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Computer simulation studies of anisotropic systems XXII. An equimolar mixture of rods and discs: a biaxial nematic?

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In principle, binary mixtures of rod-like and disc-like particles should exhibit a biaxial nematic phase, but in practice phase separation into two uniaxial nematic phases prevents this. Here, we report the results of a computer simulation study of an equimolar mixture of rods and discs in which phase separation is not allowed. The particles are confined to the sites of a simple cubic lattice in which each rod is surrounded by six discs and vice versa. Neighbouring particles interact such that they prefer to align with their respective symmetry axes orthogonal to each other. In contrast, the interaction between next nearest neighbours, which are either rods or discs, is such that their symmetry axes tend to be parallel. Monte Carlo simulations of this model mixture show that an orientationally ordered phase exists at low temperatures. This nematic phase has overall uniaxial symmetry and the particles have a negative second rank orientational order parameter, indicating that they tend to align at right angles to the director. The two interpenetrating sub-lattices containing either rods or discs, however, exhibit a biaxial nematic phase. The results of the simulation are found to be in reasonable agreement with the predictions of a molecular field theory for this model mixture. We have also investigated the behaviour of this mixture when the rods and discs are allowed to exchange between their lattice sites. The mixture is found to separate into two uniaxial nematic phases composed essentially of either rods or discs, as expected.

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1. Introduction

The constituent molecules of virtually all thermotropic nematogens depart from the high symmetry often assumed for them and yet the resulting nematic phase is non-polar and usually possesses cylindrical symmetry. This observation together with the elongated form of most nematogenic molecules has often prompted theoretical analyses to assume that the particles have $D_{\infty h}$ symmetry. Nonetheless, departure of the molecules from such symmetry can have important consequences for their liquid crystalline behaviour, as various theoretical treatments have demonstrated. Perhaps the most dramatic prediction is the existence of a biaxial nematic phase which can be formed directly from the isotropic or, for molecules with a smaller deviation from cylindrical symmetry, from the uniaxial nematic phase. This general behaviour has

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been predicted by a variety of molecular field theories [1–5] originating with the seminal work of Freiser [1]; these predictions have also been confirmed by the results of computer simulaton studies of particles with D_{2h} symmetry interacting via attractive [6] as well as purely repulsive forces [7]. Experimentally, biaxial nematic phases have been found for several lyotropic phases [8], but the situation is far less clear for thermotropic nematics. Several claims have been made to have discovered such a biaxial nematic phase [9], but evidence to substantiate these claims has not always been forthcoming [10].

An alternative route to the formation of the elusive biaxial nematic phase was proposed many years ago by Alben [11] and this is to mix both rod-like and disc-like particles. There are several predictions of the phase diagram to be expected from this binary mixture and the existence of a biaxial nematic is clearly observed for molecular field theories [11], hard particle systems [12, 13] and a van der Waals approach [14]. However, it was subsequently noted by Palffy-Muhoray and his colleagues that, on thermodynamic grounds alone, such mixtures should separate into two uniaxial nematic phases, one rich in discs and the other in rods [15]. This expected behaviour has been observed in a computer simulation study of a binary mixture of rod-like and disc-like particles [16] and also for a real mixture of calamatic and discotic mesogens, although the phase diagram here is somewhat more involved than that predicted [17]. It is, of course, possible to inhibit phase separation if the scalar interaction between unlike particles is sufficiently larger than the geometric mean of the scalar interactions between like particles [18]. The molecular engineering necessary for the creation of molecules with these particular properties has yet to be achieved. However, an alternative route is to use a computer simulation of a model system in which the constituent particles are not able to migrate and so the formation of a phase separated sample is prevented.

Here we report a Monte Carlo simulation study of such a model mixture of rods and discs. The nature of the model is described in the following section and a molecular field theory for this is given in § 3. The computational details of the simulation are listed in § 4, together with the properties used to characterize the phases and their structures. We also wished to see if the model mixture would undergo phase separation and the procedures used to allow translational motion of the particles are described in this section. Our results are gathered in § 5 where contact is made with the predictions of the molecular field theory, as well as with the results of simulation studies of related model systems. The main conclusions of our investigation are given in § 6.

2. The model mixture

To achieve a homogeneous phase, the particles, rods and discs, are confined to the sites of a simple cubic lattice. Each site, k, is characterized by dimensionless site coordinate $\mathbf{x}_x$ which have been scaled by the lattice parameter. The simple cubic lattice is bipartite, that is it consists of two interpenetrating sub-lattices which are defined as follows: for each lattice site the parameter ζ_k is equal to ± 1 depending on whether the sum of the coordinates $\mathbf{x}_k$ is even or odd. The two sub-lattices consist of nodes with the same parity; each lattice node is surrounded by six nearest neighbours belonging to the other sub-lattice and then by the twelve next nearest neighbours belonging to the same sub-lattice and so on. The opportunity for the observation of phase biaxiality is clearly maximal when the rods occupy one sub-lattice and the discs the other; we have, therefore, confined our attention to this equimolar mixture.

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Lattice models have proved to be valuable for enhancing our understanding of liquid crystals since the pioneering study by Lebwohl and Lasher [19]. In this, only nearest neighbours were allowed to interact and then via the continuous soft potential

$$U_{ij} = -\epsilon P_2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j), \tag{1}$$

where $\hat{\mathbf{u}}_i$ is a unit vector defining the orientation of the molecular symmetry axis. The strength parameter ϵ is positive and sets the temperature scale; $T^* = k_B T/\epsilon$. The model exhibits an orientational order–disorder transition which has been identified as a nematic–isotropic transition. Indeed, many of the properties of the system are found to have much in common with those of real nematics [19–22].

Within this model, it is not possible to distinguish between rod-like and disc-like particles since the potential is equation (1) will force both to align with their symmetry axes parallel. In an equimolar mixture in which the rods occupy the sites of one sub-lattice and the discs those of the other, such a distinction is possible, for only unlike particles are nearest neighbours and these interact so that their symmetry axes tend to be orthogonal. This can be achieved by simply replacing the minus sign in the Lebwohl–Lasher potential by a plus,

$$U_{ij} = \epsilon P_2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j). \tag{2}$$

Such a system has been considered by Kohring and Shrock [23] who found evidence for an ordering transition at T^* of $0{\cdot}65 \pm 0{\cdot}05$. In the low temperature phase the particles on the two sub-lattices are orientationally ordered, although the nature of this order is not clear and neither is it apparent if the two sub-systems have biaxial order. Part of this problem stems from the fact that the potential does not influence the ordering of particles on the same sub-lattice directly. All that is required in the ground state is that the neighbouring particles on the two sub-lattices are orthogonal; as Kohring and Shrock noted [23] this can be achieved by many configurations.

To overcome this difficulty we had previously modified the potential for rods and discs by the addition of a term for the like next nearest neighbours such that they align with their symmetry axes parallel [16]. This potential takes the form

$$U_{ij} = \epsilon f(r) P_2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j), \tag{3}$$

where $r = |\mathbf{x}_i - \mathbf{x}_j|$ and the function $f(r)$ is assigned the value 1 for nearest neighbours and $-1/8$ for next neighbours. This latter value results because we assume that the interaction decays as r^{-6} [16], in keeping with the Lennard–Jones 12–6 potential for atomic systems. This variation in the sign can be accommodated using the ζ_k parameters by writing the potential as

$$U_{ij} = -\epsilon \zeta_i \zeta_j |f(r)| P_2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j). \tag{4}$$

We expect that with this model, over a certain temperature range, molecules in the sub-lattices will align with their symmetry axes parallel, but that particles in different sub-lattices will tend to have their symmetry axes orthogonal. In defining the potential we have used a single energy parameter to control the anisotropic interactions between both unlike and like particles. Of course, the like interactions differ in magnitude from those for unlike particles because of their greater separation; our assumption concerning the nature of this distance dependence can be viewed as introducing a difference between like and unlike interactions. In principle, we could also have employed separate parameters for the rod–rod and disc–disc interactions, but this appears to be an unnecessary complication of our model and without any apparent

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benefits. We can now speculate on the nature of the orientational ordering in the ground state and at low temperatures. It is convenient to introduce three unit vectors $\hat{\mathbf{e}}_1$, $\hat{\mathbf{e}}_2$ and $\hat{\mathbf{e}}_3$, which can be identified with the lattice axes without any loss of generality because of the independence of the potential on the interparticle vector. In the ground state all of the particles in the even sub-lattice (say) point along $\hat{\mathbf{e}}_1$ and particles in the odd sub-lattice point along $\hat{\mathbf{e}}_2$. The $\hat{\mathbf{e}}_3$ direction is then not populated and the $(\hat{\mathbf{e}}_1\ \mathbf{e}_2)$ plane contains the symmetry axes of both the rods and the discs. As the temperature is increased, this picture is not expected to change significantly; $\hat{\mathbf{e}}_3$ will be sparsely populated while $\hat{\mathbf{e}}_1$ $\hat{\mathbf{e}}_2$ will contain the bulk of the symmetry axes. Such organization suggests a global order with the director along $\hat{\mathbf{e}}_3$ and with the symmetry axes of both rods and discs orthogonal to it. In the limit of perfect order, the usual second rank orientational order parameter $\bar{P}_2$ should be $-\frac{1}{2}$ while the fourth rank order parameter should be 3/8. More importantly, given our decision to make the interactions between like particles equivalent, the overall symmetry of the equimolar mixture is expected to be uniaxial. In constrast, the particles on a neighbouring sub-lattice will reduce the symmetry of the molecular environment on the other sub-lattice and so introduce a local phase biaxiality.

It is also of some interest to study the ability of this system to undergo phase separation, and so we have relaxed the condition of retaining the rods and discs on separate sub-lattices. Under these conditions it is necessary to modify the pair potential for like and unlike particles irrespective of whether they are nearest neighbours or next nearest neighbours. To achieve this the pair potential is written as

$$U_{ij} = -c|f(r)|P_2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j), \tag{5}$$

for like particles and

$$U_{ij} = \epsilon|f(r)|P_2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j) \tag{6}$$

for unlike particles where, as before, the interaction strength is taken to decay as r^{-6} and the interaction is restricted to nearest and next nearest neighbour particles [16].

In the remainder of the paper we shall refer to the homogeneous or uniform system of rods and discs as model I and to the system where the particles can exchange between sites as model II.

3. The molecular field theory

Here we present the molecular field theory for the model mixture of rods and discs defined in the previous section. Our starting point is the pair potential in equation (3) which gives the interaction energy of say a rod with a neighbouring disc and then with a next nearest neighbour which is a rod. Given the symmetry of the model, there is an entirely analogous expression for a disc interacting with a rod as its nearest neighbour and another disc as its next neighbour. The potential of mean torque for a rod is obtained by averaging the pair potential over the shells of surrounding molecules and over their orientations. This is achieved by writing the second Legendre polynomial, in equation (3), in terms of the orientations of the individual molecules using the spherical harmonic addition theorem

$$P_2(\cos\beta_{ij}) = \sum_m (-)^m C_{2m}(\omega_i) C_{2-m}(\omega_j). \tag{7}$$

The $C_{2m}(\omega)$ are modified spherical harmonics and ω_i denotes the spherical polar angles of the symmetry axis of particle i in the laboratory frame. This frame is defined with the

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major director for the rod sub-system along the z axis and that for the discs along the y axis. Within the context of our previous discussion, z would correspond to $\hat{\mathbf{e}}_1$ and y to $\hat{\mathbf{e}}_2$.

The single particle potential for a rod is then

$$U_{\mathrm{R}}(\omega)=6\epsilon\sum_m(-)^m\bar{C}^{\mathrm{D}}_{2m}C_{2-m}(\omega_{\mathrm{R}})-(3\epsilon/2)\sum_m(-)^m\bar{C}^{\mathrm{R}}_{2m}C_{2-m}(\omega_{\mathrm{R}}), \tag{8}$$

where the factor of 6 results from the number of nearest neighbours and (3/2) is a combination of 12 from the number of next nearest neighbours and the reduction of the interaction by 1/8. The averages $\bar{C}^{\mathrm{R}}_{2m}$ and $\bar{C}^{\mathrm{D}}_{2m}$ are the orientational order parameters for rods and discs, respectively, expressed in a common laboratory frame. The frame which we have chosen corresponds to the principal axis system for the nematic phase formed on each sub-lattice and so the order parameters with $m=\pm 1$ vanish. In addition, the components with m equal to ± 2 are real and identical. Given these results, the potential of mean torque can be written as

$$\begin{aligned}U_{\mathrm{R}}(\omega)=&\,\epsilon[6\bar{P}^{\mathrm{D}}_2-(3/2)\bar{P}^{\mathrm{R}}_2]P_2(\cos\beta)\\&+\epsilon[12\overline{(d^2_{20}\cos 2\alpha)^{\mathrm{D}}}-3\overline{(d^2_{20}\cos 2\alpha)^{\mathrm{R}}}]d^2_{20}(\beta)\cos 2\alpha,\end{aligned} \tag{9}$$

where $d^2_{20}(\beta)$ is a small Wigner rotation matrix. This expression involves the ordering tensor for both the rods and the discs, but for our model, with its equivalence of these particles, there is a simple geometric relationship between the two tensors. This is most easily seen in terms of the cartesian Q tensors describing the orientational order of the molecular symmetry axes in the laboratory frame

$$\mathbf{Q}^{\mathrm{R}}=\begin{bmatrix} Q^{\mathrm{R}}_{xx} & 0 & 0\\ 0 & Q^{\mathrm{R}}_{yy} & 0\\ 0 & 0 & Q^{\mathrm{R}}_{zz}\end{bmatrix} \tag{10}$$

and

$$\mathbf{Q}^{\mathrm{D}}=\begin{bmatrix} Q^{\mathrm{D}}_{xx} & 0 & 0\\ 0 & Q^{\mathrm{D}}_{yy} & 0\\ 0 & 0 & Q^{\mathrm{D}}_{zz}\end{bmatrix}. \tag{11}$$

For the rods, the major director is along the z axis, while for the discs it is along y; thus

$$Q^{\mathrm{R}}_{zz}=Q^{\mathrm{D}}_{yy} \tag{12}$$

Similarly

$$Q^{\mathrm{R}}_{yy}=Q^{\mathrm{D}}_{zz} \tag{13}$$

and

$$Q^{\mathrm{R}}_{xx}=Q^{\mathrm{D}}_{xx}. \tag{14}$$

We can now see that, although the Q tensors for particles on the two sub-lattices have biaxial symmetry, the entire mixture has uniaxial symmetry with principal components Q^{R}_{xx}, $(Q^{\mathrm{R}}_{yy}+Q^{\mathrm{R}}_{zz})/2$ and $(Q^{\mathrm{R}}_{zz}+Q^{\mathrm{R}}_{yy})/2$. The overall uniaxial symmetry of the phase has resulted from our decision to treat the anisotropic interactions between rods and between discs as identical.

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The irreducible form of the ordering tensor is related to the cartesian tensor via

$$\bar{P}_2^{\mathrm{R}} = Q_{zz}^{\mathrm{R}} \tag{15}$$

and

$$(\overline{d_{20}^2 \cos 2\alpha})^{\mathrm{R}} = (1/\sqrt{6})(Q_{xx}^{\mathrm{R}} - Q_{yy}^{\mathrm{R}}). \tag{16}$$

We can now write the potential of mean torque for a rod as

$$U_{\mathrm{R}}(\omega) = \epsilon[aP_2(\cos\beta) + 2bd_{20}^2(\beta)\cos 2\alpha], \tag{17}$$

where the coefficients a and b are related to the components of the ordering tensor by

$$a = (3/2)\bar{P}_2^{\mathrm{R}} + 3\sqrt{6}(\overline{d_{20}^2 \cos 2\alpha})^{\mathrm{R}}, \tag{18}$$

$$b = \sqrt{3/8}\bar{P}_2^{\mathrm{R}} + (3 - \sqrt{3/8})(\overline{d_{20}^2 \cos 2\alpha})^{\mathrm{R}}. \tag{19}$$

The order parameters are then obtained by solving the consistency equations

$$\bar{P}_2^{\mathrm{R}} = 2\pi Z^{-1} \int_0^{\pi} P_2(\cos\beta) I_0[2\epsilon b d_{20}^2(\beta)/k_{\mathrm{B}}T] \exp[\epsilon a/k_{\mathrm{B}}T)P_2(\cos\beta)] \sin\beta d\beta, \tag{20}$$

$$(\overline{d_{20}^2 \cos 2\alpha})^{\mathrm{R}} = 2\pi Z^{-1} \int_0^{\pi} d_{20}^2(\beta) I_1[2\epsilon b d_{20}^2(\beta)/k_{\mathrm{B}}T] \exp[(\epsilon a/k_{\mathrm{B}}T)P_2(\cos\beta)] \sin\beta d\beta, \tag{21}$$

where the orientational partition function is

$$Z = 2\pi \int_0^{\pi} I_0[2\epsilon b d_{20}^2(\beta)/k_{\mathrm{B}}T] \exp[(\epsilon a/k_{\mathrm{B}}T)P_2(\cos\beta)] \sin\beta d\beta. \tag{22}$$

Here $I_m[2\epsilon b d_{20}^2(\beta)/k_{\mathrm{B}}T]$ is an nth order modified Bessel function. These forms for the order parameters ensure that the orientational Helmholtz free energy

$$A = -(\epsilon/2)[a\bar{P}_2^{\mathrm{R}} + 2b(\overline{d_{20}^2 \cos 2\alpha})^{\mathrm{R}}] - k_{\mathrm{B}}T \ln Z \tag{23}$$

is a minimum with respect to fluctuations in the order parameters.

The form of the potential of mean torque has much in common with that predicted by molecular field theory for a biaxial particle in a uniaxial nematic phase [24]. However, in this theory it is possible to make a further approximation which results in the ratio b/a being independent of the orientational order and this facilities the solution of the consistency equations. Such an approximation is not possible for the binary mixture considered here, and so the consistency equations (20) and (21) were solved numerically. Solutions to the two non-linear equations were found for a given scaled temperature $k_{\mathrm{B}}T/\epsilon$ by using a NAG library minimization routine EO4CCF which employs the SIMPLEX $N+1$ points method. The order parameters were observed to decrease with increasing temperature and to vanish simultaneously and continuously at T^* of 1·5. Evaluation of the orientational free energy using these order parameters shows that the transition from the biaxial nematic phase to the isotropic phase is predicted to be second order and to occur when T^* is 1·5. We shall make contact with this and other predictions of the molecular field theory when we consider the results of our computer simulation studies.

4. Computational aspects

The Monte Carlo simulations were performed using standard periodic boundary conditions and sample sizes of 10^3 and 16^3 particles for model I and 10^3 for model II; our reasons for using a larger sample for model I will become apparent shortly.

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Random rotations were attempted on randomly selected particles with the aid of the Barker–Watts algorithm [25]. In addition, for model II we introduced a move with which to exchange particles; this was chosen to be implemented with a probability p, where p is an input parameter and determines the fraction of moves $(1-p)$ in which an attempt is made to change the orientation of a particle. The equilibrium runs took typically 5000 cycles, where one cycle or sweep corresponds to a number of attempted moves equal to the number of particles in the sample. The production runs took up to 250 000 cycles especially near the phase transition; the sub-averages which were employed to evaluate the statistical errors were calculated over macrosteps consisting of 250 cycles.

The exchange routine necessary for model II can be implemented in a variety of ways, each of which is consistent with microscopic reversibility. These methods include

(*a*) selecting a pair of unlike particles at random,
(*b*) choosing a pair of nearest neighbours at random,
(*c*) choosing a pair of nearest neighbours or next nearest neighbours at random,
(*d*) selecting a pair of particles at random.

The last three procedures include the possibility of exchanging like particles, in contrast to the first method. The four methods were tested over a wide range of scaled temperatures ($T^*=0{\cdot}2$, 0·4, 0·6, 0·8, 1·0 and 1·25); they were found to give the same results for the major order parameter of the total mixture and of the biaxial components, to within the statistical error. However, at low temperatures, method (*b*) was found to be slow to converge, and in practice we have used procedure (*a*) which selects a pair of unlike particles for all of the temperatures [26].

To facilitate the simulations, the configuration at the end of the equilibrium stage was used to start both the production run at that temperature and the equilibrium stage at the next temperature. The starting configuration for model I was the ground state configuration with the symmetry axes of the discs pointing along the x axis of the simulation box and those for the rods aligned along the y axis. For model II, where we wished to explore the possibility of phase separation, three different starting configurations were employed. These were

(i) a random mixture of the rods and discs on the lattice;
(ii) a homogeneous mixture, that is, with the rods on one sub-lattice and the discs on the other;
(iii) a layered arrangement in which the rods occupy the lattice sites in one half of the simulation box and the discs occupy the other half.

Even at the lowest temperatures the mixed configurations (i) and (ii) converged within a few thousand cycles to a phase separated mixture, in agreement with a previous simulation study [16].

The configurational heat capacity, which is important in locating any phase transitions, was evaluated from the fluctuations in the potential energy as well as by fitting the temperature dependence of the internal energy to a cubic spline. In addition our procedures were checked by using a polynomial fit to $\bar{U}^*$.

The extent of the orientational order of the total mixture and of the individual components was evaluated at both the second and fourth rank level. The second rank orientational order parameter was evaluated from the Q tensor

$$Q_{\alpha\beta}=(3\overline{\hat{\mathbf{u}}_\alpha\hat{\mathbf{u}}_\beta}-\delta_{\alpha\beta})/2 \tag{24}$$

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introduced by Vieillard-Baron [27]. The fourth rank order parameter comes from the analogous quantity [22]

$$B_{\lambda\mu\nu\rho}=\{35\hat{\mathbf{u}}_\lambda\hat{\mathbf{u}}_\mu\hat{\mathbf{u}}_\nu\hat{\mathbf{u}}_\rho-5[\delta_{\nu\rho}\overline{\hat{\mathbf{u}}_\lambda\hat{\mathbf{u}}_\mu}+\delta_{\mu\rho}\overline{\hat{\mathbf{u}}_\lambda\hat{\mathbf{u}}_\nu}$$
$$+\delta_{\mu\nu}\overline{\hat{\mathbf{u}}_\lambda\hat{\mathbf{u}}_\rho}+\delta_{\lambda\rho}\hat{\mathbf{u}}_\mu\hat{\mathbf{u}}_\nu+\overline{\delta_{\lambda\nu}\hat{\mathbf{u}}_\mu\hat{\mathbf{u}}_\rho}+\overline{\delta_{\lambda\mu}\hat{\mathbf{u}}_\nu\hat{\mathbf{u}}_\rho}]+\delta_{\lambda\mu}\delta_{\nu\rho}+\delta_{\lambda\nu}\delta_{\mu\rho}+\delta_{\lambda\rho}\delta_{\mu\nu}\}8. \quad (25)$$

In both cases, the Greek subscripts refer to cartesian components of the various tensors. These quantities were originally formulated to deal with the observation that, during a computer simulation, the main director, as well as the minor director for biaxial systems can change their orientation within the simulation box. In order to allow for this, the Q tensor is averaged over a number of cycles, selected so that the director orientation does not change. It is then diagonalized, which is equivalent to a tranformation from the frame fixed in the simulation box to the director frame and the eigenvalues are averaged over the production stage of the simulation. For a uniaxial phase formed from a single component, this procedure presents few problems, for the largest eigenvalue is readily identified as the order parameter for the system and can be averaged during the simulation.

The situation is not so straightforward for the binary mixture which we have studied, first, because it is necessary to define order parameters for the two components as well as for the entire system; secondly and more importantly, we need to allow for fluctuations in the orientations of the major and minor directors for both the global system and the individual components. To illustrate the problems, we consider the second rank ordering tensor $\mathbf{Q}^{s,m}$ obtained for the mth macrostep and for the system s where this label denotes the entire mixture ($s=3$) or just the rods ($s=1$) or discs ($s=2$). The eigenvalues of this Q tensor are denoted by $q_k^{s,m}$ and the associated eigenvectors are $\mathbf{v}_k^{s,m}$. To simplify the notation, we label the three eigenvalues as η_k; the problem is to decide which of these eigenvalues should be averaged over the various macrosteps. As we have indicated, there is no difficulty for the major order parameter, for we simply select the largest eigenvalue, except perhaps in the isotropic phase where this procedure necessarily overestimates the orientational order [28]. The real difficulty arises when we come to average the other two eigenvalues, for there are two extreme ways in which this might be achieved. First, we could reorder the eigenvalues such that $|\eta_3|\geqslant|\eta_2|\geqslant|\eta_1|$ which would have the effect of artificially enhancing the biaxiality of the phase $(\eta_2-\eta_1)$. This might be expected to be a problem if the phase was uniaxial, but the method has been applied to systems where phase biaxiality is observed and no difficulties appear to have arisen [6, 7]. Of course the magnitude of the spurious biaxiality in $\mathbf{Q}$ will depend on the size of the system and should be relatively small for the number of particles usually studied. Secondly, at the other extreme, we could order the two remaining eigenvalues at random, which would have the effect of reducing the phase biaxiality. In an attempt to avoid the bias of either of these two extremes we have considered the following alternatives for the reordering of the eigenvalues of $\mathbf{Q}^{m,s}$.

(*a*) The eigenvalues were reordered via an even (or an odd) permutation such that $\eta_3\geqslant\eta_1$ and $\eta_3\geqslant\eta_2$.

(*b*) An even (or odd) permutation of the eigenvalues is used to give $|\eta_3|\geqslant|\eta_1|$ and $|\eta_3|\geqslant\eta_2|$. However, for normal nematics, η_3 is positive and so here this method would be equivalent to (*a*).

(*c*) The previous methods were motivated by the aim to have some unbiased ordering of the eigenvalues of the Q tensor from one macrostep to the next.

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However, a more physical approach to the problem is also possible and that is to assume that the director orientation should not change significantly between macrosteps. Thus at the end of the mth macrostep, we look at the eigenvectors $\mathbf{v}_k^{s,m}$ and associate them with the eigenvalues from the previous macrostep $\mathbf{v}_k^{s,m-1}$ to which they are closest orientationally. Equivalent eigenvalues are then assigned to the equivalent eigenvectors. This assignment was achieved by forming the sum of scalar products

$$\Omega^{s,m} = \sum_k (\mathbf{v}_k^{s,m-1} \cdot \mathbf{v}_k^{s,m})^2 \tag{26}$$

and selecting the labels k for the eigenvectors for the mth macrostep from the six possible combinations such that $\Omega^{s,m}$ is a maximum. To apply this procedure we need simply to assign the labels to the eigenvalues for the first macrostep, and we can do this, without loss of generality, using procedure (*a*). After reordering the eigenvalues during the production stage and performing the necessary averages we obtained the major order parameters $\overline{\eta_3}$ and the biaxial order parameter $\overline{\eta_1} - \overline{\eta_2}$ for the total system as well as for the individual components.

During the simulation, the three methods used to order the eigenvalues were compared. For model I, procedures (*b*) and (*c*) were found to give essentially the same results, both qualitative and quantitative, for the total system for all temperatures within the ordered phase. That is the second rank order parameter for the mixture is negative and the phase has uniaxial symmetry. For the two components on their individual sub-lattices there is a low temperature range where the eigenvalue largest in magnitude is positive, the two sub-lattices are biaxial and the major directors are orthogonal. In addition, there is a high temperature range ($T^* \geqslant 0{\cdot}7$), where the eigenvalue largest in magnitude can have either sign; this corresponds to a system with maximal phase biaxiality so that the major and biaxial order parameters are simply equal and opposite in sign. In this regime, method (*b*), which uses the magnitude, but not the signs of the eigenvectors, failed although methods (*a*) and (*c*) gave results in more or less good agreement. We shall return to this unexpected and fascinating behaviour of the particles on the sub-lattices in the following section.

For model II, the three methods gave the same result for both the rod and disc components, that is uniaxial phases with positive second rank order parameters. The symmetry of the total mixture was also found to be uniaxial, although now the overall second rank order parameter is negative, and so method (*b*) cannot be employed for this system; the remaining two methods gave identical results.

The fourth rank orientational order parameter was evaluated from the B tensor in the following way [22]. At the end of each macrostep, the eigenvectors associated with the reordered eigenvalues define the column vectors of an orthogonal matrix $\mathbf{A}$. This is then used to transform $\mathbf{B}$ into the director frame and the diagonal element B_{3333} is then averaged over the production run and identified with $\bar{P}_4$. This procedure was used to determine $\bar{P}_4$ for the two components in model I, as well as for the total mixture. The values obtained were found to be rather insensitive to the choice of reordering procedure used, which is perhaps to be expected, because we are only concerned with the major fourth rank order parameter and not in the departure of this ordering tensor from cylindrical symmetry.

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The orientational correlations were also investigated for model I via the second and fourth rank correlation functions which are defined by

$$G_L(r) = \overline{P_L(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)}, \tag{27}$$

where L is 2 or 4. The average is evaluated for pairs of particles i and j separated by $r = |\mathbf{x}_i - \mathbf{x}_j|$. The results are shown as functions of r^2 rather than r, since this has the advantage that even values of r^2 belong to sites on the same sub-lattice, whereas odd values correspond to sites on different sub-lattices. The behaviour of these orientational correlation functions for particular limiting situations are considered in § 5.

The primary interest in model II is in its ability to undergo phase separation and to monitor this, we have calculated the spatial distribution function for like and unlike particles $g^{RR}(r)$, $g^{DD}(r)$ and $g^{RD}(r)$ [16]. These distributions give the probability of finding a particle of a particular type at a distance r from a given particle. For example

$$g^{RR}(r) = N_R(r)/N(r)x_R, \tag{28}$$

where $N_R(r)$ is the average number of rod-like particles separated by r from a rod, $N(r)$ is the total number of lattice sites at the distance r and x_R is the mole fraction of rods in the mixture. In the limit of a random mixture, $g^{RR}(r)$, as well as the other spatial distribution functions, are independent of r and equal to 1. In general, the unlike distribution functions are equal ($g^{RD}(r) = g^{DR}(r)$), and they are related to the like distributions by, for example,

$$x_R g^{RR}(r) + x_D g^{RD}(r) = 1. \tag{29}$$

For an equimolar mixture of rods and discs $g^{RR}(r)$ and $g^{DD}(r)$ are necessarily equal. In the limit of an infinite system separated into two pure phases, the unlike distributions vanish and the like distribution functions are equal and independent of r. The value of the constant depends on the composition of the binary mixture and for an equimolar mixture takes the value 2. However, for the relatively small numbers of particles used in a simulation, $g^{RR}(r)$ is found to deviate significantly from this limit; for a layered system, it starts at small separations close to the value of 2 for an infinite system, but then decays rapidly to a value close to unity. The decay is not monotonic, but exhibits a structure which is characteristic of the lattice [16].

Finally, the orientational order in model I was characterized by calculating the singlet orientational distribution function for the total mixture at a single temperature T^* of 0·6, using procedures described elsewhere [29]; this involved the analysis of one configuration every cycle of the production run. For model I, $f(\beta)$ is an even function of $\cos\beta$ and so can be expanded in a basis of even Legendre functions as

$$f(\beta) = (\tfrac{1}{2})\left\{1 + \sum_{L>0} (2L+1) f_L P_L(\cos\beta)\right\}, \tag{30}$$

where the expansion coefficients f_L are the even rank order parameters $\bar{P}_L$ [30].

5. Results and discussion

We begin the discussion of our results with the global properties of model I in which the equimolar mixture of rods and discs is constrained to retain its uniform distribution. The temperature dependence of the heat capacity is shown in figure 1. This was calculated for the two system sizes (10^3 and 16^3) using various methods; the results are in close agreement and the cusp suggests a phase transition in the vicinity of T^*

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equal to $1{\cdot}0 \pm 0{\cdot}025$. The shape of the temperature dependence and the insensitivity of C_v to the system size suggest that the transition is not first order. However, C_v does not exhibit a jump at the transition which would be expected for a second order transition and which is predicted by molecular field theory for this transition. Given the relatively small system size, we can only conclude from C_v that the transition is higher than first order. We have also shown in figure 1 the heat capacity predicted by the molecular field theory with the temperature scaled to that at the transition. Within the nematic phase, there is remarkably good agreement between theory and simulation; this is less impressive in the isotropic phase where C_v is predicted to drop to zero from the nematic phase and to remain at this value. Such failures of molecular field theories are not surprising and result from the short range orientational order in the isotropic phase which is not predicted by theory.

The agreement between theory and the simulations for the transition temperature is not so good; thus T^*_{NI} is found to be 1·0, whereas the predicted value is 1·5. This tendency of the molecular field approximation to yield transition temperatures which are far too large seems to be a common feature for phase transitions which are higher than first order [31]. In those other examples, the higher order character of the transitions stems from the two dimensional nature of the systems, but our result for a system in three dimensions suggests that the failure of the molecular field approximation to predict the transition temperature stems from the higher order nature of the transition. The agreement is usually better for systems exhibiting a first order transition, albeit weak, as in the Lebwohl–Lasher model [20]. The failure of the theory to predict the transition temperature necessarily complicates the comparison of

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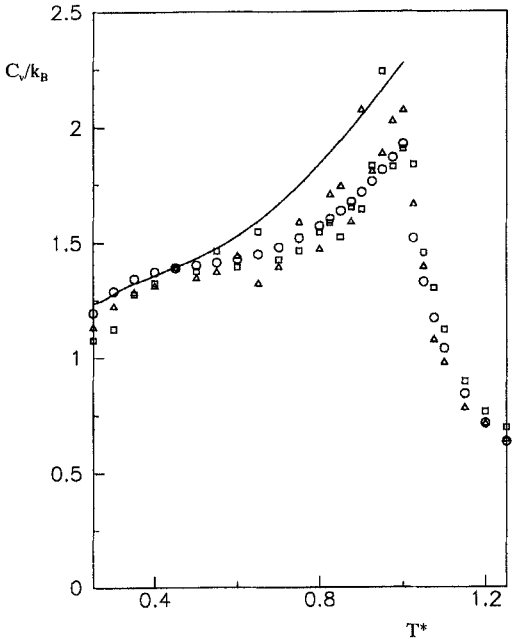

Figure 1. The temperature dependence of the configurational heat capacity for model I. The results were obtained via fluctuations in the internal energy for 10^3 (□) and 16^3 (○) particles; in addition, C_v was determined from a least squares fit to the internal energy and subsequent differentiation (○). The prediction of the molecular field theory, with the temperature scaled to the transition, is shown as the solid line.

simulation and theory for the other properties which we have determined. To overcome this difficulty we shall, as for the heat capacity, scale the temperature occurring in the molecular field theory so that the transition temperatures match.

The nature of the low temperature phase and the extent of the orientational order is available from the Q tensor for the total mixture. The tensor is found to be cylindrically symmetric within the statistical error, and the major order parameter for the molecular symmetry axes of both rods and discs is found to be negative; both of these findings are in agreement with the predictions of the molecular field theory. The temperature dependence of the order parameter $\bar{P}_2$ for the global system is shown as the triangles in figure 2. The negative order parameter is seen to go continuously to zero at the transition, as expected from its higher order character. In addition, the dependence of $\bar{P}_2$ on temperature is essentially linear, which is an unexpected feature, at least for conventional nematics and their mixtures. Nonetheless, the molecular field theory is able to predict this unusual temperature dependence, as the dashed line in figure 2 clearly shows. At low temperatures, theory predicts a slighly less negative value for $\bar{P}_2$ than is observed in the simulations; we have no explanation for this small difference.

The temperature dependence of the fourth rank order parameter of the mixture is shown in figure 3 as the open triangles. It is positive but small, as expected for a mixture where the molecules tend to align with their symmetry axes perpendicular to the director. Again in accord with the higher order nature of the transition, $\bar{P}_4$ passes continuously to zero; in addition there is an unusual upward curvature of this order parameter with decreasing temperature. The molecular field theory is, however, able to account for this feature, as the dashed line in figure 3 clearly shows.

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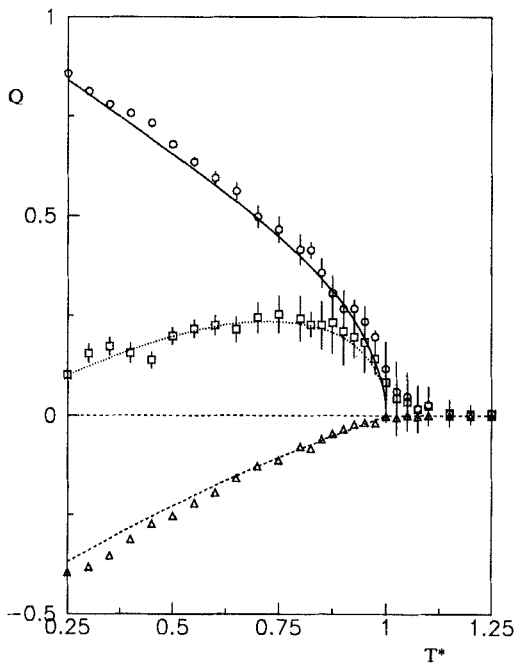

Figure 2. The second rank orientational ordering tensor for model I as a function of temperature; (○) major order parameter Q_{zz} for the sub-lattice (□) biaxial order parameter $Q_{xx}-Q_{yy}$ for the sub-lattice and (△) major order parameter Q_{zz} for the total system. The lines show the predictions of all three quantities obtained from the molecular field theory with the temperature scaled to that of the transition.

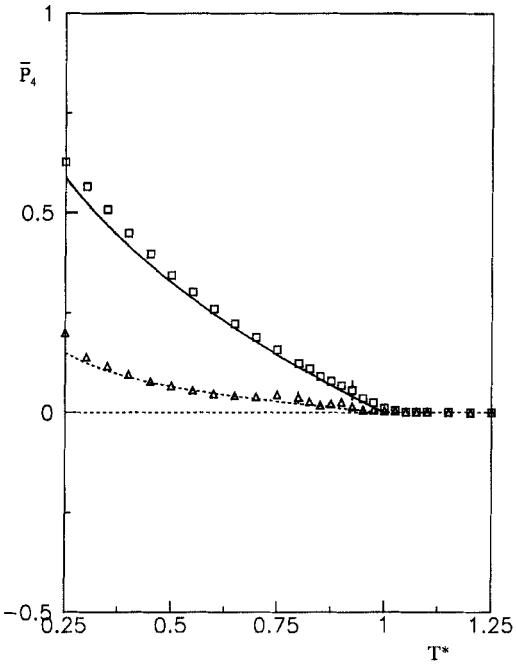

Figure 3. The temperature dependence of the fourth rank order parameter for model I obtained for (□) the sub-lattice and (△) the total system. The predictions of the molecular field theory with the temperature scaled to the transition are shown as the solid and dashed lines.

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Information on both $\bar{P}_2$ and $\bar{P}_4$, as well as all of the higher rank orientational order parameters, is contained in the singlet orientational distribution function for the mixture. This was calculated at a scaled temperature of 0·6 with the result shown in figure 4. The maximum in $f(\beta)$ at 90° is, of course, entirely expected, but it is still unusual for normal nematics where the molecular symmetry axes tend to be parallel to the director [32]. The distribution function for the mixture does contain a very small additional maximum when β is zero. In terms of the molecular interactions, the origin of the secondary maximum is obscure, although it is presumably related to the strong interaction between nearest neighbours which tends to keep their symmetry axes perpendicular. The expansion in equation (30) provides a good fit to the orientational distribution function when the series contains just four terms. The coefficients for these yield the order parameters $\bar{P}_2 = -0{\cdot}195 \pm 0{\cdot}003$; $\bar{P}_4 = 0{\cdot}053 \pm 0{\cdot}004$; $\bar{P}_6 = -0{\cdot}0063 \pm 0{\cdot}002$ and $\bar{P}_8 = 0{\cdot}0017 \pm 0{\cdot}002$. The quality of the fit with these four values is excellent as we can see from the distribution function calculated from them; this is shown as the solid line in figure 4. The error in the order parameter $\bar{P}_8$ is rather high, but if this term is excluded, then the small maximum in $f(\beta)$ at 0° is not reproduced, although the fit in all other regions remains excellent. The first two order parameters are in good agreement with those obtained from the Q and B ordering tensors where the statistics are far better; the results are $\bar{P}_2 = -0{\cdot}195 \pm 0{\cdot}002$ and $\bar{P}_4 = 0{\cdot}047 \pm 0{\cdot}001$.

We turn now to the individual ordering of the rods and discs on the two sub-lattices. As we have noted for temperatures less than 0·7, the ordering tensors are equivalent, with the eigenvalue largest in magnitude positive, corresponding to a nematic phase which is made biaxial via its interaction with the particles on the neighbouring sub-lattice. The main directors for the biaxial nematics are orthogonal and so it is possible

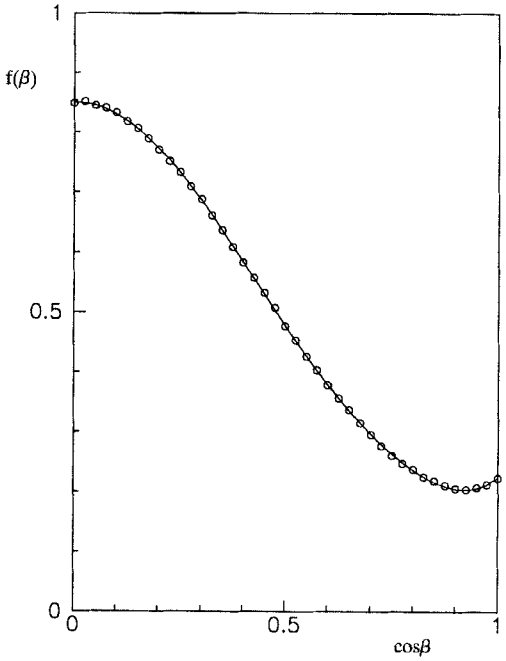

Figure 4. The singlet orientational distribution function for model I calculated for the total system at T^* of 0·6. The solid line shows the fit to equation (30) truncated after the first four terms.

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to think of the molecular field of one nematic being aligned orthogonal to the director of the other and hence creating the phase biaxiality, just as an external field can induce biaxiality in a single component system [33]. Above T^* of 0·7, the phase biaxiality associated with the particles on either lattice is found to approach its maximum value, so that two eigenvalues are essentially equal but opposite in sign, and the third is approximately zero. In addition, it was found that the ordering tensors for the rods and discs were not equivalent, but tended to oscillate out of phase with one another. The period for this oscillation appears to be of the order of several hundred cycles. In an attempt to see if this unexpected oscillatory behaviour was some artefact of the simulation as the transition to the isotropic phase was approached, we tried several modifications to the simulations. Thus, we increased the number of particles from 10^3 to 16^3; we used extremely long production runs amounting to 250 000 cycles and we reduced the number of cycles between diagonalization of the Q tensor in case the director reorientation was occurring more rapidly as the order in the system was reduced. However, none of these measures altered the basic behaviour in which the two sub-lattices appear to exchange their order. In fact, a similar exchange of order between sub-lattices has also been reported by Kohring and Shrock [23] for their model in which there are only interactions between nearest neighbours. It seems likely that our system is behaving in an analogous manner because, at these higher temperatures, the interaction between next nearest neighbours is no longer sufficient to retain the conventional nematic order on the sub-lattices. If this is the case, then we may be seeing the retention of nematic order on one sub-lattice while the particles on the other simply fan out so that they satisfy the constraint of remaining orthogonal to their nearest neighbours. There is clearly no reason why the nematic order should be confined to one

sub-lattice rather than the other and so the order will exchange between the sub-lattices. Given that the order for the particles on the two sub-lattices must, on average, be the same, and because their order seems to oscillate out of phase, we have decided to average the major and biaxial order parameters for the sub-lattices at each macrostep. It is these averages which are reported in figure 2 above T^* of 0·7 and it is presumably the exchange of order which is responsible for the rather high level of noise on the order parameters in this region. However, we should note that the individual values for the sub-lattices averaged over the production stage do not differ in any significant way from those found by first averaging the results for the two sub-lattices, provided, of course, that the production run is sufficiently long.

The results for both the major order parameter Q^{R}_{zz} and the biaxial order parameter $(Q^{\mathrm{R}}_{xx}-Q^{\mathrm{R}}_{yy})$ fall continuously to zero as the transition to the isotropic phase is approached. Below this transition, Q^{R}_{zz} grows with decreasing temperature as we had expected. However, the biaxiality $(Q^{\mathrm{R}}_{xx}-Q^{\mathrm{R}}_{yy})$ first increases, passes through a maximum and then decreases with decreasing temperature. Such behaviour is analogous to that predicted and observed for the ordering of biaxial molecules in a uniaxial phase [24, 34]. It results from essentially the same effect. As Q^{R}_{zz} approaches its limiting value of 1, both Q^{R}_{xx} and Q^{R}_{yy} must tend to the limiting negative value of $-\frac{1}{2}$ in order to ensure that the Q tensor is traceless; as this occurs, so the biaxiality must vanish. Another way of visualizing this dependence is to plot the phase biaxiality against the major order parameter, thus eliminating temperature; an entirely analogous plot is used in studies of molecular biaxiality in uniaxial phases [24, 34]. Our data are plotted in this way in figure 5; they show that when Q^{R}_{zz} vanishes, so must the biaxiality $(Q^{\mathrm{R}}_{xx}-Q^{\mathrm{R}}_{yy})$. The results pass through a maximum when Q^{R}_{zz} is just less than 0·5 and then decrease to approach the other limiting case when Q^{R}_{zz} is unity and the phase biaxiality must again vanish.

Both representations of our results can be used to provide a further test of the molecular field theory which we have developed. The biaxiality plot shown in figure 5 provides a less searching test of the theory, because temperature has been eliminated from the comparison and so the failure of the theory to predict T_{NI} is not apparent. The curve given in the figure was obtained from the molecular field theory and it is clearly in very good agreement with the results obtained from the simulation. In contrast, the theory is not able to fit the temperature dependence of the order parameters unless we compensate for its failure to predict the transition temperature by scaling the temperatures to this point. If we do this then we obtain the two curves shown in figure 2 which are again in extremely good agreement with the simulation. Indeed, the quality of this fit can be taken as some justification for our apparently *ad hoc* procedure of averaging the ordering tensors for the two sub-lattices.

The final quantity which we have calculated to probe the single particle order of the sub-lattices is the major fourth rank orientational order parameter $\bar{P}_4$. This was also determined by averaging the results for the two sub-lattices, and the results are shown as a function of the scaled temperature T^* in figure 3. As we have come to expect, this passes continuously to zero at the transition and the temperature variation has a slight upward curvature. This behaviour is entirely in keeping with the molecular field theory, as the theoretical prediction shown as the solid line in figure 3 clearly demonstrates.

We now consider the results for the orientational correlation functions $G_L(r)$; these were calculated for model I containing 10^3 particles at the five temperatures 0·4, 0·6, 0·8, 1·0 and 1·25 with the results shown in figures 6 (*a*)–6 (*e*), respectively. In these the values of the second rank correlation function $G_2(r)$ are denoted by squares and those for the

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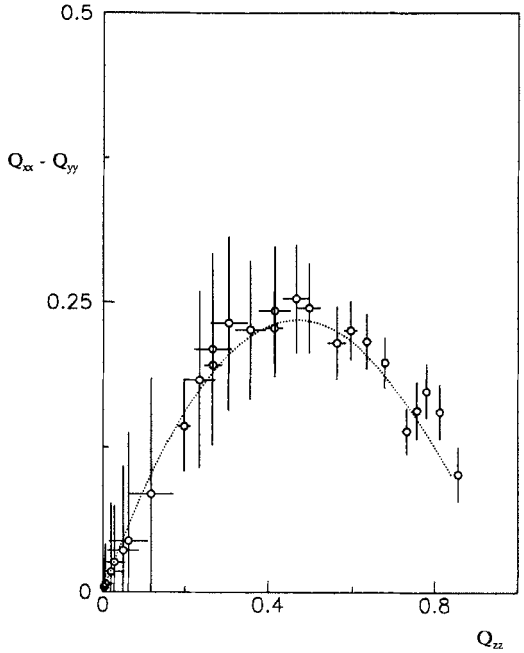

Figure 5. The dependence of the second rank phase biaxiality parameter $(Q_{xx}-Q_{yy})$ on the major order parameter Q_{zz} for a sub-lattice. The dotted line shows the prediction of the molecular field theory.

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fourth rank $G_4(r)$ are denoted by triangles. To appreciate the significance of our results it is instructive to consider a number of limiting situations. In the limit of the perfectly ordered ground state for like particles, $G_2(r)$ and $G_4(r)$ are unity independent of r and for unlike particles $G_2(r)$ is $-\frac{1}{2}$ and $G_4(r)$ is 3/8, again independent of r. This difference in behaviour for the correlations between like and unlike particles, together with the fact that r^2 for like particles is even, but odd for unlike particles means that both $G_2(r)$ and $G_4(r)$ are expected to exhibit a pronounced alternation. This, in itself, is of little physical significance, and in considering the correlation functions we shall confine our attention either to those for like or those for unlike particles. In the limit of large separations, when all direct angular correlations are lost, the correlation functions are related to the single particle order parameters. Thus, by using the spherical harmonic addition theorem

$$\lim_{r\to\infty} G_L^{AB}(r)=\sum_m (-)^m \bar{C}^A_{Lm}\bar{C}^B_{L-m}, \tag{31}$$

where $C_{Lm}(\omega)$ is a modified spherical harmonic and $\bar{C}^A_{Lm}$ is the ordering tensor for a molecule of type A. In a phase composed of uniaxial particles subject to a uniaxial ordering potential the $\bar{C}_{Lm}$ vanish unless m is zero and so [35]

$$\lim_{r\to\infty} G_L^{AB}(r)=\bar{P}^A_L\bar{P}^B_L. \tag{32}$$

For a single component system the limiting value of $G_L(r)$ provides a valuable route to the single particle order parameter $\bar{P}_L$ as shown by Zannoni [27]. This does not prove

to be the case for our system, for although the particles are cylindrically symmetric, they are subject to a biaxial ordering potential and so

$$\lim_{r\to\infty} G_L^{AB}(r) = \bar{P}_L^A \bar{P}_L^B + \sum_{m\neq 0} (-)^m \bar{C}_{Lm}^A \bar{C}_{L-m}^B. \tag{33}$$

Here, the presence of these biaxial terms removes the formal use of $G_L^{AB}(r)$ to obtain the order parameters. Nonetheless the additional terms are often small and we can obtain a useful check on the values of $\bar{P}_L^A$ and $\bar{P}_L^B$ from the limiting value of $G_L^{AB}(r)$.

At the lower temperature of 0·4, the behaviour of the second rank correlation functions for both like and unlike particles is in general accord with the description we have just given (see figure 6 (*a*)). For like particles, $G_2(r)$ is both large and positive; it decays rapidly, that is within a few lattice spacings, to a plateau value which is consistent with the major and biaxial order parameters determined at this temperature for the particles on individual sub-lattices. In fact the contribution of the biaxial terms to the plateau value is rather small in comparison with that from $\bar{P}_2^2$; the values are 0·008 and 0·574 which combine to give a limiting plateau value of 0·582 in good agreement with the observed value of 0·589. Unlike particles tend to be orthogonal to each other and so $G_2(r)$ is negative; though unlike particles have a stronger interaction than like particles, the decay to the plateau value also takes place within a few lattice spacings, as for like particles. Again the biaxial terms make a moderate contribution to the plateau value of $G_2(r)$; the values now are $-0{\cdot}056$ in comparison with $-0{\cdot}347$ coming from the $\bar{P}_2^D \bar{P}_2^R$ term; this gives a total of $-0{\cdot}403$ which is in equally good agreement with the observed value of $-0{\cdot}396$. The fourth rank correlation functions for like and unlike particles are both positive as we had anticipated. They are significantly smaller than their second rank counterparts, presumably because of the larger number of nodes in $P_4(\cos\beta)$ than $P_2(\cos\beta)$. It is this significant reduction from the ground state limit which may well cause the correlation functions for like and unlike particles to be so similar. Again the $G_4(r)$ decay to their limiting values within a few lattice spacings. We are not able to calculate the value of the plateau because we do not have the fourth rank order parameters which reflect the departure of the phase from cylindrical symmetry. However, for like particles, the contribution of the $\bar{P}_4^2$ term to the plateau is 0·202; the observed value is 0·233 which suggests that the biaxial contributions are somewhat small. This may not be the case for unlike particles; indeed, ignoring any biaxiality leads to a value of 0·076 which is significantly smaller than the value extracted from the simulation of 0·176.

As the temperature is increased and the transition to the isotropic phase approached, so we expect and observe that the orientational correlations decrease in magnitude (see figure 6). Such reductions are clearly far more pronounced for the fourth rank correlation functions; indeed, they adopt quite small values in keeping with the low values of the fourth rank single particle order parameter. In consequence, they may not be of particular value in studying the molecular organization in a mesophase. The changes in the limiting values of the second rank orientational correlation functions prove to be entirely in keeping with the reduction in the major order parameter and the modest variation in the biaxial order parameter. At short range, the correlation functions for both like and unlike particles deviate from their long range limit; indeed, the magnitude of this deviation is a measure of the validity of the molecular field approximation for the system. From the plots in figure 6, the deviations seem to be rather small, although they increase with increasing temperatures as the transition is

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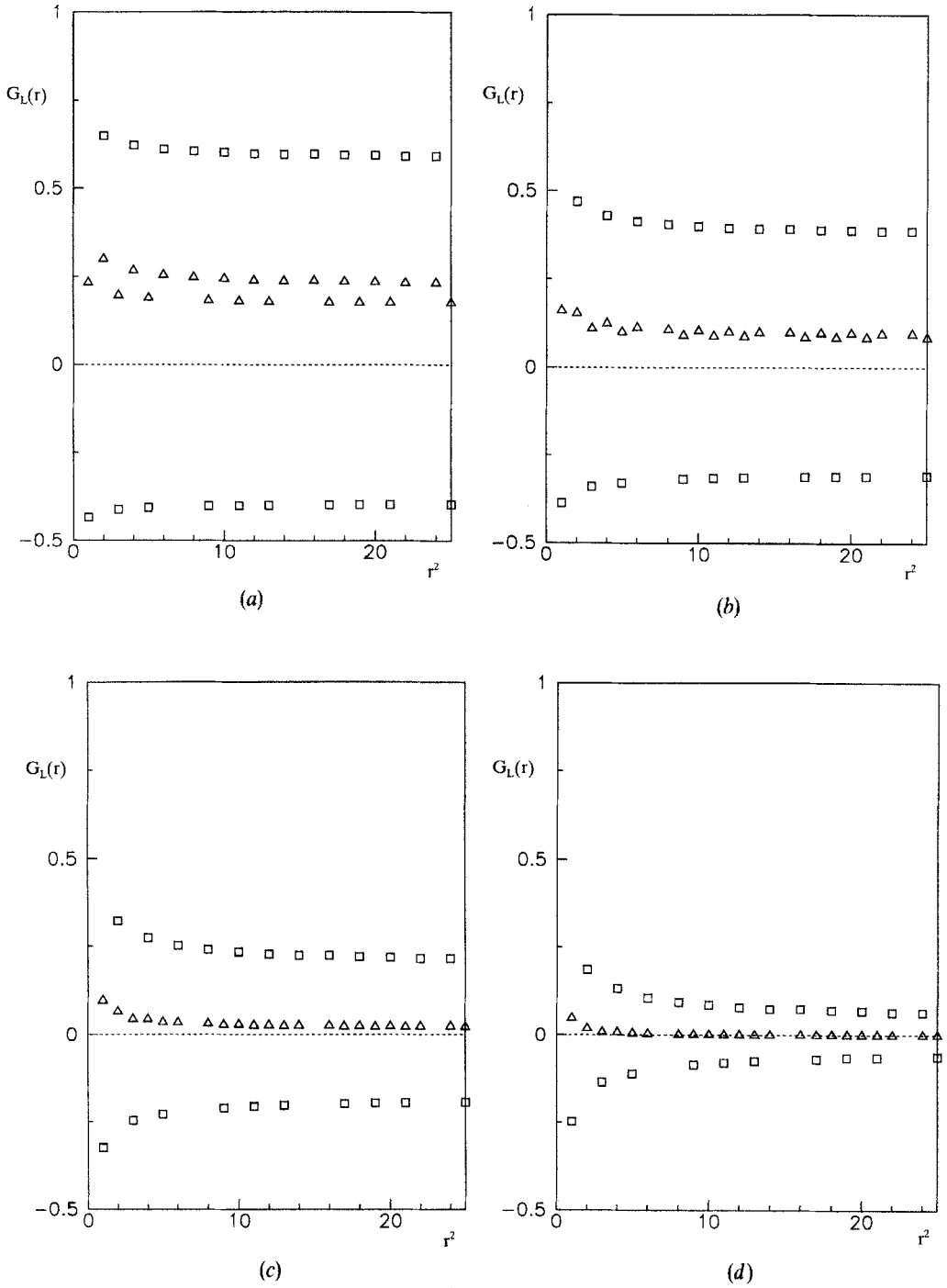

Figure 6.

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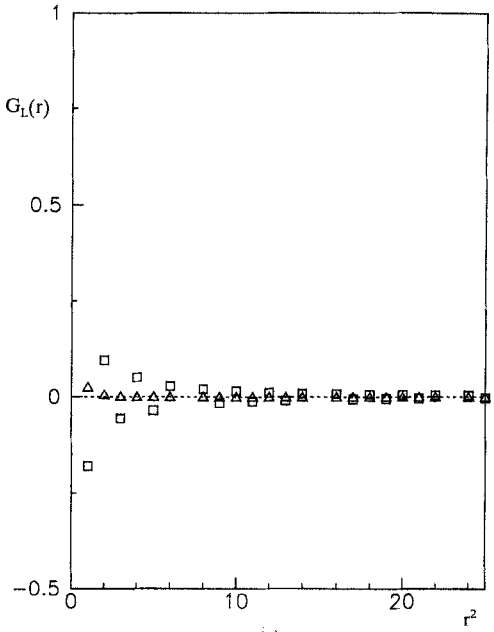

(*e*)

Figure 6. The distance dependence of the orientational correlation functions $G_L(r)$ for $L=2$ (□) and $L=4$ (△) calculated for model I at temperatures T^* of (*a*) 0·4, (*b*) 0·6, (*c*) 0·8, (*d*) 1·0 and (*e*) 1·25.

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approached, but then decrease in the isotropic phase with further increases in temperature. Such variations in the excess angular correlations have also been observed for the Lebwohl–Lasher model [20].

Our simulations of model I clearly demonstrate the biaxiality of the nematic phases formed by the rods and discs confined to the two sub-lattices; indeed, it is this confinement in a uniform mixture which creates the biaxility. We now come to the results for model II in which this constraint is no longer imposed and phase separation becomes possible. To study this possibility we have monitored the distribution of the two components within the mixture by calculating the spatial distribution functions for like and unlike particles, $g^{RR}(r)$ and $g^{RD}(r)$, respectively. Initially, however, we wished to explore the state of the system by evaluating the distribution functions, $g^{RR}(1)$ and $g^{RD}(1)$, for the nearest neighbour separation as a function of temperature and the results of our calculations are shown in figure 7. For a finite system of 10^3 particles separated into two layers of pure discs and pure rods, $g^{RR}(1)$ takes the value 1·86 and $g^{RD}(1)$ is just 0·14 [16]; at the other extreme of a uniform mixture, both spatial distribution functions are unity. The simulation results show that at low temperatures the mixture is indeed separated into two pure phases, one composed of rods and the other of discs. This situation is stable until a temperature of about 0·5; at this point $g^{RR}(1)$ starts to decrease, while $g^{RD}(1)$ increases. These changes signal a variation in the composition of the separate phases with rods progressively dissolving in the disc rich phase and vice versa. This process continues until, at a temperature of approximately 1·25, $g^{RR}(1)$ and $g^{RD}(1)$ are both unity and the two mixtures have the same composition. In other words, a homogeneous phase has been formed. Such changes in the composition of the coexisting phases with temperature for an equimolar mixture appear to be in qualitative agreement with the predictions of molcular field theory [15].

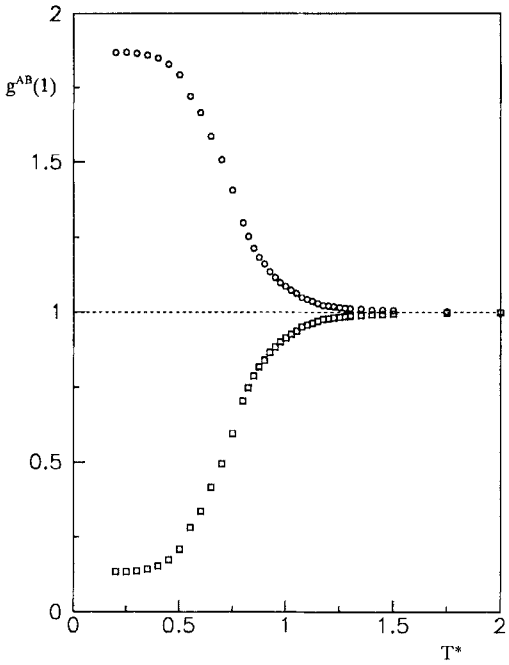

Figure 7. The temperature dependence of the spatial distribution functions for like (○) $g^{RR}(1)$ and unlike components (□) $g^{RD}(1)$ evaluated for nearest neighbour separations for model II.

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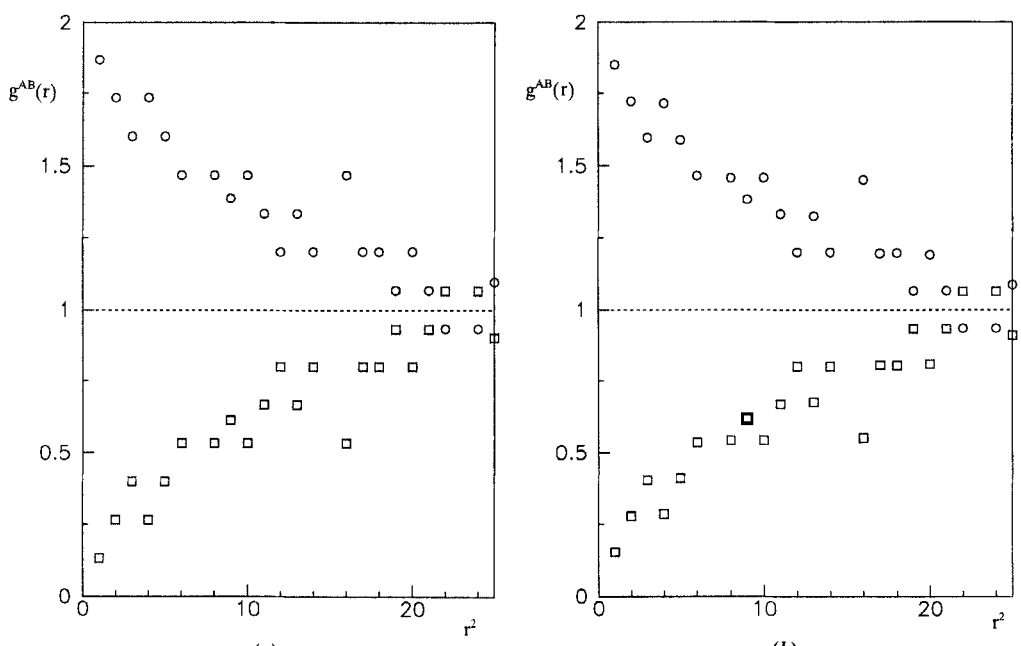

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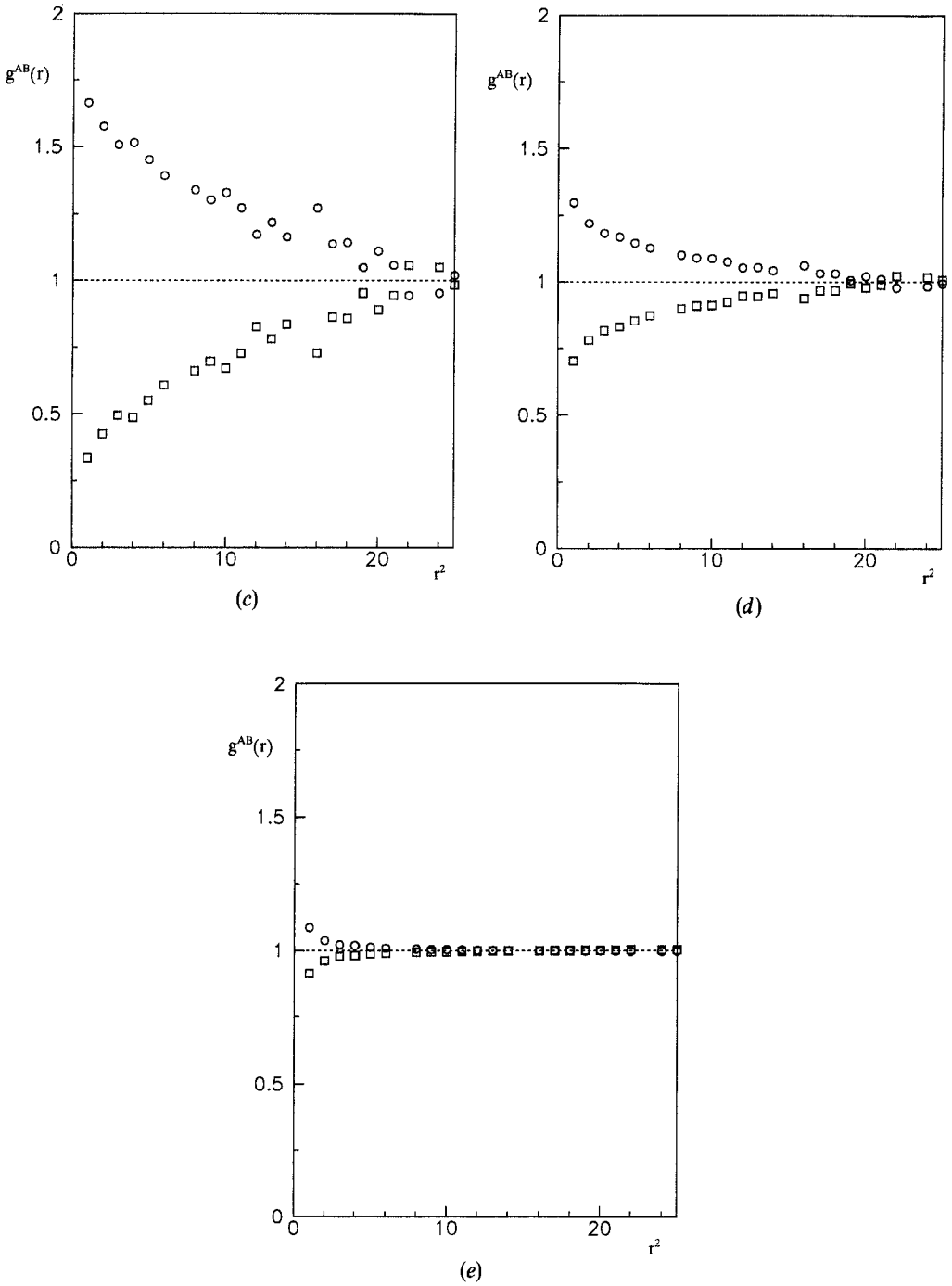

Figure 8. The distance dependence of the spatial distribution functions (○) $g^{RR}(r)$ and (□) $g^{RD}(r)$ for model II evaluated at the temperatures (*a*) 0·2, (*b*) 0·4, (*c*) 0·6, (*d*) 0·8 and (*e*) 1·0.

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To describe the nature of the phases in more detail, we show in figure 8 the two spatial distribution functions $g^{RR}(r)$ and $g^{RD}(r)$ for selected temperatures of 0·2, 0·4, 0·6, 0·8 and 1·0. The distribution functions observed at low temperatures appear to exhibit a scatter in the data. However, this does not result from statistical error, but rather from the finite size of the sample. Indeed the two distribution functions which we have observed at T^* of 0·2 are identical to those calculated for two slabs of pure discs and pure rods each containing 500 particles [16]. This comparison also confirms that the decrease in the distribution function $g^{RR}(r)$ with increasing separation does not result from an increase in the number of discs in the mixture, but rather from the finite size of the system. At the higher temperature of 0·4, the distribution functions have not changed to any significant extent and the system still consists of two pure phases. There is, however, a change in the distribution functions at the slightly higher temperature of 0·6. First, $g^{RR}(r)$ has decreased in magnitude while $g^{RR}(r)$ has increased, and secondly, the structure on the distributions has been reduced. These changes are associated with the creation of a phase rich in rods but containing some discs and vice versa. Such changes continue with increasing temperature, and this is certainly apparent at T^* of 0·8, although the deviation of $g^{RR}(r)$ and $g^{RD}(r)$ from unity suggests that the mixture is still not uniform. The formation of this uniform mixture appears to have taken place by T^* of 1·0; now both spatial distribution functions are essentially independent of the separation and equal to unity. There are, however, the remnants of some structure at short range which hints at the slight preferential attraction of rods rather than discs by another rod.

The temperature dependence of the spatial distribution functions suggests that there is a transition from a phase separated system to a uniform mixture of rods and discs at a temperature somewhere between 1·0 and 1·25. In order to locate the transition

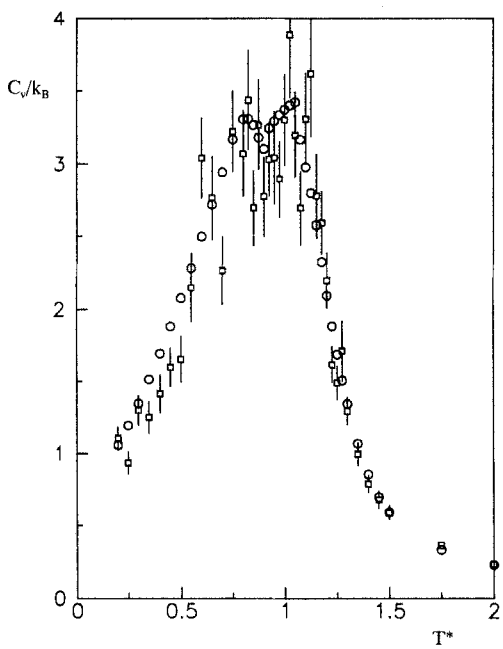

Figure 9. The temperature dependence of the configurational heat capacity evaluated for model II from (□) fluctuations in the internal energy and (○) differentiation of the internal energy with respect to temperature.

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more accurately as well as to probe its nature, we have calculated the heat capacity as a function of temperature, with the results shown in figure 9. There is clearly a peak in C_v at $1{\cdot}050 \pm 0{\cdot}025$, but the lack of divergence, which is found, for example, for the Lebwohl–Lasher model [20], suggests that the transition is of second or higher order; this is in accord with the molecular field predictions for an equimolar mixture of rods and discs [15]. The theory also predicts that the transition temperature should be 0·9 times that of the pure system; for our model II, there are no results for the transition temperature of the pure system in which the interactions extend over two shells of neighbours. For the Lebwohl–Lasher model, the interactions are confined to nearest neighbours on a simple cubic lattice and T^*_{NI} is 1·127. However, Luckhurst, Romano and Simpson have extended this model to include three shells of neighbours in which the interaction decays as r^{-6} and find T^*_{NI} of $1{\cdot}54 \pm 0{\cdot}02$ [36]. Interpolating between these values using the coordination number weighted sum of r^{-6} for the shells of neighbours gives T^*_{NI} of 1·44 for a pure system in which nearest and next nearest neighbours interact. Accordingly, the theory developed by Palffy–Muhoray *et al.* [15], predicts a phase separated nematic–isotropic transition temperature of 1·30, which is somewhat greater than that given by our simulation of 1·05.

The heat capacity data in figure 9 also reveals another weak maximum at a temperature of approximately 0·75. This coincides with the point at which the compositions of the coexisting phases are changing most rapidly (see figure 7). Such variations in the composition will result in corresponding changes to the internal energy and hence, to an additional feature in the temperature dependence of the heat capacity. This interpretation of the additional peak in the heat capacity is certainly consistent with the temperature dependence of the orientational order in the mixture, as we shall now see.

The second and fourth rank orientational order parameters were calculated for the individual components and the total mixture by using the appropriate Q and B tensors. This allowed us to determine both the symmetry of the coexisting phases as well as the orientation of the directors for these and that of the mixture. For an infinite system, the directors of the coexisting phases would be unrelated and so the director for the mixture would be devoid of any physical significance. However, for the finite system studied in this simulation, there is a significant interaction between the rods and discs across the interface of the coexisting phases. This feature is further enhanced by the periodic boundary conditions, because the interface is at the centre of the simulation box and parallel to the xy face. Thus, for example, the phase consisting largely of discs is bounded on either side by that composed largely of rods. We might anticipate, therefore, that the directors for the coexisting phases will in fact, be correlated. This proves to be the case, for we have found that the directors are orthogonal and, in consequence, the director for the complete mixture is well defined and perpendicular to those of the coexisting phases. In addition, the Q tensors for the individual components reveal that the coexisting phases are essentially cylindrically symmetric and so their orientational order can be characterized by the order parameters $\bar{P}_2$ and $\bar{P}_4$. Further, these order parameters for the two components are observed to be equivalent as indeed they should be. The results for $\bar{P}_2$ of one component and of the mixture are given in figure 10 as a function of temperature. At the lowest T^*, the orientational order in the coexisting phases is seen to be practically complete and $\bar{P}_2$ is almost unity. As the temperature increases, so $\bar{P}_2$ decreases until T^* is about 0·5, at which point there is an increase in the rate of decrease; this can be attributed to the change in the composition of these phases. Thus, for example, as the concentration of discs in the phase which is

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rich in rods grows, so the mean anisotropic interaction, or potential of mean torque, acting on a rod will diminish and the associated order parameter will fall. Since the internal energy is quadratic in $\bar{P}_2$, at least in the molecular field limit, we expect a change in its slope which is then reflected by the maximum in the heat capacity at T^* of 0·75. As the temperature is further increased, so $\bar{P}_2$ continues to fall both as a result of the increase in T^* and the increase in the concentration of unlike species in the phase rich in the other component. As a consequence of these changes, the order parameter $\bar{P}_2$ appears to pass continuously to zero at a temperature of about 1·0, in accord with our previous observation that the transition is of second or higher order.

At the lowest temperatures, when the coexisting phases are essentially pure discs and pure rods the order parameter for the mixture should be simply related to that of the phases. This situation obtains because the two phases are uniaxial and their directors are orthogonal. For the case of the second rank order parameter, $\bar{P}_2$ for the mixture should be just $-\frac{1}{2}$ that of a coexisting phase. This relationship holds quite well until T^* is about 0·75 and then there is an increasing deviation from this prediction, with $\bar{P}_2$ for the mixture being less negative than anticipated. This departure results from the way in which we have defined the order parameters for the coexisting phases. Since it is a difficult task to monitor the spatial extent of these phases, we have identified their order parameters simply as those of the two components. This is likely to be a reasonable approximation, as long as the two phases are rich in their respective components. When this ceases to be the case, then the significance of the order parameters for the components tends to be lost, especially as the same component in the different phases will be ordered with respect to directors which are orthogonal. The only well-defined quantity is then the order parameter for the total mixture.

The corresponding results for the fourth rank order parameter are given in figure 11 and they reflect the behaviour found for the second rank order parameter. Thus, the

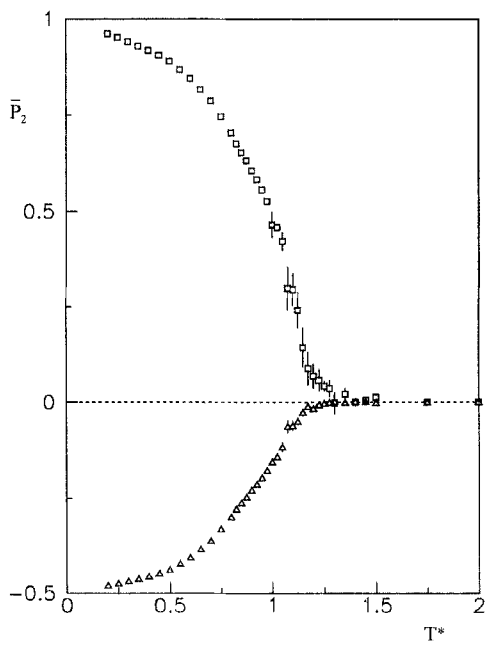

Figure 10. The dependence on temperature of the second rank order parameter $\bar{P}_2$ for (□) the individual components and (△) the total system.

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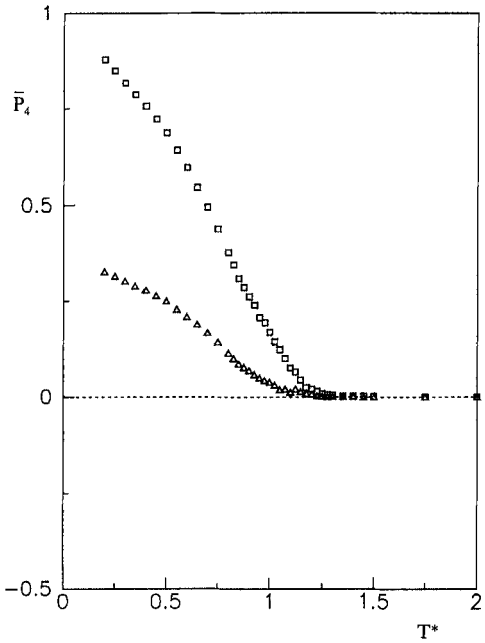

Figure 11. The variation with temperature of the fourth rank order parameter $\bar{P}_4$ for (□) the individual components and (△) the total system.

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value of $\bar{P}_4$ for the components is close to unity at the lowest temperature. It then decreases, albeit more rapidly than $\bar{P}_2$, with a change in slope at T^* of about 0·5, before passing continuously to zero at a temperature of approximately 1·1. As we have seen this corresponds to the second or higher order transition from the phase separated nematic to the uniform isotropic phase. The total fourth rank order parameter for the mixture is also related to those of the components and, by analogy with the geometric transformation for $\bar{P}_2$, the value of $\bar{P}_4$ for the mixture should be just 3/8 that for the individual components; here we use the result

$$\bar{P}_L^{\text{mixture}} = \bar{P}_L^{\text{component}} P_L(\cos 90°) \tag{34}$$

obtained via the spherical harmonic addition theorem. At the lowest temperatures, this prediction is obeyed quite accurately because the coexisting phases are essentially pure. However, at T^* of about 0·75, $\bar{P}_4$ for the mixture begins to depart from this relationship, because the composition of the coexisting phases begins to change dramatically. As for the second rank order parameter, the only quantity of significance under these conditions is $\bar{P}_4$ for the total mixture.

6. Conclusions

Here we bring together the main conclusions of our Monte Carlo simulation study of an equimolar mixture of rods and discs. We have developed two models for this mixture; in model I the rods are confined to the sites of one sub-lattice and the discs to those of the other, thus representing a uniform mixture for which phase separation is unable to occur. For model II exchange of particles between lattice sites is allowed and so phase separation can occur. For model I we observe a second or higher order transition between an orientationally ordered and an isotropic phase. The overall

symmetry of this nematic phase is uniaxial, although the two nematic phases with the sub-lattices of rods and of discs are biaxial. The major and biaxial second rank order parameters characterizing these phases are in good agreement with the predictions of a molecular field theory provided allowance is made for the failure of the theory to predict the nematic–isotropic transition temperature. At low temperatures, the ordering tensors for the particles on the two sub-lattices are identical, but as the temperature is increased, so they become unequal at any instant and the extent of the order is exchanged between the sub-lattices in an oscillatory manner. This unusual behaviour occurs because the term in the anisotropic potential between particles on the same sub-lattice becomes relatively unimportant at higher temperatures and the potential is dominated by that between particles on neighbouring sub-lattices. When the constraint on the exchange of particles is relaxed, the system separates into two coexisting uniaxial nematic phases. As a result of the finite size of the system, there is a significant interaction of rods with discs across the interface of the coexisting phases and as a result the directors for these are orthogonal. At low temperatures the phases are composed essentially of discs or of rods, but the composition of the two phases changes with increasing temperature at an ever increasing rate. This change in composition is clearly discernible via the temperature dependence of the orientational order parameters for the coexisting phases and the total mixture, as well as in the heat capacity. Unlike model I, the orientational order for the two components in model II is always identical. The coexisting nematic phases eventually undergo a second or higher order transition to a uniform isotropic phase. The behaviour of model II is in good qualitative agreement with the predictions of the molecular field theory for such a system.

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