divergence temperature, $kT_b^*/\bar{u}_{200}$, the nematic–isotropic transition temperature, $kT_{NI}/\bar{u}_{200}$, their ratio and the entropy of transition, $\Delta S/R$ [11] on the molecular biaxiality, λ.

λ	$kT_b^*/\bar{u}_{200}$	$kT_{NI}/\bar{u}_{200}$	T_b^*/T_{NI}	$\Delta S/R$
0	0·2000	0·2203	0·9079	0·417
0·1	0·2040	0·2220	0·9189	0·384
0·2	0·2160	0·2280	0·9474	0·275
0·3	0·2360	0·2404	0·9817	0·112
$1/\sqrt{6}$	0·2666	0·2666	1·0000	0

the entropy of transition. The maximum biaxiality for a molecule occurs when λ is $1/\sqrt{6}$, for this the phase transition is predicted to be second order and the nematic phase is biaxial [12]; it is here that T_b^* and T_{NI} are found to be equal.

The precise form for the temperature dependence of the field-induced order parameters can be obtained from numerical solutions to equations (19). However to perform these calculations we should need to assume particular values for the ratio χ^{22}/χ^{20} as well as for λ. Since our major objective is to develop a molecular field theory for binary mixtures we shall not report such calculations here. Instead we now proceed, in the following section, to present a theory of pretransitional behaviour in nematogenic mixtures.

3. Binary mixtures

We shall develop the molecular field theory for a variety of binary mixtures. For the most general case which we shall consider one component, *A*, is taken to have cylindrically symmetric molecules and so may be thought of as the nematogenic solvent while the other component, *B*, is assumed to be formed from biaxial molecules and so could be considered as the solute. To determine the field-induced order parameters we require the potential of mean torque experienced by each. As we have seen, there are two contributions to these, one from the interaction of the magnetic flux density with the anisotropic magnetic susceptibility and the other from the molecular field created by the anisotropic molecular interactions.

The magnetic contributions are equivalent to those which we have encountered for the pure nematogens although we rewrite them, in a common notation, as

$$U^A_{\text{mag}}(\omega_A) = -\chi^{20}_A C_{20}(\omega_A) \tag{24}$$

for the uniaxial component and

$$U^B_{\text{mag}}(\omega_B) = -[\chi^{20}_B C_{20}(\omega_B) + \chi^{22}_B\{C_{22}(\omega_B) + C_{2-2}(\omega_B)\}] \tag{25}$$

for the biaxial species. Here ω_A and ω_B denote the spherical polar angles made by the magnetic field with the molecular frames of *A* and *B*, respectively. These frames are chosen to reflect the molecular symmetry assumed for the two components. The molecular field contributions to the potentials of mean torque are taken from the theory of nematogenic mixtures developed by Humphries *et al.* [13] and later extended by Humphries and Luckhurst [14]. For the uniaxial component

$$U^A_{\text{mol}}(\omega_A) = -\{(1-x)\bar{u}^{AA}_{200}\bar{C}^A_{20} + x\bar{u}^{AB}_{200}\bar{C}^B_{20} + 2x\bar{u}^{AB}_{202}\bar{C}^B_{22}\}C_{20}(\omega_A); \tag{26}$$

here x is the mole fraction of *B*. This simple dependence of the potential of mean torque on the composition results from the random mixing approximation [13] although if the molecular volumes of *A* and *B* were different the mole fraction would need to be replaced by a volume fraction [15]. The single, second-rank order parameter for component *A* is written as $\bar{C}^A_{20}$ instead of $\bar{P}^A_2$ to conform with the notation for the elements of the ordering tensor, $\bar{C}^B_{20}$ and $\bar{C}^B_{22}$, for the biaxial component *B*. The coefficients $\bar{u}_{2mn}$ determine the strength of the molecular field contribution to the potential of mean torque; the first subscript is simply the rank of the interaction. Of the other two subscripts in, for example, $\bar{u}^{AB}_{2mn}$ the first is associated with component *A* and the other with component *B*; since component *A* is cylindrically symmetric, m is therefore confined to the value zero while n can take values 0 and ± 2. The molecular field experienced by A and given in equation (26) results from three interactions: the first term involving $\bar{u}^{AA}_{200}$ comes from the A–A interactions and so depends on the orientational order parameter for A as well as on its mole fraction; the second term involving $\bar{u}^{AB}_{200}$ is a mixed, A–B, interaction associated with the major axes of both A and B and so depends on the major order parameter $\bar{C}^{B}_{20}$, for B together with its mole fraction; and the final term, in $\bar{u}^{AB}_{202}$, is another mixed interaction but now associated with the major axis of A and the minor axes of B; it necessarily involves the biaxial order parameter, $\bar{C}^{B}_{22}$, for B and its mole fraction. The potential of mean torque for component B has a similar structure to that for A although there is an additional term, in $\bar{u}^{BB}_{222}$, which results from the B–B interaction associated with the minor axes; the potential is

$$\begin{aligned} U^{B}_{\mathrm{mol}}(\omega_B) \;=\; & -\{x\bar{u}^{BB}_{200}\bar{C}^{B}_{20} + 2x\bar{u}^{BB}_{202}\bar{C}^{B}_{22} + (1-x)\bar{u}^{AB}_{200}\bar{C}^{A}_{20}\}C_{20}(\omega_B) \\ & -\{x\bar{u}^{BB}_{220}\bar{C}^{B}_{20} + 2x\bar{u}^{BB}_{222}\bar{C}^{B}_{22} + (1-x)\bar{u}^{AB}_{202}\bar{C}^{A}_{20}\} \\ & \times\{C_{22}(\omega_B) + C_{2-2}(\omega_B)\}. \end{aligned} \qquad (27)$$

In writing these expressions for the potential of mean torque we have used the relationships between the interaction coefficients contained in equation (17) based on the assumed molecular symmetry, together with the identity

$$\bar{u}^{AB}_{2mn} = \bar{u}^{BA}_{2nm} \qquad (28)$$

for the mixed interactions. In general the potential of mean torque may also contain terms of higher rank but as we have seen they do not contribute to the second-rank field-induced order parameters.

These order parameters are determined from the total potential of mean torque in exactly the same way as for the pure nematogens. Indeed the potentials have the same dependence on the molecular orientations and so we find, for component A,

$$\bar{C}^{A}_{20} = (1/5kT)\{\chi^{20}_{A} + (1-x)\bar{u}^{AA}_{200}\bar{C}^{A}_{20} + x\bar{u}^{AB}_{200}\bar{C}^{B}_{20} + 2x\bar{u}^{AB}_{202}\bar{C}^{B}_{22}\}. \qquad (29)$$

However unlike the result in equation (7) the field-induced order parameter for A now depends on the ordering tensor for B. The components $\bar{C}^{B}_{2m}$ take the same form as for the nematogen composed of biaxial particles (cf. equation (18)) and so for the major order parameter we have

$$\bar{C}^{B}_{20} = (1/5kT)\{\chi^{20}_{B} + x\bar{u}^{BB}_{200}\bar{C}^{B}_{20} + 2x\bar{u}^{BB}_{202}\bar{C}^{B}_{22} + (1-x)\bar{u}^{AB}_{200}\bar{C}^{A}_{20}\} \qquad (30)$$

and for the biaxial order parameter

$$\bar{C}^{B}_{22} = (1/5kT)\{\chi^{22}_{B} + x\bar{u}^{BB}_{220}\bar{C}^{B}_{20} + 2x\bar{u}^{BB}_{222}\bar{C}^{B}_{22} + (1-x)\bar{u}^{AB}_{202}\bar{C}^{A}_{20}\}. \qquad (31)$$

There are then three simultaneous equations for the three field-induced order parameters and we can rewrite these in matrix form as

$$\begin{pmatrix} 5kT - (1-x)\bar{u}^{AA}_{200} & -x\bar{u}^{AB}_{200} & -2x\bar{u}^{AB}_{202} \\ -(1-x)\bar{u}^{AB}_{200} & 5kT - x\bar{u}^{BB}_{200} & -2x\bar{u}^{BB}_{202} \\ -(1-x)\bar{u}^{AB}_{202} & -x\bar{u}^{BB}_{220} & 5kT - 2x\bar{u}^{BB}_{222} \end{pmatrix}\begin{pmatrix} \bar{C}^{A}_{20} \\ \bar{C}^{B}_{20} \\ \bar{C}^{B}_{22} \end{pmatrix} = \begin{pmatrix} \chi^{20}_{A} \\ \chi^{20}_{B} \\ \chi^{22}_{B} \end{pmatrix}. \qquad (32)$$

The solutions to this equation can be expressed in determinental form as

$$\bar{C}^A_{20} = \Delta^{-1}\begin{vmatrix} \chi^{20}_A & -x\bar{u}^{AB}_{200} & -2x\bar{u}^{AB}_{202} \\ \chi^{20}_B & 5kT - x\bar{u}^{BB}_{200} & -2x\bar{u}^{BB}_{202} \\ \chi^{22}_B & -x\bar{u}^{BB}_{220} & 5kT - 2x\bar{u}^{BB}_{222} \end{vmatrix}, \tag{33}$$

$$\bar{C}^B_{20} = \Delta^{-1}\begin{vmatrix} 5kT - (1 - x)\bar{u}^{AA}_{200} & \chi^{20}_A & -2x\bar{u}^{AB}_{202} \\ -(1 - x)\bar{u}^{AB}_{200} & \chi^{20}_B & -2x\bar{u}^{BB}_{202} \\ -(1 - x)\bar{u}^{AB}_{202} & \chi^{22}_B & 5kT - 2x\bar{u}^{BB}_{222} \end{vmatrix} \tag{34}$$

and

$$\bar{C}^B_{22} = \Delta^{-1}\begin{vmatrix} 5kT - (1 - x)\bar{u}^{AA}_{200} & -x\bar{u}^{AB}_{200} & \chi^{20}_A \\ -(1 - x)\bar{u}^{AB}_{200} & 5kT - x\bar{u}^{BB}_{200} & \chi^{20}_B \\ -(1 - x)\bar{u}^{AB}_{202} & -x\bar{u}^{BB}_{220} & \chi^{22}_B \end{vmatrix}, \tag{35}$$

where the denominator is

$$\Delta = \begin{vmatrix} 5kT - (1 - x)\bar{u}^{AA}_{200} & -x\bar{u}^{AB}_{200} & -2x\bar{u}^{AB}_{202} \\ -(1 - x)\bar{u}^{AB}_{200} & 5kT - x\bar{u}^{BB}_{200} & -2x\bar{u}^{BB}_{202} \\ -(1 - x)u^{AB}_{202} & -x\bar{u}^{BB}_{220} & 5kT - 2x\bar{u}^{BB}_{222} \end{vmatrix}. \tag{36}$$

In the vicinity of the nematic–isotropic transition the numerators in these expressions are non-zero and their temperature dependence is relatively weak; in consequence the divergence temperature for the order parameters is obtained by setting the denominator equal to zero. Since Δ is common to all three order parameters they are predicted to diverge at the same temperature, as we should expect. To illustrate the significance of these general predictions for the pretransitional behaviour of binary nematogenic mixtures we shall now consider certain limiting situations.

3.1. *Infinite dilution*

In the limit that x tends zero or unity we recover from equation (36) the divergence temperatures for the pure nematogens formed from uniaxial and biaxial particles, respectively. In addition we can also determine the temperature dependence of the solute order parameter in this infinite dilution limit. Of particular interest is a uniaxial solvent with a biaxial solute since the pretransitional behaviour of such systems have been studied by N.M.R. spectroscopy [4, 10]. For this mixture we take the limit as x goes to zero and from equations (33) to (36) we obtain the order parameter for the solvent as

$$\bar{C}^A_{20} = \chi^{20}_A/5k(T - T^*_A), \tag{37}$$

where T^*_A is the divergence temperature for pure A, namely $\bar{u}^{AA}_{200}/5k$ (cf. equation (10)). The components of the ordering tensor for the solute are of potentially greater importance and these are found to be

$$\left.\begin{aligned} \bar{C}^B_{20} &= (1/5kT)(\chi^{20}_B + \bar{u}^{AB}_{200}\bar{C}^A_{20}) \\ &\text{and} \\ \bar{C}^B_{22} &= (1/5kT)(\chi^{22}_B + \bar{u}^{AB}_{202}\bar{C}^A_{20}), \end{aligned}\right\} \tag{38}$$

where the order parameter for the solvent is given by equation (37). We see that there are two contributions to each solute order parameter. The first is the direct alignment via the coupling of the magnetic flux density to the anisotropic magnetic susceptibility of the solute. The second results from the indirect alignment caused by a combination of the anisotropic solute–solvent interaction and the direct alignment of the solvent by the magnetic field. From the structure of the equations we can see that the molecular field plays an analogous role to the magnetic field, with $\bar{u}_{200}^{AB}\bar{C}_{20}^{A}$ and $\bar{u}_{202}^{AB}\bar{C}_{20}^{A}$ being equivalent to χ_B^{20} and χ_B^{22}, respectively. The major difference between these strength parameters is that the molecular field is strongly temperature dependent via the solvent order parameter whereas the magnetic susceptibility is temperature independent. In consequence the direct contribution to the solute ordering tensor is expected to be negligible in comparison to the indirect mechanism except at temperatures far from the phase transition. We also note that the temperature dependence of the solvent order only contains information concerning the anisotropic interactions via the divergence temperature T_A^*. In contrast the solute ordering tensor yields the solute–solvent interaction parameters, $\bar{u}_{200}^{AB}$ and $\bar{u}_{202}^{AB}$, as well as the divergence temperature. Thus close to the nematic–isotropic transition the ratio $\bar{C}_{22}^{B}/\bar{C}_{20}^{B}$ is essentially equal to $\bar{u}_{202}^{AB}/\bar{u}_{200}^{AB}$, a result which was suggested but not derived previously [10].

3.2. *Rods and spheres*

The simplest binary nematogenic mixture is formed by the addition of a spherically symmetric solute to a uniaxial solvent. Despite its apparent simplicity the phase diagram for the mixture is predicted to be somewhat complex exhibiting as it does a re-entrant biphasic regime [16] as well as an extensive normal biphasic range [17]. In contrast the composition dependence of the divergence temperature obtained from the isotropic phase prior to the formation of the coexisting nematic and isotropic phases is predicted to be quite straightforward, as we shall now see. For spherical solutes the interaction parameters $\bar{u}_{20n}^{AB}$ and $\bar{u}_{2mn}^{BB}$ vanish and so the determinant controlling the divergence of $\bar{C}_{20}^{A}$ (cf. equation (36)) reduces to

$$\Delta = \begin{vmatrix} 5kT - (1-x)\bar{u}_{200}^{AA} & 0 & 0 \\ 0 & 5kT & 0 \\ 0 & 0 & 5kT \end{vmatrix}. \tag{39}$$

The divergence temperature T_{M}^* for the mixture is then just

$$T_{\mathrm{M}}^* = (1-x)T_A^*, \tag{40}$$

and so the addition of the spherical solute simply scales the divergence temperature for the solvent T_A^* with its mole fraction. It is possible to test this prediction by using the results obtained by Rosenblatt [5] for a mixture of 4-*n*-pentyl-4′-cyanobiphenyl and carbon tetrachloride. However the molecular volumes of these components are not the same and so the mole fraction in equation (40) must be replaced by the volume fraction of the solute. With this change the predicted composition dependence of T_{M}^* is found to be in good agreement with experiment. Indeed this composition dependence of the divergence temperature had been postulated but not derived by Rosenblatt [5].

In the absence of phase separation the nematic–isotropic transition temperature for the mixture is also predicted to be linear in the mole fraction of nematogenic solvent [13]

$$T^{\mathrm{M}}_{\mathrm{NI}} = (1 - x)T^{A}_{\mathrm{NI}}. \tag{41}$$

The difference $(T^{\mathrm{M}}_{\mathrm{NI}} - T^{*}_{\mathrm{M}})$ should therefore be linear in the solvent mole fraction also

$$(T^{\mathrm{M}}_{\mathrm{NI}} - T^{*}_{\mathrm{M}}) = (1 - x)(T^{A}_{\mathrm{NI}} - T^{*}_{A}) \tag{42}$$

and should tend to zero as the mole fraction of solute is increased. This intriguing behaviour has not been observed for thermotropic systems where, in any event, the biphasic regime is expected to be extensive. However this regime is considerably smaller for a micellar liquid crystal formed from caesium perfluorooctanoate and water; for this system the difference $(T^{\mathrm{M}}_{\mathrm{NI}} - T^{*}_{\mathrm{M}})$ has been determined and is found to decrease significantly with increasing water concentration [18]. Provided we make the major assumption that the water plays the role of the spherical solute and the micelles that of the uniaxial solvent then these measurements support, at least qualitatively, the theoretical predictions.

3.3. *Laths and spheres*

The majority of nematogenic molecules are lath-like rather than rod-like and so it is relevant to consider the divergence temperature for a mixture of a biaxial solvent with a spherical solute. This system is described by setting $\bar{u}^{AA}_{200}$ and $\bar{u}^{AB}_{20n}$ equal to zero in equations (33) to (36); thus the determinant governing the divergence temperature becomes

$$\Delta = \begin{vmatrix} 5kT & 0 & 0 \\ 0 & 5kT - x\bar{u}^{BB}_{200} & -2x\bar{u}^{BB}_{202} \\ 0 & -x\bar{u}^{BB}_{220} & 5kT - 2x\bar{u}^{BB}_{222} \end{vmatrix}. \tag{43}$$

We see that the mole fraction of component B scales all of the interaction parameters equally and so T^{*}_{M} for the mixture is simply

$$T^{*}_{\mathrm{M}} = xT^{*}_{B}, \tag{44}$$

where the divergence temperature for the biaxial solvent is obtained from the solution to equation (20). As a consequence the result for the divergence temperature for the mixture does not demand any assumption concerning the relationships between the interaction coefficients, $\bar{u}^{BB}_{2mn}$. In contrast to the simple composition dependence of the divergence temperature for the mixture the phase diagram is expected to be rather complex [16, 17] because the system separates into two phases at the transition; an analogous situation also obtains for mixtures of rods and spheres. However at the level of the molecular field theory the parameters determining the composition dependence of T^{*}_{M} and the phase diagram are entirely comparable. The additional complexity of the phase diagram results primarily from the contributions of the entropy of mixing as well as the orientational entropy to the total free energy and not because there is more information concerning the anisotropic molecular interactions.

3.4. *Rods and rods*

We now turn to the pretransitional behaviour for a mixture of two nematogens each composed of cylindrically symmetric particles. For such a system the biaxial interaction parameters, $\bar{u}_{222}^{BB}$, $\bar{u}_{220}^{BB}$, $\bar{u}_{202}^{BB}$, $\bar{u}_{202}^{AB}$ and $\bar{u}_{220}^{BA}$ vanish, and the determinant Δ (cf. equation (36)) is therefore reduced to

$$\Delta = \begin{vmatrix} 5kT - (1-x)\bar{u}_{200}^{AA} & -x\bar{u}_{200}^{AB} & 0 \\ -(1-x)\bar{u}_{200}^{AB} & 5kT - x\bar{u}_{200}^{BB} & 0 \\ 0 & 0 & 5kT \end{vmatrix} . \tag{45}$$

The field-induced order parameters diverge when the determinant vanishes and the temperature at which this occurs is given by the solution to the equation

$$(5kT_{\mathrm{M}}^*)^2 - 5kT_{\mathrm{M}}^*\{(1-x)\bar{u}_{200}^{AA} + x\bar{u}_{200}^{BB}\} + x(1-x)\{\bar{u}_{200}^{AA}\bar{u}_{200}^{BB} - (\bar{u}_{200}^{AB})^2\} = 0. \tag{46}$$

Humphries *et al.* [13] have suggested that the mixed anisotropic interaction can be approximated by the geometric mean of the interactions for the pure components; with this Berthelot combining rule T_{M}^* is given by the simple result

$$T_{\mathrm{M}}^* = (1-x)T_A^* + xT_B^*. \tag{47}$$

The nematic–isotropic transition temperature for the mixture is also found to have the same linear dependence on the composition when the components have similar transition temperatures but only in the absence of phase separation [13]. However this result is obtained by numerical evaluation of the molecular field expressions for the orientational free energy and is not analytic.

We have explored the influence of departures of $\bar{u}_{200}^{AB}$ from the geometric mean by solving equation (46) for the divergence temperature of the mixture numerically. To do this we write the mixed anisotropic interaction as

$$(\bar{u}_{200}^{AB})^2 = \bar{u}_{200}^{AA}\bar{u}_{200}^{BB}\delta, \tag{48}$$

where the parameter δ is used to control the departure from the geometric mean. The results of such calculations for the composition dependence of T_{M}^* for a mixture with T_B^* equal to 0·8 T_A^* where δ takes the values 1·1 and 0·9 are shown in figure 1 together with the linear dependence found when δ is unity. Deviations from the geometric

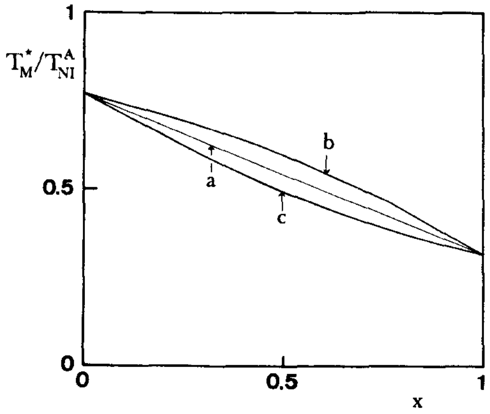

Figure 1. The composition dependence of the divergence temperature, T_{M}^*, for a binary mixture of cylindrically symmetric particles with T_B^*/T_A^* equal to 0·8 calculated from equation (46) when the mixed interaction parameter, $\bar{u}_{200}^{AB}$, (*a*) obeys the geometric mean combining rule, (*b*) exhibits a positive deviation from it (δ = 1·1) and (c) has a negative deviation (δ = 0·9).

mean clearly result in a non-linear dependence of the divergence temperature for the mixture on its composition. Positive deviations, corresponding to $\delta > 1$, produce an increase in the value of T^*_{M} while negative deviations ($\delta < 1$) lower the divergence temperature; the deviations from the linear dependence of T^*_{M} appear to be essentially symmetric in the parameter δ. Similar deviations from the linear dependence of the nematic–isotropic transition temperature on composition are also observed when there are deviations of the mixed interaction parameter from the Berthelot combining rule [13].

Although we have presented the theory for mixtures of rods and rods, the equations are equally valid for nematogenic mixtures composed of rod-like and disc-like particles. The only difference is that the mixed interaction, $\bar{u}^{AB}_{200}$, is negative for rods and discs because these particles tend to align at right angles to each other, whereas for rod-like particles it is positive, as are the pure interactions. The phase diagram for such a mixture is predicted [19] to be intricate because the system separates into two uniaxial nematic phases rather than form a single biaxial nematic phase [20] when the mixed interaction obeys the geometric mean combining rule. If this restriction is relaxed then the phase diagram becomes more complex and a biaxial nematic phase can be stabilized [21]. In contrast the divergence temperature obtained from the isotropic phase prior to the biphasic region is predicted to have a linear dependence on the composition, in the geometric mean limit (cf. equation (47)). Indeed since the mixed interaction parameter enters equation (46) for T^*_{M} as the square then the results obtained when the geometric mean rule no longer holds, and shown in figure 1 for rods and rods, should still be valid for rods and discs. We have been unable to locate any measurements of pretransitional behaviour for mixtures of rods and discs, or indeed for rods and rods. However Rosenblatt [5] has studied the binary mixture of 4-*n*-pentyl-4′-cyanobiphenyl and tetraethyl tin over a relatively wide concentration range. Deuterium N.M.R. measurements of comparable mixtures suggest that within the nematic phase the flexible tetraethyl tin tends to adopt a planar conformation [22]. If this is indeed the case then T^*_{M} should be given by equation (47) but with the mole fraction replaced by the volume fraction because the two components do not have the same molecular volume. Tetraethyl tin is not mesogenic and so its divergence temperature T^*_B is not known; if this is taken therefore as an adjustable parameter then, to a reasonable approximation, it proves possible to fit Rosenblatt's data [22].

3.5. *Rods and laths*

For the sake of completeness we now consider the divergence temperature for a binary mixture of uniaxial and biaxial particles, corresponding to the most general case dealt with by the theory. This temperature is obtained by setting the determinant in equation (36) equal to zero; however as the resultant cubic equation in T^*_{M} contains six interaction coefficients we have first sought to reduce this number. Thus the mixed interaction coefficients have been related to those for the pure components via the geometric mean approximation

$$(\bar{u}^{AB}_{20n})^2 = \bar{u}^{AA}_{200}\bar{u}^{BB}_{2nn}; \tag{49}$$

a specialized version of this approximation had been introduced earlier for interactions between different rod-like particles. The pure uniaxial–biaxial interaction coefficient, $\bar{u}^{BB}_{202}$, is approximated in a similar way (cf. equation (21)). The number of unknown interaction parameters is then reduced to just three, $\bar{u}^{AA}_{200}$, $\bar{u}^{BB}_{200}$ and $\bar{u}^{BB}_{222}$, for the pure components and with these the divergence temperature is found to be linearly dependent on the composition of the binary mixture

$$T^*_{\mathrm{M}} = (1 - x)T^*_A + xT^*_B; \tag{50}$$

here the divergence temperatures for the pure components are given by equations (10) and (23). We have also investigated the effect of deviations from the geometric mean approximation for the mixed interactions on the composition dependence of T^*_{M}; as for mixtures of rods and rods the linear dependence on x is lost and for positive deviations T^*_{M} is increased while for negative deviations it is reduced.

4. The temperature dependence of the field-induced order parameters

In the previous section we have been concerned, predominantly, with the divergence temperatures for various nematogenic binary mixtures. These temperatures could then be compared with those determined from studies of the isotropic phase prior to the formation of the biphasic regime. However an N.M.R. investigation of the field-induced order within the isotropic phase of the biphasic regime has revealed a totally different pretransitional behaviour to that in the preceding homogeneous isotropic phase [4]. To undertstand this marked change in behaviour we now develop expressions for the field-induced order parameters in both regimes. To do this we shall consider two particular mixtures; firstly rods and spheres which serves to illustrate the procedure and then rods and laths which is analogous to that studied experimentally.

4.1. *Rods and spheres*

The field-induced order parameter, $\bar{C}^A_{20}$, for the nematogenic solvent is obtained from equations (33) and (36) as

$$\bar{C}^A_{20} = \chi^{20}_A/\{5kT - (1 - x)\bar{u}^{AA}_{200}\}, \tag{51}$$

by setting χ^{20}_B, χ^{22}_B, $\bar{u}^{AB}_{20n}$ and $\bar{u}^{BB}_{2mn}$ equal to zero. It is convenient to work with a scaled order parameter and so we rewrite equation (51) as

$$(5k\bar{C}^A_{20}/\chi^{20}_A)^{-1} = T - (1 - x)T^*_A. \tag{52}$$

The inverse, scaled order parameter is predicted therefore to be linear in temperature, with unit slope and intercept $(1 - x)T^*_A$, prior to the formation of the coexisting isotropic and nematic phases. At this temperature, T_{I}, the composition of the isotropic phase starts to change, becoming richer in the spherical component B, and so there is an additional contribution to the temperature dependence of $\bar{C}^A_{20}$. To predict this new contribution we take the solute concentration to be sufficiently small that the mixture is within the Henry's Law regime [3]. In other words the phase boundaries shown in figure 2 are linear in the mole fraction of the solute, x. The composition, x_{I}, of the coexisting isotropic phase is related to the slope, $\beta^{\infty}_{\mathrm{I}}$, of the upper phase boundary by

$$x_{\mathrm{I}} = (T_{\mathrm{I}}(x_{\mathrm{I}}) - T^A_{\mathrm{NI}})/\beta^{\infty}_{\mathrm{I}}; \tag{53}$$

here the superscript ∞ indicates the Henry's Law regime, formally valid in the infinite dilution limit [3]. The nematic–isotropic transition temperature of the pure nematogenic solvent is denoted by T^A_{NI}, and $T_{\mathrm{I}}(x_{\mathrm{I}})$ is the upper transition temperature for a mixture with a solute mole fraction x_{I} (cf. figure 2). In principle the slope of the phase

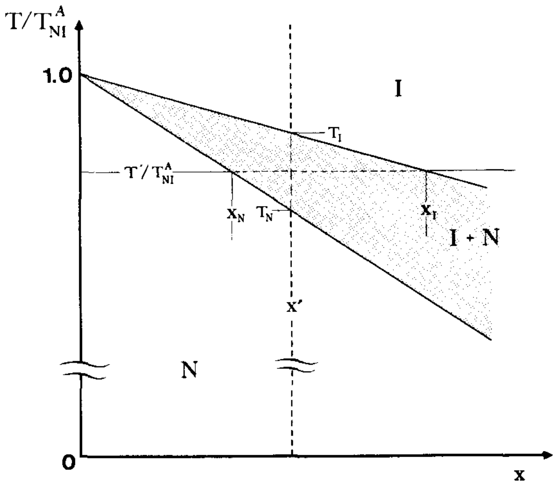

Figure 2. The phase diagram for a binary nematogenic mixture within the Henry's Law regime. The solute, *B*, is taken to be less anisotropic than the nematogenic solvent, *A*.

boundaries can be predicted by the molecular field theories of nematogenic mixtures [15, 16]; however we do not wish, at this stage, to combine our theory of the pretransitional behaviour of mixtures with that for the transitional properties which necessarily contains additional approximations. We shall therefore treat the slope, β_I^∞, as a parameter to be entered into the theory. None the less we note that for a mixture of rods and spheres the slope is predicted to equal $-T_{NI}^A$ in the absence of phase separation [13]; when phase separation is allowed $|\beta_I^\infty|$ is found to be reduced to $0{\cdot}817T_{NI}^A$ provided the solvent and solute have the same molecular volumes [15, 16].

To obtain $\bar{C}_{20}^A$ at a temperature T within the biphasic regime we need the composition of the coexisting isotropic phase x_I; this is given by equation (53) with T_I replaced by T (cf. figure 2). The scaled field-induced order parameter of the solvent within this region is, therefore, given by

$$(5k\bar{C}_{20}^A/\chi_A^{20})^{-1} = \{(1 + T_A^*/\beta_I^\infty)T - (1 + T_{NI}^A/\beta_I^\infty)T_A^*\}. \qquad (54)$$

We see then that within the biphasic regime the inverse of the scaled order parameter is also predicted to be linear in the temperature; however the slope has changed from 1 to $(1 + T_A^*/\beta_I^\infty)$ and the intercept is now $(1 + T_{NI}^A/\beta_I^\infty)(1 + T_A^*/\beta_I^\infty)^{-1}T_A^*$ instead of $(1 - x)T_A^*$. These changes are predicted to be particularly dramatic for as we have seen β_I^∞ is expected to be negative and less than T_{NI}^A; in consequence the slope should be negative and small. Clearly, if the sign of the slope for the inverse plot is not to change on entering the biphasic regime then β_I^∞, the slope of the phase boundary, has to be greater in magnitude than T_{NI}^A. In addition because T_A^* is approximately equal to T_{NI}^A the intercept for the inverse order parameter plot should be about T_A^*, the divergence temperature for the pure nematogen, and not that for the mixture, $(1 - x)T_A^*$.

We show in figure 3 the temperature dependence of (*a*) the scaled order parameter and (*b*) its inverse within the homogeneous isotropic phase and the biphasic regime; the parameters used in these model calculations were $\beta_I^\infty = -0{\cdot}6\,T_{NI}^A$ and $\beta_N^\infty = -4{\cdot}8\,T_{NI}^A$ which simply determines T_N^A at the lowest phase boundary, for a

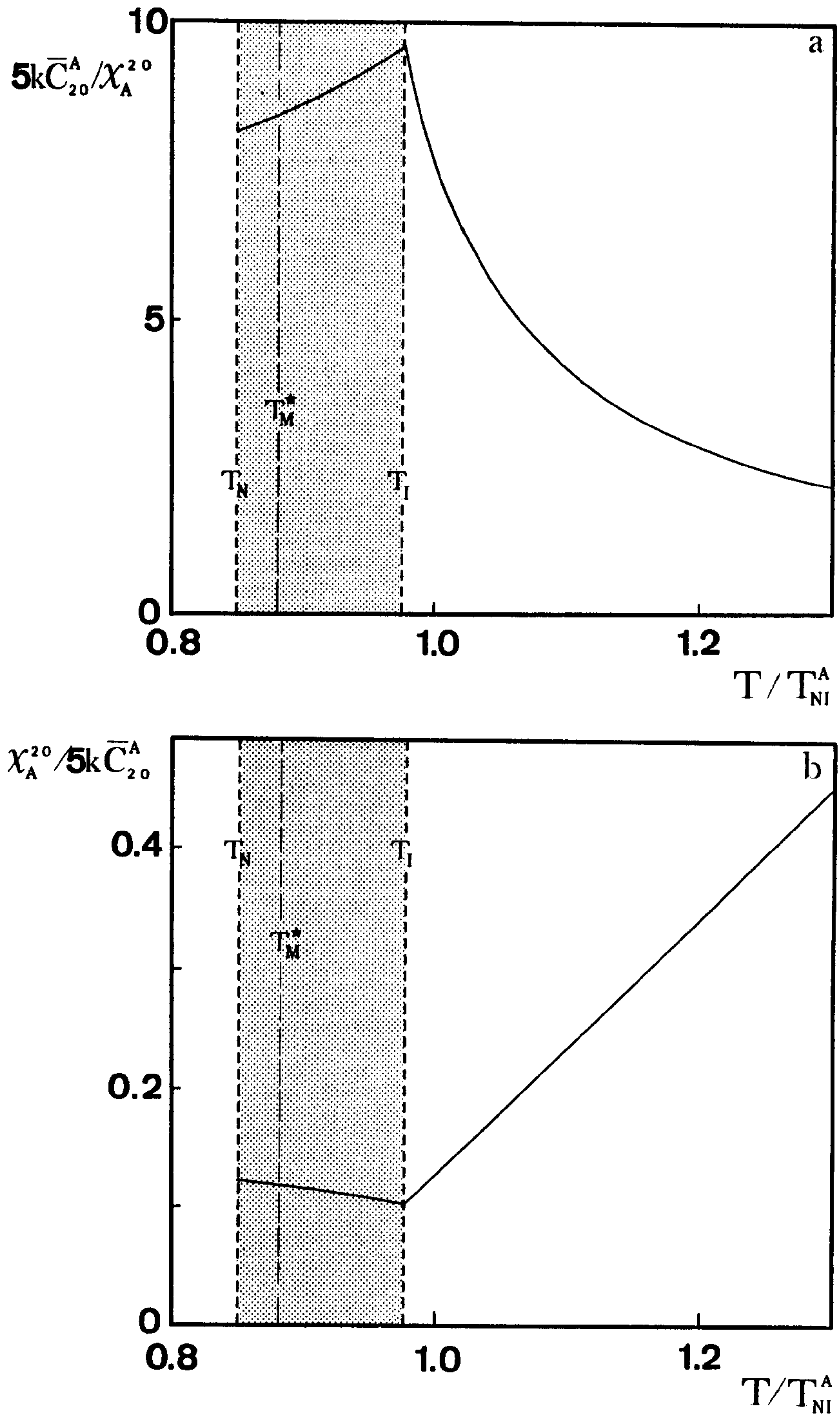

Figure 3. The dependence of (*a*) the scaled, field-induced order parameter, $5k\bar{C}^A_{20}/\chi^{20}_A$, and (*b*) its inverse on the scaled temperature, T/T^A_{NI} prior to and in the biphasic regime calculated from equations (52) and (54) respectively, with $\beta_I^\infty = -0{\cdot}6\,T^A_{NI}$, $\beta_N^\infty = -4{\cdot}8\,T^A_{NI}$ and $x = 0{\cdot}03$.

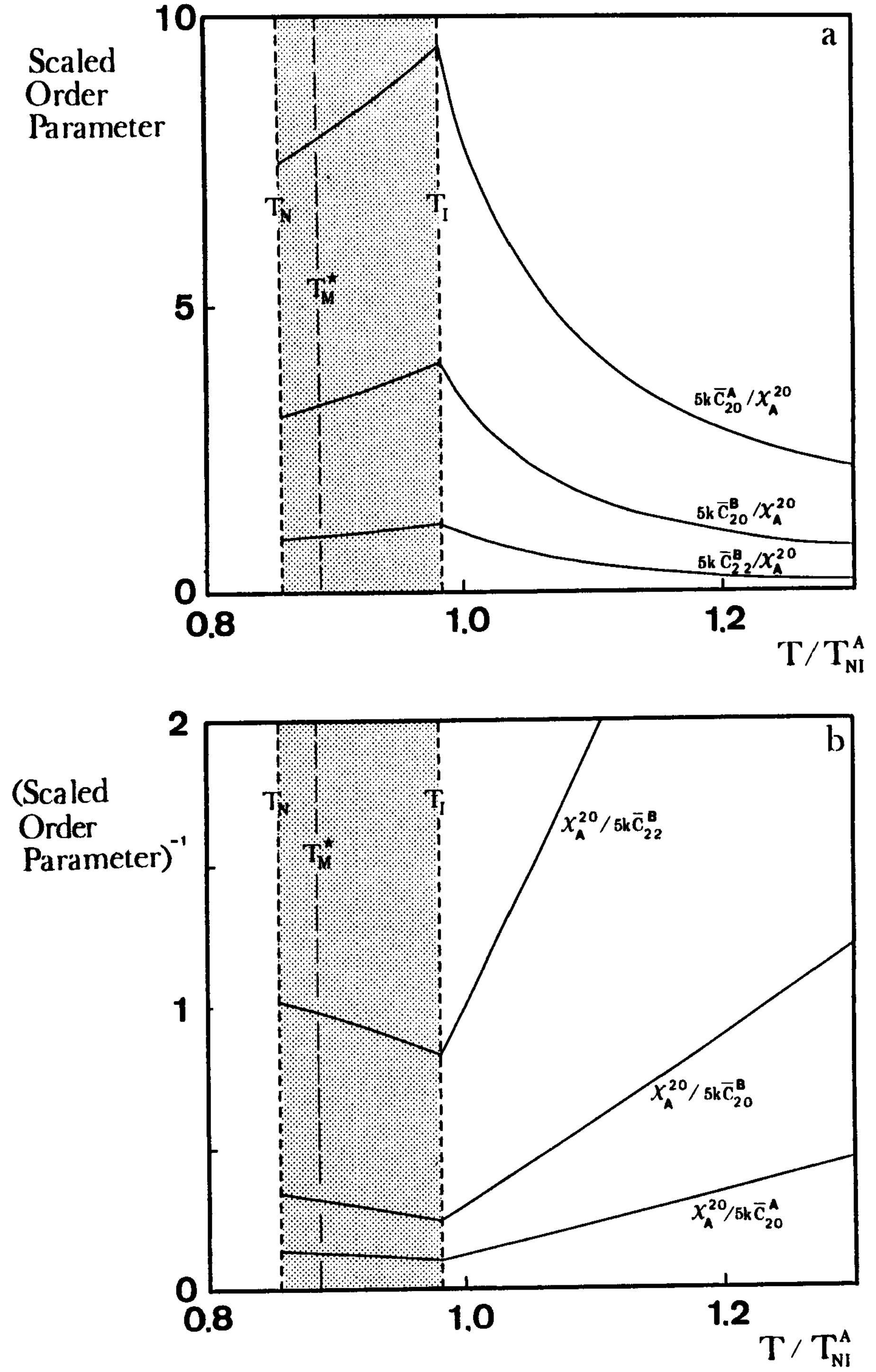

Figure 4. The scaled temperature dependence of (*a*) the scaled, field-induced order parameter for the solvent, $5k\bar{C}^{A}_{20}/\chi^{20}_{A}$ and the ordering tensor $5k\bar{C}^{B}_{20}/\chi^{20}_{A}$, $5k\bar{C}^{B}_{22}/\chi^{20}_{A}$ for the solute and (*b*) their inverses calculated from equations (33) to (36) and equation (53) using the parameters listed in the text.

solute mole fraction of 0·03. In figure 3 (*a*) we see that the divergence of $\bar{C}^A_{20}$ is quenched at the upper phase boundary and decreases as the temperature is lowered within the biphasic regime. The linear plots for the inverse order parameter, given in figure 3 (*b*), reveal that the sign of the slope is changed at the phase boundary and is reduced in the biphasic regime. Similarly the intercept is found to increase to a value above that for the pure nematogen. The predicted variations of the field-induced solvent order parameter is reminiscent of that observed for *p*-xylene dissolved in the nematogen Phase 5 [4]. However for this mixture it was the field-induced order parameters for the biaxial solute which were measured, although as we saw in §3.1 these are expected to parallel that of the rod-like solvent, at least in the limit of infinite dilution. None the less it is of importance to include the solute–solvent interactions in the calculations and this we do in the following section.

4.2. *Rods and laths*

The field-induced order parameters for the two components in this mixture of uniaxial and biaxial particles are not readily obtained in analytic form from equations (33) to (36). This is especially difficult when the temperature dependence of the composition is allowed for within the biphasic regime from equation (53). We have, therefore, found numerical solutions to these equations using the geometric mean approximations and typical values for the remaining parameters

$$x = 0{\cdot}03,$$

$$\bar{u}^{BB}_{200}/\bar{u}^{AA}_{200} = 0{\cdot}2, \qquad \bar{u}^{BB}_{222}/\bar{u}^{BB}_{200} = 0{\cdot}1,$$

$$\chi^{20}_B/\chi^{20}_A = 0{\cdot}2, \qquad \chi^{22}_B/\chi^{20}_B = 0{\cdot}1,$$

$$\beta^{\infty}_{\mathrm{I}} = -0{\cdot}6\,T^A_{\mathrm{NI}}, \qquad \beta^{\infty}_{\mathrm{N}} = -4{\cdot}8\,T^A_{\mathrm{NI}}.$$

The parameters are shown as scaled quantities because the results obtained as a function of the sealed temperature, T/T^A_{NI}, are also scaled quantities, namely $5k\bar{C}^A_{20}/\chi^{20}_A$, $5k\bar{C}^B_{20}/\chi^{20}_A$ and $5k\bar{C}^B_{22}/\chi^{20}_A$. These results for the scaled order parameters are shown in figure 4 (*a*); the divergence of all three within the homogeneous isotropic phase is clearly apparent as is the reversal of this trend when the biphasic regime is formed. The solute order parameters appear to parallel that for the solvent, as we had anticipated for this relatively low solute concentration. The plots of the inverse order parameters against the scaled temperature are given in figure 4 (*b*); they are linear and show the dramatic change in behaviour on entering the biphasic regime, thus the slopes are considerably reduced in magnitude and their signs are reversed. The linear plots for the three inverse order parameters have a common intercept and this is increased significantly within the biphasic regime.

Finally we note that the predicted temperature dependence for the solute order parameters bears a striking resemblance to those determined for *p*-xylene dissolved in Phase 5 [4], especially when allowance is made for the much smaller biphasic regime of the real nematogenic mixture.

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