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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Bates, M. A. and Luckhurst, G. R.(1998) 'Computer simulation studies of anisotropic systems XXIX. Quadrupolar Gay-Berne discs and chemically induced liquid crystal phases', Liquid Crystals, 24: 2, 229 — 241

To link to this Article: DOI: 10.1080/026782998207406

URL: http://dx.doi.org/10.1080/026782998207406

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LIQUID CRYSTALS, 1998, VOL. 24, NO. 2, 229–241

Computer simulation studies of anisotropic systems XXIX. Quadrupolar Gay–Berne discs and chemically induced liquid crystal phases

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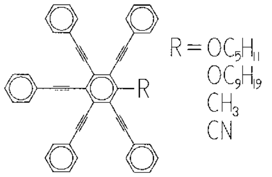
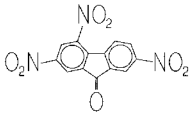
(*Received 20 August 1997; accepted 10 September 1997*)

Liquid crystal phases can be induced chemically by mixing compounds whose specific interactions are such that the transition temperature for the induced phase is higher than the melting points of the two compounds. A particularly dramatic example of such behaviour is the creation of a columnar nematic and a hexagonal columnar phase on mixing discotic multiynes with 2,4,7-trinitrofluorenone. Although the intense colour of the mixture indicates a strong charge-transfer band, it is uncertain as to whether the charge-transfer interaction between unlike molecules is enough to stabilize the induced liquid crystal phases. An alternative explanation for the formation of such phases involves an electrostatic quadrupolar interaction between the components, whose quadrupole moments differ in sign. This interaction weakens the face-to-face attraction for like particles while strengthening it for unlike particles. We have explored this possible explanation for chemically induced liquid crystal phases in discotic systems by modelling the basic interaction between discs with a Gay–Berne potential, to which is added a point quadrupolar interaction. We have determined the phase behaviour of the pure systems and their binary mixtures with constant pressure Monte Carlo simulations. It would seem that the quadrupolar interaction can account for many of the features of chemically induced liquid crystals.

1. Introduction

New liquid crystal phases can be revealed and their ranges frequently extended by the use of binary mixtures of materials. The enhancement of the liquid crystal behaviour usually results from the depression of the melting point, which reaches a minimum at the eutectic composition. However, perhaps more intriguing is the observation made by Praefcke and co-workers that for certain mixtures of disc-like molecules, new liquid crystal phases could be formed by the alternative strategy of increasing the liquid crystal–isotropic transition temperature [1–3]. The phases so formed are known as chemically induced phases and are strictly defined as those occurring above the melting point of either compound, to avoid the possibility that they result simply from the depression of the melting point on forming the mixture. One of the first observations of such chemically induced liquid crystal phases [2] in low molar mass systems was for mixtures of the multiynes (I) with 2,4,7-trinitrofluorenone (TNF):





Neither TNF nor any of the multiynes (I) exhibit liquid crystal phases, but their binary mixtures form both nematic and columnar phases. The phase diagram for TNF with penta(2-phenylethynyl)toluene ($R = –CH_3$) is sketched in figure 1 and we can see that a hexagonal, ordered columnar phase (Col_{ho}) is formed with a maximum transition temperature close to the equimolar mixture [3]. As the concentration of TNF is increased, so the transition temperature falls and a nematic phase appears. X-ray diffraction studies of the two mesophases show that, within the columns of the Col_{ho} phase, the molecules of TNF and I alternate along the column [3]. The structure of the nematic phase is more intriguing, for it is thought to consist of short columns, again with the molecules of the two components alternating along the column. It is then the anisotropic interaction between these assemblies which should create the nematic phase; this has therefore been called a columnar nematic.

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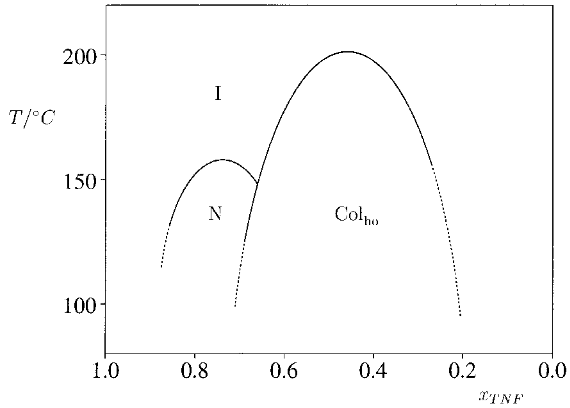


Figure 1. A sketch of the phase diagram for a binary mixture of the multiyne I (R=–CH$_3$) and trinitrofluorenone (TNF), whose mole fraction is denoted by x_{TNF}.

It seems that the formation of chemically induced liquid crystal phases in these and similar systems should result from a stronger interaction between unlike molecules in comparison with the average interaction between like molecules. This is especially the case when the discotic molecules are in their face-to-face configuration. One candidate which has been proposed to account for this is that a charge-transfer interaction occurs between unlike molecules. The argument in support of this is that, whereas both TNF and I (R=–CH$_3$) are pale yellow in colour, the binary mixture is bright red, this change in colour coming from a charge-transfer band. However, although the colour is intense, there is some doubt as to whether the associated charge-transfer interaction is sufficiently strong to induce a liquid crystal phase. An alternative explanation has its origins in an electrostatic quadrupolar interaction, which stabilizes a face-to-face arrangement provided the quadrupole moments of the unlike molecules are opposite in sign. The evidence in support of this interaction derives from the behaviour of the more well-known binary system of benzene and hexafluorobenzene. Whereas both benzene and hexafluorobenzene are liquid at room temperature, their equimolar mixture is crystalline at the same temperature [4]. In other words, the mixture exhibits a chemically induced crystalline phase. The crystal structure of the mixture is essentially columnar with benzene and hexafluorobenzene molecules alternating along the columns [5]. In contrast, the crystal structure of benzene has the molecules assembling with edge-to-face pairs as well as pairs in which the discs are parallel, but displaced with respect to their face-to-face arrangement. These observations are now accepted to be consistent with an electrostatic quadrupolar interaction playing a dominant role in determining the crystal structure of both the pure system and the binary mixture [5]. It seems likely that the same quadrupolar interaction could be responsible for the formation of the chemically induced liquid crystal phases. The chemical structures of the two components would lead us to expect that the quadrupole moment for I is negative, as for benzene [6], whilst that for TNF is positive, as for hexafluorobenzene [6]. In the pure systems, the quadrupolar interaction would tend to destabilize the columnar structure, whereas in the mixture it would favour the columnar organization, thus leading to a chemically induced liquid crystal phase.

To explore this idea in more detail we have undertaken a Monte Carlo computer simulation study of systems of discotic particles interacting through a quadrupolar potential. In addition to this, the underlying interaction between the discotic particles is represented by the Gay–Berne pair potential [7]. This model potential has been found to be especially valuable in studies of calamitic liquid crystals [8, 9] and is proving to be equally useful for the investigation of discotic liquid crystals [10, 11]. Thus a system of Gay–Berne discs has been found to exhibit isotropic, nematic and hexagonal columnar phases [11]. The paper is arranged as follows. In § 2, we describe the form of the pair potential together with the parametrizations employed in the simulations. The properties which are used to characterize the various phases formed are given in § 3, together with the essential details of the constant pressure Monte Carlo simulations. The results of the simulations are described and their significance is discussed in § 4. A summary of our work and conclusions are presented in § 5.

2. The pair potential and its parametrization

The Gay–Berne model is a single site intermolecular potential representing the interaction between a pair of uniaxial particles and takes the form [11]

$$U_{\mathrm{GB}}(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\mathbf{r})=4\varepsilon(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}})\left\{\left[\frac{\sigma_{\mathrm{f}}}{r-\sigma(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}})+\sigma_{\mathrm{f}}}\right]^{12}-\left[\frac{\sigma_{\mathrm{f}}}{r-\sigma(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}})+\sigma_{\mathrm{f}}}\right]^{6}\right\}. \qquad (1)$$

The orientations of the two particles are denoted by the unit vectors $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_j$ and $\mathbf{r}$ is the vector joining the particles. The expressions for the functions $\varepsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}})$ and $\sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}})$, which describe the orientational dependence of the well depth and the contact separation, have been discussed in detail elsewhere. These functions are given in the Appendix for those not familiar with the Gay–Berne model. To the potential in equation (1) we have added a point quadrupolar interaction, located at the centre of the disc. This maintains the cylindrical symmetry of the particles and is also consistent with the single site character of the Gay–Berne potential. The quadrupolar component of the total potential is

$$U_Q(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\mathbf{r}) = \frac{3Q_iQ_j}{16\pi\epsilon_0 r^5}\,[1+2(\hat{\mathbf{u}}_i\,\hat{\mathbf{u}}_j)^2-5(\hat{\mathbf{u}}_i\,\hat{\mathbf{r}})^2 - 5(\hat{\mathbf{u}}_j\,\hat{\mathbf{r}})^2-20(\hat{\mathbf{u}}_i\,\hat{\mathbf{u}}_j)(\hat{\mathbf{u}}_i\,\hat{\mathbf{r}})(\hat{\mathbf{u}}_j\,\hat{\mathbf{r}}) + 35(\hat{\mathbf{u}}_i\,\hat{\mathbf{r}})^2(\hat{\mathbf{u}}_j\,\hat{\mathbf{r}})^2] \qquad (2)$$

where Q_i and Q_j are the quadrupole moments of particles i and j, respectively and ϵ_0 is the permittivity of free space [12, 13].

In principle, the parameters in the pair potentials for the two components should be different, as they are for real systems. However, to reduce the number of adjustable parameters within the simulations, we have decided that the two components should differ only in the sign of their quadrupole moments. Since the quadrupolar interaction is quadratic in Q, the pure systems of the two components are identical. The different behaviour of the mixture compared with that of the pure systems then results solely from the negative sign of the product Q_iQ_j for unlike particles, in contrast to the positive sign for like particles. The Gay–Berne potential parameters were set equal to those used in our previous study of discotic particles [11]. Thus the ratio of the contact separations σ_f/σ_e for the face-to-face (f) and edge-to-edge (e) arrangements was given the value 0·345, which is typical of that for real discotic mesogens. The ratio $\varepsilon_f/\varepsilon_e$ for the well depths for the same arrangements was set equal to 5; the exponents μ and ν in the expression for the well depth were given the values 1 and 2, respectively. A system of particles interacting via the Gay–Berne potential with these parameters is found to form isotropic, nematic and hexagonal columnar phases, with transition temperatures which increase with increasing pressure [11].

It is more difficult to select the quadrupole moments for the components. However, the influence of the quadrupolar interaction on the total potential suggests values for $Q^*[=Q/(4\pi\epsilon_0\varepsilon_0\sigma_0^5)^{1/2}]$ of about 0·10. We have, therefore, studied in detail the behaviour of two systems, one with Q^* set equal to 0·05 and the other with Q^* equal to 0·10. In order to compare these values with quadrupole moments of real molecules we need to know the Gay–Berne scaling parameters ε_0 and σ_0. These have been estimated to be 1·63 kJ mol^{-1} and 26 Å, respectively, for typical discotic mesogens [11]. Using these values, we estimate Q^* of 0·05 to correspond to a quadrupole moment Q of $1{\cdot}1\times10^{-38}$ C m^2 and Q^* of 0·10 to be twice this value. The quadrupole moments for benzene and naphthalene have been measured as $-3{\cdot}0\times10^{-39}$ and $-4{\cdot}5\times10^{-39}$ C m^2, respectively [14]. These are close to but somewhat smaller than the values which we have selected, but such a difference is consistent with the larger size of the multiynes I and the greater polarity of 2,4,7-trinitrofluorenone.

To illustrate the influence of the quadrupolar interaction on the total potential, the potential energy contours for interactions between like and unlike particles are shown in figure 2 for both values of Q^*. The configuration chosen to calculate these contours was with the symmetry axes of the two particles parallel ($\hat{\mathbf{u}}_i\,\hat{\mathbf{u}}_j=1$), since we expect this to be the most common arrangement for discs in a liquid crystal phase. In addition the quadrupolar contribution depends upon the separation between the particles and not on the shifted separation as in the Gay–Berne potential itself, and so the quadrupolar interaction is greatest for the smallest separation. This is achieved for the face-to-face arrangement when the particles are necessarily parallel; the influence of the quadrupolar interaction on other arrangements, such as the edge-to-edge or face-to-edge, is found to be considerably reduced. For the smaller value of the quadrupole moment, the energy minimum occurs when the particles are face-to-face for interactions between both like and unlike particles. However, we can see from the number of contours, that the energy minimum is slightly deeper for the unlike than for the like interaction. In addition the well is narrower for the interaction between unlike particles when they are displaced away from the face-to-face arrangement [see figures 2(*a*) and 2(*b*)]. The situation is qualitatively different for the particles with the larger scaled quadrupole moment. For a pair of like particles there is no longer an energy minimum when the particles are face-to-face; the minimum occurs when they have been displaced by about 30° from the face-to-face arrangement [see figure 2(*c*)]. In addition, the potential well is rather shallow. In marked contrast, the contours for unlike particles now show a maximum attraction when the particles have a face-to-face arrangement [see figure 2(*d*)]. The well depth for this arrangement is also very large, corresponding to a strong attraction between the particles. Qualitatively at least, it would seem that Gay–Berne discs with a quadrupolar interaction with Q^* of 0·10 should destabilize a columnar phase for the pure system and create a columnar structure for a binary mixture in which the Q^* for the two components differ in only their sign.

The models which we have chosen to study, therefore, are quadrupolar Gay–Berne discs with $|Q^*|$ equal to 0·05 and 0·10. In addition to the pure system, we have also investigated two binary mixtures, the components of which we denote by the letters A and B. Given the equivalence of these components, the transition temperature for a chemically induced liquid crystal phase will be greatest for the equimolar mixture, which we refer to as the 50 : 50 mixture. The induced phase for this mixture

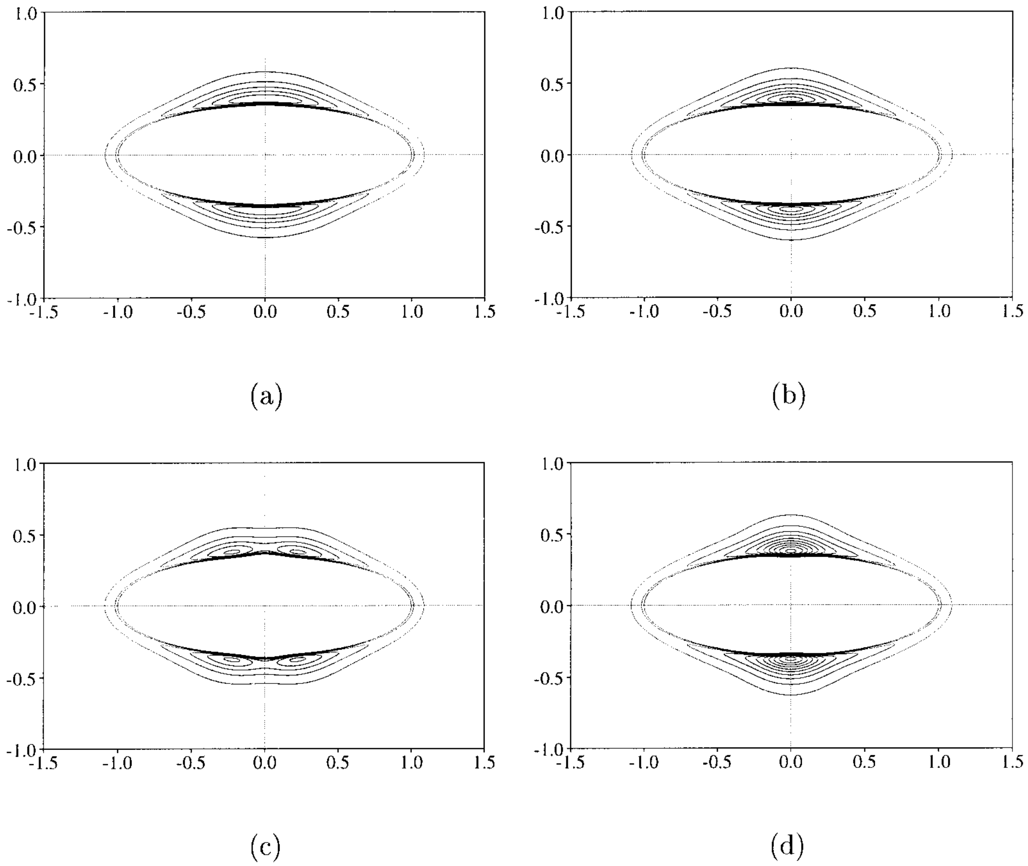


Figure 2. The potential energy contours calculated for a pair of particles with their symmetry axes parallel; with the quadrupole moment, Q^*, equal to 0·05 for (*a*) like and (*b*) unlike interactions, and Q^* equal to 0·10 for (*c*) like and (*d*) unlike interactions. The innermost contour corresponds to zero potential energy and the other contours are for values of the scaled potential energy decreasing in steps of 2·0.

is likely to have a columnar structure, but as we also wish to investigate an induced columnar nematic phase, we have also studied a 75:25 mixture. Comparison with the behaviour of real systems (see figure 1) suggests that this should form a nematic as well as a columnar phase, presumably because the unequal amounts of the two components will tend to destabilize the columnar structure.

3. The constant pressure Monte Carlo simulations

The isothermal–isobaric Monte Carlo simulation technique used in our studies of the quadrupolar Gay–Berne discs is described in detail elsewhere [11]. This paper also discusses the advantages of using constant pressure simulations in which the dimensions of the simulation box can change for systems exhibiting transitions to phases with long range translational order. The number of particles employed in the simulation was 2000 and the system was studied at a scaled pressure $P^*(=P\sigma_0^3/\varepsilon_0)$ of 25. At this pressure, a system of discs interacting solely through the Gay–Berne potential was found to exhibit a hexagonal columnar–nematic transition at a scaled temperature $T^*(=k_BT/\varepsilon_0)$ of 2·525 ± 0·025 and a nematic–isotropic transition at a temperature of 2·675 ± 0·025. It seemed appropriate, therefore, to start the simulations of the quadrupolar systems at a temperature of 3·5 in the isotropic phase using a configuration taken from our previous simulation of Gay–Berne discs. The temperature was then lowered in steps of 0·1 using a configuration taken from the previous temperature as a starting configuration until the temperature was 2·0. This is significantly lower than the temperature for the transition to the hexagonal columnar phase found for the Gay–Berne system. In the simulations, a cut-off r_c^* $(=r_c/\sigma_0)$ of 2·0 was used; this is somewhat longer than that employed for the Gay–Berne system because of the longer range nature of the quadrupolar interaction. The equilibration stage of the simulations consisted typically of 100 000 cycles and was followed by a production stage of 50 000 cycles. Such lengthy runs were required because the systems proved slow to equilibrate, especially close to the transition to the columnar phase. In view of this, we were concerned to ensure that the distribution of the two components within the columns does correspond to that for an equilibrated system. We have, therefore, repeated some of the simulations with an additional step within the Monte Carlo cycle. This was an attempted exchange of two unlike particles selected at random within the system. We found that the use of this step for the columnar phase formed by the equimolar mixture with $|Q^*|$ of 0·10 did not change the translational distribution function along the column. It seems reasonable, therefore, to assume that the columnar phases formed during the simulations were adequately equilibrated.

In order to locate the phase transitions and to characterize their strength, we have calculated the scaled enthalpy per particle $\langle H^*\rangle$ $(=\langle H\rangle/N\varepsilon_0)$ and the scaled volume per particle $\langle V^*\rangle(=\langle V\rangle/N\sigma_0^3)$ from the simulations. The extent of the long range orientational order of the phases was characterized by the second rank orientational order parameter $\langle P_2\rangle$, where $P_2(\cos\beta)$ is the second rank Legendre polynomial and β is the angle between the director and the symmetry axis of the particle. The order parameter was evaluated from the Q-tensor introduced by Vieillard-Baron to allow for the change in the director orientation during the course of the simulation [15]. In our work, the averaged Q-tensor was evaluated and diagonalized after every cycle. The eigenvalues of **Q** were then averaged and the order parameter identified with minus twice the middle eigenvalue. This quantity was used in preference to the largest eigenvalue because, as Eppenga and Frenkel have shown, this presents a better description of the orientational order within the isotropic phase and the error with which it is evaluated is less sensitive to the number of particles studied [16]. In the orientationally ordered phases, we have observed that there is no significant difference between the order parameter calculated from the middle eigenvalue and that determined from the largest eigenvalue. This is consistent with the expected cylindrical symmetry of these phases.

The translational order and, in particular, the columnar structure of the phases exhibited by quadrupolar Gay–Berne discs and their binary mixtures have been explored with an extension of the columnar distribution function, introduced by Veerman and Frenkel [17], to mixtures. For a single component system, $g_c(r_\parallel)$ gives the probability of finding a particle in a cylinder of radius R with the cylinder axis parallel to the symmetry axis of the particle at the origin and at a resolved distance $r_\parallel$ from this in a volume element $\delta r_\parallel$. The distribution function is normalized so that, in the absence of positional correlations, it tends to a limiting value of unity. In a simulation, $g_c(r_\parallel)$ is evaluated from a histogram composed of the number of particles separated by resolved distances in the range $r_\parallel-\frac{1}{2}\delta r_\parallel$ and $r_\parallel+\frac{1}{2}\delta r_\parallel$ within a cylinder located on the particle at the origin. Since the number, $n(r_\parallel)$, of such pairs of particles is proportional to the number of particles in the system, this enters the definition of $g_c(r_\parallel)$, which is

$$g_c(r_\parallel)=n(r_\parallel)/2N\rho\pi R^2\delta r_\parallel \tag{3}$$

where ρ is the number density. To extend this definition to mixtures of discotic particles, we require the probability $g_c^{\alpha\beta}(r_\parallel)$ of finding a particle of type β confined within a cylinder located on α. To ensure that this is still normalized in the absence of positional correlations, it is necessary to replace N in equation (3) by N_α and introduce the mole fraction of β, x_β. This is analogous to the normalization proposed by Hashim *et al.* [18] and leads to

$$g_c^{\alpha\beta}(r_\parallel)=n_{\alpha\beta}(r_\parallel)/2N_\alpha\rho x_\beta\pi R^2\delta r_\parallel \tag{4}$$

$$=n_{\alpha\beta}(r_\parallel)V/2N_\alpha N_\beta\pi R^2\delta r_\parallel \tag{5}$$

where V is the volume of the system and $n_{\alpha\beta}(r_\parallel)$ is the number of pairs of particles with β separated from α by a distance $r_\parallel$. This normalization removes the concentration dependence of $g_c^{\alpha\beta}(r_\parallel)$ which would result even in the absence of positional correlations. The columnar distribution functions for unlike particles, $g_c^{\alpha\beta}(r_\parallel)$ and $g_c^{\beta\alpha}(r_\parallel)$, are necessarily the same for the 50:50 mixture of quadrupolar Gay–Berne discs which we have studied. They are also found to be the same for the 75:25 mixture. In consequence, only the results for $g_c^{\alpha\beta}(r_\parallel)$ will be given in the following section.

4. Results and discussion

Here, we shall find it convenient to present the results for the quadrupolar Gay–Berne systems and their mixtures in two parts. We begin with the system having the smaller scaled quadrupole moment of 0·05 and, as we shall discover, the quadrupolar interaction has a relatively modest effect on the behaviour of the systems, certainly in comparison with that of the Gay–Berne potential alone. In contrast, we shall also see that the system having the larger scaled quadrupole moment of 0·10 behaves in a qualitatively different manner from a system of Gay–Berne discs. This is perhaps to be anticipated given that the quadrupolar interaction is quadratic in Q^*, which means that this is four times larger for the system with Q^* of 0·10; the significant effect this has on the energy contours is clearly seen in figure 2.

4.1. *Quadrupolar Gay–Berne discs with Q^* of 0·05*

The enthalpy per particle $\langle H^*\rangle$, the volume per particle $\langle V^*\rangle$ and the second rank orientational order parameter $\langle P_2\rangle$ of the pure system and the two binary mixtures are shown as functions of the scaled temperature in figure 3. Above T^* of 2·7, all three systems exhibit an isotropic phase; we observe that the values of $\langle P_2 \rangle$ are essentially zero, indicating the orientationally disordered nature of the systems at these temperatures. We also note that there are no significant differences in the values of $\langle H^* \rangle$ and $\langle V^* \rangle$ for the three systems; we can therefore conclude that the quadrupolar interaction has essentially no influence on the local molecular environment in the isotropic phase. This is not unexpected, given that the quadrupolar interaction has only a slight influence on the attractive forces in the face-to-face arrangement and that these forces play only a minor role in determining the structure of the isotropic phase. Indeed, the local structure in the isotropic phase observed for non-quadrupolar discotic particles can be traced back to the excluded volume of the particles, and therefore to their shape, which is related to the repulsive and not the attractive nature of the potential. Each system is found to undergo a weak first order phase transition at T^* of $2{\cdot}65 \pm 0{\cdot}05$; these transitions are similar in strength to that observed at essentially the same temperature in the analogous system of Gay–Berne discs. We notice, however, that the value of $\langle P_2 \rangle$ is slightly larger in the 50:50 mixture than in the other systems and that the values of $\langle H^* \rangle$ and $\langle V^* \rangle$ are slightly lower. We can relate these observations for the narrow nematic range to the enhanced interaction for unlike particles aligning in the face-to-face arrangement. Indeed, the presence of a relatively large face-to-face peak at $r_{\|}^*$ of 0·4 in the columnar distribution function, $g_c(r_{\|}^*)$, for Gay–Berne discs suggests [11] that the attractive face-to-face interaction does have an influence on the stability of the discotic nematic phase, and therefore we expect that any modification in this interaction will influence the local structure of the orientationally ordered phases.

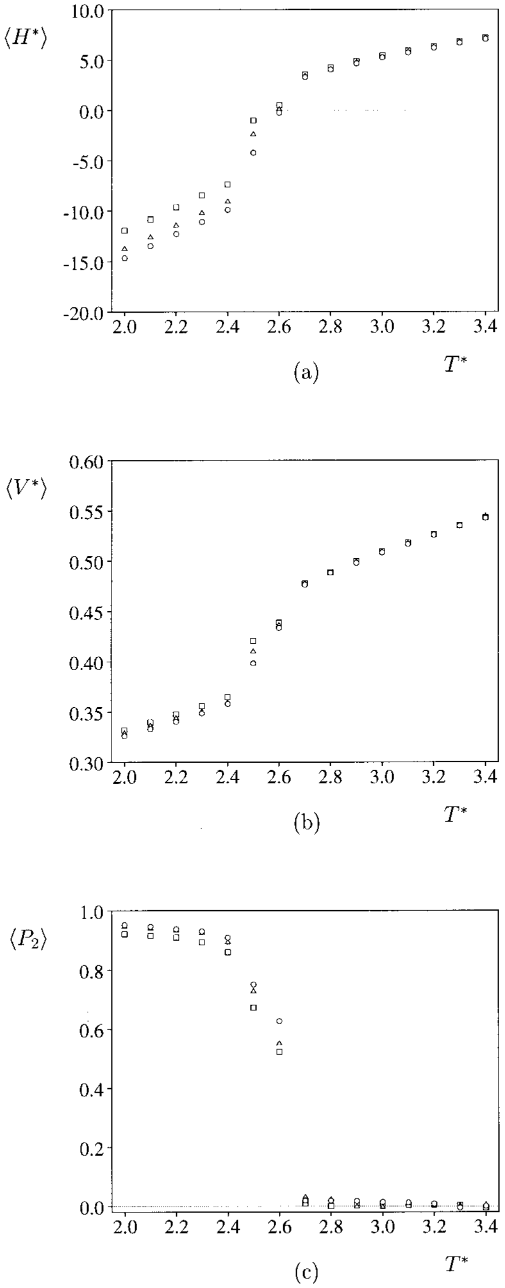


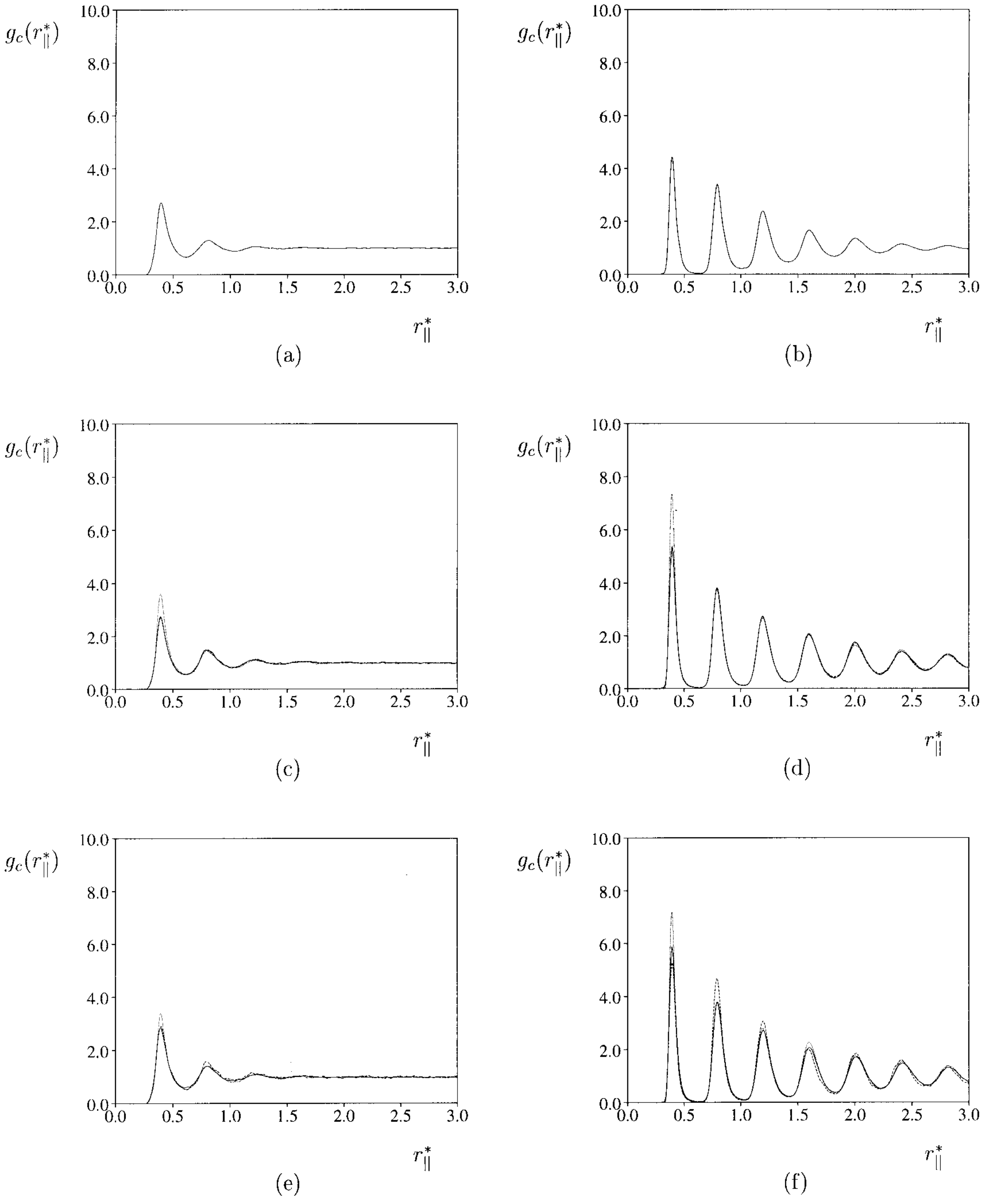
Figure 3. The dependence of (*a*) the scaled enthalpy per particle, $\langle H^* \rangle$, (*b*) the scaled volume per particle, $\langle V^* \rangle$, and (*c*) the second rank orientational order parameter $\langle P_2 \rangle$ on the scaled temperature T^* for quadrupolar Gay–Berne discs with Q^* of 0·05. (□) the pure system, (○) the 50:50 mixture and (△) the 75:25 mixture.

A further transition occurs in each system at T^* of $2{\cdot}45 \pm 0{\cdot}05$; this transition temperature is comparable with that of the hexagonal columnar–nematic phase transition observed for Gay–Berne discs, as are the transitional entropy and volume changes in all three systems [11]. The enthalpy for the columnar phase of the equimolar mixture is somewhat more negative than for that of the pure quadrupolar discs; such stabilization of the phase is entirely consistent with the increased attraction between unlike particles in the face-to-face arrangement which occurs in a columnar phase. As we might have expected, the enhancement of the attraction between particles in the columnar phase will also reduce the volume of the equimolar mixture, although the change is relatively modest. Thus we conclude that the three systems exhibit the same phase behaviour as the system of Gay–Berne discs which we have studied previously. This is not unexpected, given the relatively small contribution of the quadrupolar term to the total interaction potential [see figure 2 (*a*) and 2 (*b*)]. Nonetheless, we may expect a minor change in the local structure of the phases exhibited by these systems due to the slightly enhanced interaction between unlike particles, which we now explore with the aid of the columnar distribution function, $g_c(r_\parallel^*)$. The dependence of $g_c(r_\parallel^*)$ on the scaled, resolved separation $r_\parallel^*$ for the phases of the three systems on either side of the hexagonal columnar–nematic transition is shown in figure 4. The form of the columnar distribution function calculated for the pure system in the nematic phase at T^* of 2·6 is similar to that found for Gay–Berne discs at the same temperature. Indeed, the only difference is that the peak at $r_\parallel^*$ of 0·4 is reduced by approximately 10%, which is consistent with the weaker face-to-face interaction for the quadrupolar discs. The anisotropic repulsive forces between such Gay–Berne discs require that particles with a resolved separation of about 0·4 must be in a face-to-face arrangement and so we shall describe the first peak in $g_c(r_\parallel^*)$ which corresponds to this separation as the face-to-face peak. In both binary mixtures, the form of $g_c(r_\parallel^*)$ for pairs of like (AA and BB) particles is essentially the same as that determined for the pure system. However, we observe that the face-to-face peak for pairs of unlike (AB) neighbours at $r_\parallel^*$ of 0·4 is slightly more intense than that for pairs of like particles; this higher probability is associated with the enhanced attraction between unlike particles in a face-to-face arrangement [see figure 2 (*b*)]. It is clear, however, that the quadrupolar contribution to the potential only changes the local structure of the system slightly and does not influence significantly the long range structure or the phase behaviour. The form of $g_c(r_\parallel^*)$ in the columnar phase of each system at T^* of 2·4 is similar to that observed for the columnar phase of the Gay–Berne discs at the same temperature [11]. However, we do note that this function decays more rapidly in the pure quadrupolar Gay–Berne system than in the binary mixtures, which indicates that the quadrupolar interaction does affect the translational order in the columnar phase, but only weakly. The height of the face-to-face peak for unlike particles in the 50:50 mixture at $r_\parallel^*$ of 0·4 is larger than that for like particles; in other words, given a particle of type A, there is a slightly larger probability that the neighbouring particle is of type B rather than A. This is clearly related to the enhanced face-to-face attraction between unlike particles in comparison to that between like particles. However, this interaction appears to affect the local structure only weakly. The equal heights of the peaks corresponding to next nearest like and unlike neighbours, which occur at a separation $r_\parallel^*$ of 0·8, indicate that the longer range structure within a column is essentially random. The face-to-face peak shows that a similar effect occurs for the 75:25 mixture; thus the AB pairing is favoured over that for AA and BB pairs. Note, however, that the peaks associated with second and third neighbours are slightly larger for BB interactions than AA interactions. This can be related to the excess of component A in the system, an effect which will be discussed later, when we consider particles with a quadrupole moment of 0·10.

4.2. *Quadrupolar Gay–Berne discs with Q* of 0·10*

As we shall now see, increasing the scaled quadrupole moment from 0·05 to 0·10 has a qualitative effect on the behaviour of the quadrupolar Gay–Berne discs. In the pure system, we observe a weak transition from the isotropic phase to an orientationally ordered phase at T^* of $2{\cdot}65 \pm 0{\cdot}05$; this is indicated in figure 5 by a change in $\langle H^* \rangle$ of approximately $2{\cdot}0 \pm 0{\cdot}2$, which corresponds to a transitional entropy $\Delta S/R$ of $0{\cdot}75 \pm 0{\cdot}05$, and a jump in $\langle P_2 \rangle$ from zero to 0·45. On further cooling, $\langle P_2 \rangle$ gradually rises to 0·90; however, there is no evidence for further phase transitions in the temperature dependence of the order parameter or indeed that of $\langle H^* \rangle$ or $\langle V^* \rangle$, at least until a scaled temperature of 2·0, which is the lowest which we have studied. The relatively small entropy change and the low value of the orientational order parameter suggests that the transition at T^* of 2·65 is between a nematic and an isotropic phase. This interpretation is, as we shall see, consistent with the columnar distribution function for this system. Indeed, if we consider the potential energy contours for these quadrupolar Gay–Berne discs [see figures 2 (*c*) and 2 (*d*)], then it is clear that the quadrupolar interaction significantly modifies the face-to-face interaction, which is crucial for the formation of a columnar structure. Thus the particles prefer to be in the slipped parallel rather than the face-to-face arrangement. This structure, which should dominate at relatively low temperatures, might be expected to lead to a tilted columnar phase; however, this would require the displacement of the particles along the column to occur in the same sense. The quadrupolar interaction would not be able to stabilize such a tilted structure as our results suggest, although we have not investigated this intriguing possibility at lower temperatures.

We contrast the behaviour for quadrupolar Gay–Berne discs with that found for the 50:50 mixture of discs with $|Q^*|$ of 0·10. In this system, we observe an extremely strong first order transition at T^* of $2{\cdot}85 \pm 0{\cdot}05$ (see figure 5). The transitional entropy $\Delta S/R$ and the relative change in volume at this transition are estimated to be 4·5 and 30%, respectively. These large entropy and volume changes, in conjunction with a large jump in the second rank orientational order parameter $\langle P_2 \rangle$, prompt us to characterize the low temperature phase of the 50:50 mixture as a columnar phase, a conclusion which is supported by the form of the columnar distribution function. We also observe that, even in the orientationally disordered isotropic phase, the



(a) (b) (c) (d) (e) (f)

Figure 4. The columnar distribution function for quadrupolar Gay–Berne discs with Q^* of 0·05 in the nematic phase at T^* of 2·6, and in the columnar phase at T^* of 2·4; for the pure system (*a*) nematic and (*b*) columnar, for the 50:50 mixture (*c*) nematic and (*d*) columnar and for the 75:25 mixture (*e*) nematic and (*f*) columnar. The distribution function for AA particles is shown by (—), for BB particles by (---) and for AB particles by (...).

enthalpy $\langle H^* \rangle$ in this mixture is lower than that in the pure system. Thus it appears that the quadrupolar interaction has some influence on the local organization of the particles in the mixture prior to the transition into the columnar phase; again, the columnar distribution function $g_c(r^*_\parallel)$ shows this to be the case. We have found that the phase behaviour exhibited by the pure system and the 50:50 binary mixture is strongly influenced by the quadrupolar interaction. Thus the pure system forms a nematic, but not a columnar phase; in

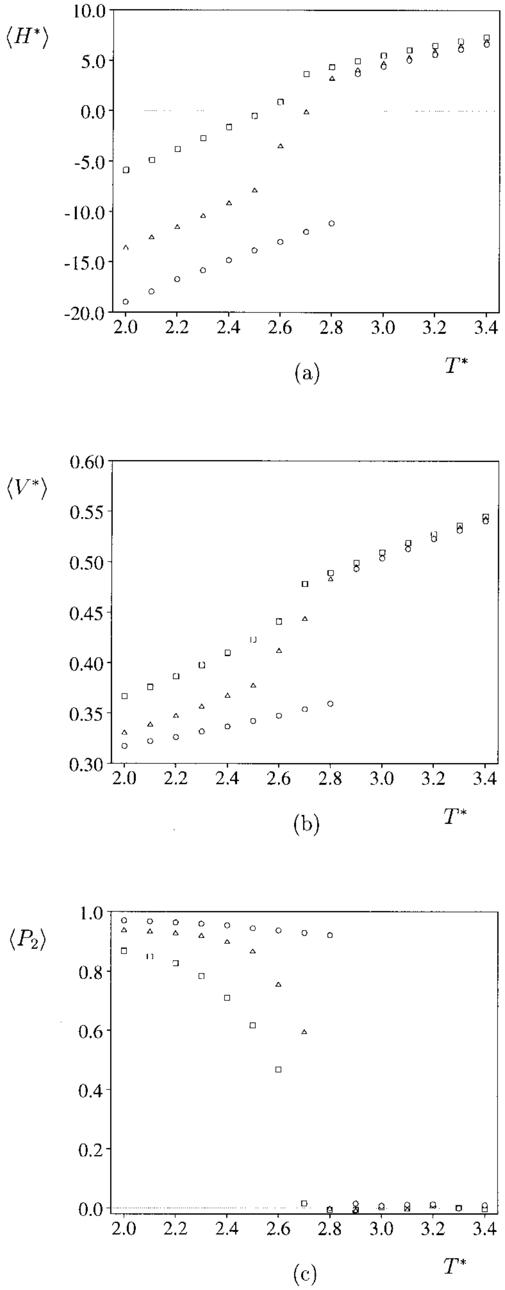


Figure 5. The dependence of (*a*) the scaled enthalpy per particle, $\langle H^* \rangle$, (*b*) the scaled volume per particle, $\langle V^* \rangle$, and (*c*) the second rank orientational order parameter $\langle P_2 \rangle$ on the scaled temperature T^* for quadrupolar Gay–Berne discs with Q^* of 0·10. (□) the pure system, (○) the 50 : 50 mixture and (△) the 75 : 25 mixture.

contrast, the mixture has a columnar, but not a nematic phase. The introduction of the quadrupolar interaction to the Gay–Berne potential has clearly created a system which exhibits chemically induced liquid crystal behaviour.

By analogy with the phase behaviour of real mixtures (see figure 1), we might speculate that the 75 : 25 mixture will form phases in a manner which is intermediate between that of the pure system and that of the 50 : 50 mixture. In the isotropic phase, the enthalpy $\langle H^* \rangle$ for the 75 : 25 mixture appears to be similar to that of the 50 : 50 mixture (see figure 5); we expect, therefore, that the local environment is similar in these two systems. It is clear that the 75 : 25 mixture undergoes a transition at a scaled temperature of $2{\cdot}75 \pm 0{\cdot}05$, at which the transitional entropy, $\Delta S/R$, and the relative change in volume, $\Delta V^*/V^*$, are estimated to be $0{\cdot}75 \pm 0{\cdot}05$ and 5%, respectively. This transition is significantly weaker than the columnar–isotropic transition observed for the 50 : 50 mixture. Indeed, the jump in $\langle P_2 \rangle$ from zero to just less than 0·60 indicates that this is almost certainly a nematic–isotropic transition, rather than a columnar–isotropic transition. We do find, however, that the orientational order parameter is larger than that in the pure system and so it would seem that the enhanced attractive forces between unlike particles do influence the orientational order in the nematic phase. It is also apparent that a further transition occurs at T^* of $2{\cdot}55 \pm 0{\cdot}05$ to a phase with high orientational order which, as we shall see, is similar in structure to the columnar phase exhibited by the 50 : 50 mixture.

We now turn to the translational structure of the phases formed by the three systems, as reflected by the columnar distribution function. In the isotropic phase of the pure quadrupolar Gay–Berne discotic system, the form of $g_c(r_{\|}^*)$, shown in figure 6, is similar to that found for the isotropic phase of the analogous Gay–Berne discs. We also observe essentially the same distribution function between pairs of like particles in the isotropic phases exhibited by the two binary mixtures. It is apparent, however, that there is a large difference in the local structure for pairs of unlike particles. The large peak at $r_{\|}^*$ of 0·40 in $g_c(r_{\|}^*)$ calculated for AB pairs in the binary mixtures indicates that there is a strong preference for these particles to be associated, on average, with an unlike neighbour. It appears, therefore, that the quadrupolar interaction for the system with Q^* of 0·10 is now sufficiently strong to have a noticeable influence on the local structure, even in the isotropic phase, where the number of face-to-face arrangements is relatively low.

In the nematic phase, at the lower scaled temperatures of 2·6 and 2·4, the form of $g_c(r_{\|}^*)$ for the pure system is virtually unchanged, see figures 7 (*a*) and 7 (*b*). Thus this function remains rather featureless, indicating the translationally disordered nature of the system so that despite the orientational order of the nematic phase, the displacement of the minima in the potential away from the face-to-face configuration by the quadrupolar interaction is sufficient to inhibit the formation of any significant

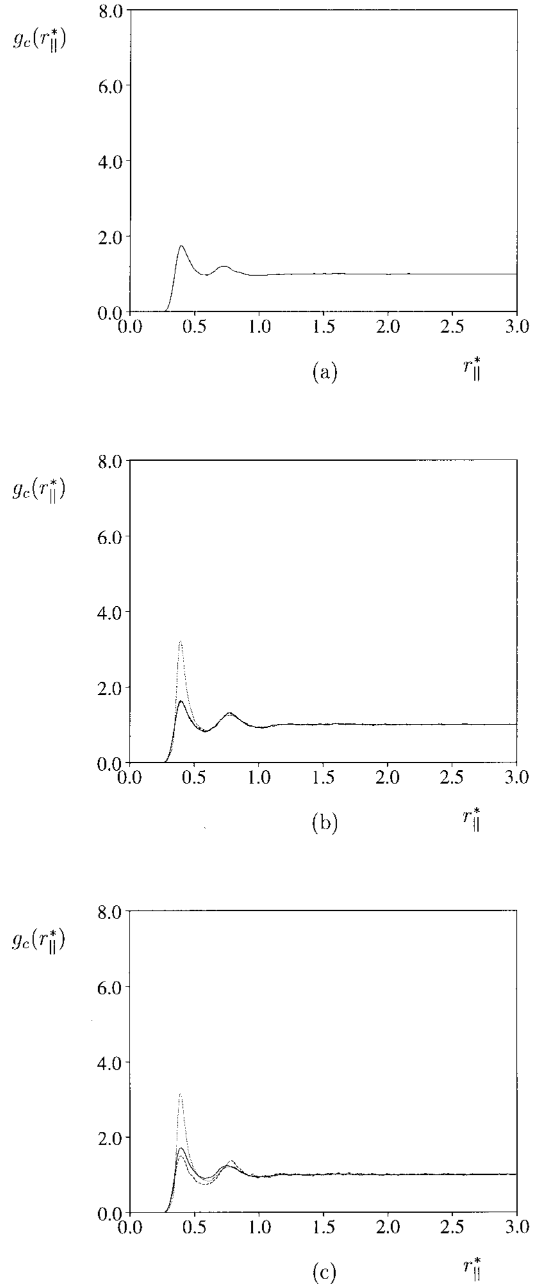
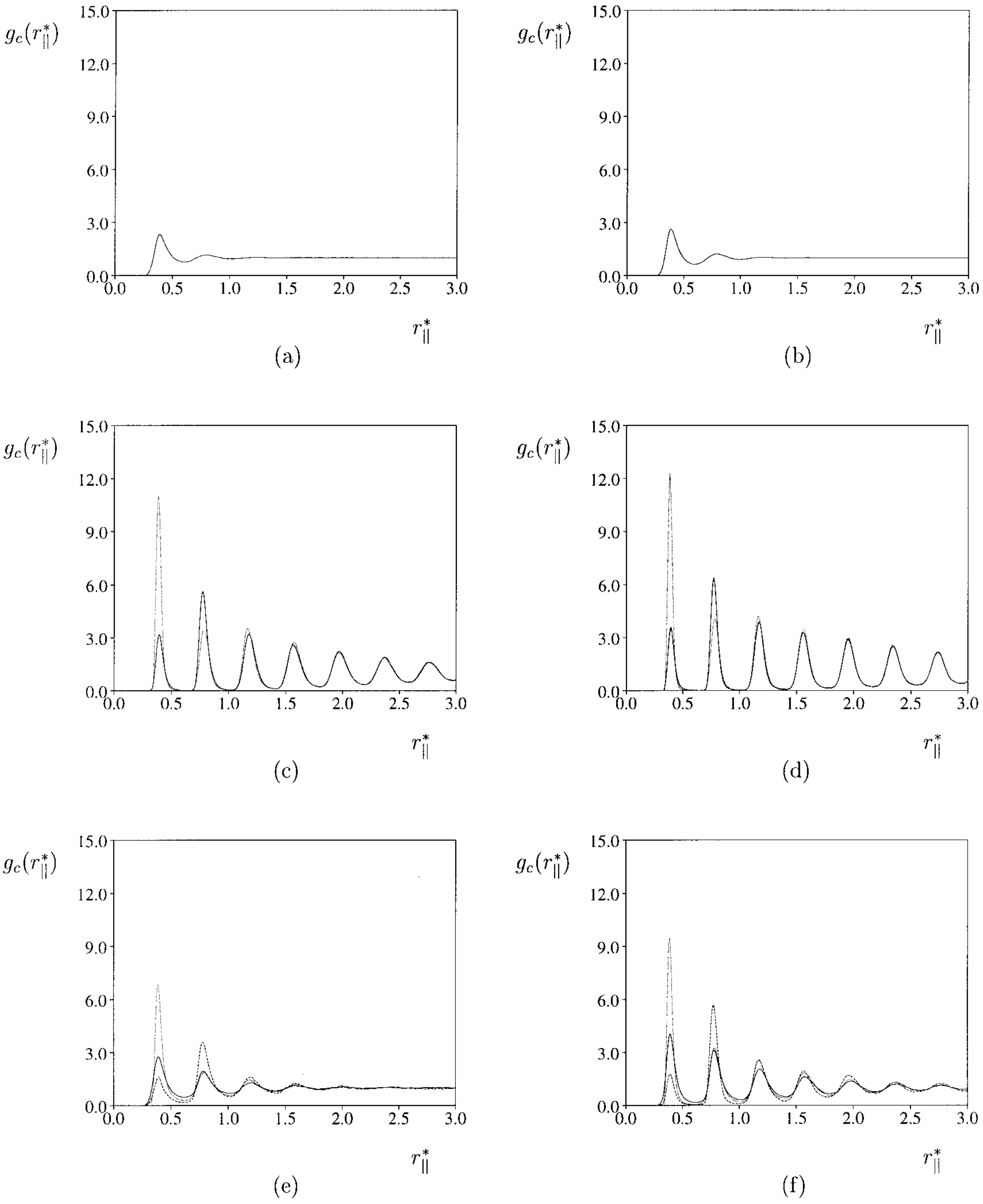


Figure 6. The columnar distribution function for quadrupolar Gay–Berne discs with Q^* of 0·10 in the isotropic phase at a scaled temperature of 3·0 in (*a*) the pure system, (*b*) the 50 : 50 mixture and (*c*) the 75 : 25 mixture. The distribution function for AA particles is shown by (—), for BB particles by (---) and for AB particles by (...).

columnar structure. This contrasts with the behaviour in the columnar phase formed by the 50 : 50 mixture at T^* of 2·6 and 2·4; $g_c(r_\parallel^*)$ clearly indicates that the particles organize themselves into columns within which there is a strong preference for the different components to stack alternately [see figures 7 (*c*) and 7 (*d*)]. Thus, given a particle of type A, there is a large probability that the neighbouring particle will be of type B and also that the next nearest neighbour will be of type A. We note, however, that the alternation of the particles along the columns is not perfect and that the probabilities of finding pairs of like and pairs of unlike particles as third nearest neighbours are essentially equal. On lowering the scaled temperature to 2·4, we see that the translational order within the columns has increased and that there is a greater tendency for the different components to alternate along the column.

The form of $g_c(r_\parallel^*)$ in the nematic phase of the 75 : 25 mixture at T^* of 2·6 is clearly different from that observed for the pure quadrupolar Gay–Berne discs [see figures 7 (*a*) and 7 (*e*)]. The long range behaviour ($r_\parallel^* > 2$) of $g_c(r_\parallel^*)$ is rather featureless, similar to that observed for the nematic phase of the pure system; this indicates that there is no long range translational order in the ordered phase exhibited by the 75 : 25 mixture and that it can be identified as a nematic phase. However, it is apparent from the strong peaks at smaller separations that there is a local columnar structure. The distribution function for pairs of unlike particles indicates that there is a strong preference for them to align, on average, in the face-to-face arrangement with a particle of the opposite type. As the face-to-face interaction between pairs of like particles is significantly weaker in comparison with that between pairs of unlike particles, the peaks at $r_\parallel^*$ of 0·4 for AA and BB pairs are also expected to be smaller, as we find [see figure 7 (*e*)]. In the columnar structure formed by the 50 : 50 mixture, we have found that there is a preference for next nearest neighbours to be of the same type; thus a pair of particles of type A are likely to be separated by one of type B and conversely a pair of type B separated by one of type A. However, in the nematic phase formed by the 75 : 25 binary mixture, the BB peak at $r_\parallel^*$ of 0·8 is larger than that for the AA distribution. We can relate this to the excess of component A and the normalization of the columnar distribution function [see equation (5)] which favours the component with the lower concentration. Thus, the particles prefer to align in the face-to-face arrangement with one of the opposite type. This is easily satisfied for the B particles because there are many of type A in the system. However, on average, not all of the A particles can find two neighbouring B particles. It is, therefore, reasonable to assume that short columnar stacks, in which the particles alternate, are formed. These columns do not associate, however, to form a columnar phase; rather the quadrupolar interactions between the A particles destabilize the long columns and instead the system forms a nematic phase in which the short columns with



(a) (b) (c) (d) (e) (f)

Figure 7. The columnar distribution function for quadrupolar Gay–Berne discs with Q^* of 0·10 in the nematic phase of the pure system at scaled temperatures of (*a*) 2·6 and (*b*) 2·4; for the columnar phase of the 50:50 mixture at T^* of (*c*) 2·6 and (*d*) 2·4; and for (*e*) the nematic phase of the 75:25 mixture at T^* of 2·60 and (*f*) the columnar phase of the 75:25 mixture at T^* of 2·4. The distribution function for AA particles is shown by (—), for BB particles by (---) and for AB particles by (...).

alternating particles are surrounded by the discs of the excess component in the mixture.

The phase formed by the 75:25 mixture below a scaled temperature of 2·55 is expected to be columnar by analogy with the behaviour of the 50:50 mixture. This identification is supported by the columnar distribution function calculated for this phase at T^* of 2·4 and shown in figure 7 (*f*). The oscillations in $g_c(r^*_\|)$ extend to large distances, although they are not as intense as those found for the 50:50 mixture at T^* of 2·6 and 2·4, see figures 7 (*c*) and 7 (*d*), respectively. This difference in the translational order could result because the systems are not being compared at equivalent temperatures. Thus for the 75:25 mixture, a scaled temperature of 2·4 is closer to the transition temperature from the columnar to the nematic phase at T^* of 2·55 than for the 50:50 mixture where the columnar transition temperature is 2·85. The columnar phases also differ in that for the 50:50 mixture, it is formed directly from the isotropic phase whereas for the 75:25 mixture it appears from the nematic phase. By analogy with the behaviour of smectic phases, it is to be expected that the columnar phase formed by the 50:50 mixture should have a higher translational order than that formed by the 75:25 mixture. There is also another explanation which is suggested by the appearance of the $g_c^{\alpha\beta}(r_\parallel^*)$ for the different components. As we now expect, the most intense of the face-to-face peaks at $r_\parallel^*$ of 0·4 is for the unlike species [see figure 7 (*f*)]. This shows that there is a strong tendency for a particle of type B to have those of type A as nearest neighbours in the column. The peak at $r_\parallel^*$ of 0·8 is most intense for BB correlations, as it is in the preceding nematic phase where the increased intensity over the AA correlations comes, in part, from the normalization. This may also account for the slightly greater intensity of the BB peak at $r_\parallel^*$ of 1·2. Given the clear preference of B particles to have those of type A as nearest neighbours, the excess of the A particles must be accommodated as nearest neighbours within the columns and this seems to be consistent with the columnar distribution function which we have calculated. The presence of a section of the column composed entirely of A particles will clearly tend to destabilize the structure and could reduce the translational order, as we have found.

5. Summary and conclusions

Our Monte Carlo simulations of quadrupolar Gay–Berne discs have shown that the introduction of the quadrupolar interaction can have a profound influence on the phase behaviour. Thus for the pure system, the quadrupolar interaction with Q^* of 0·10 destroys the columnar phase exhibited by Gay–Berne discs and gives instead a nematic phase over the wide temperature range studied. In marked contrast the 50:50 mixture forms a columnar phase directly from the isotropic phase at a temperature which is higher than the nematic–isotropic transition temperature of the pure system. In addition, there is a strong tendency for unlike particles to be nearest neighbours, giving a structure in which the nature of the particles alternates on average along the column. The 75:25 mixture has a different phase behaviour in that it forms a nematic phase before undergoing a relatively weak transition to a columnar phase. The nematic phase is of special interest as it has a columnar structure with the different components of the mixture alternating along the short columns. This local columnar structure contrasts with the translational order in the nematic phase formed by the pure systems which is extremely short ranged.

The phase behaviour of quadrupolar Gay–Berne discs clearly has much in common with discotic systems which form chemically induced liquid crystal phases. In addition, the alternate packing of the two components in the stacks of the columnar phase and the local columnar structure of the nematic phase formed by the 75:25 mixture is essentially the same as the structure proposed for the chemically induced phases formed by certain multiynes with 2,4,7-trinitrofluorenone. It would seem, therefore, that an electrostatic quadrupolar interaction between discotic particles with quadrupole moments differing in sign is entirely consistent with the formation of chemically induced liquid crystal phases. This identification of the molecular interaction responsible for such phases is further supported by the observation that the quadrupole moment used in the simulation is comparable to that expected for the discotic molecules known to form chemically induced liquid crystal phases.

We are grateful to the Engineering and Physical Sciences Research Council for the award of a research studentship to Dr M. A. Bates and for a grant (GR/J74459) towards the cost of a Silicon Graphics Power Challenge computer used to perform these simulations.

Appendix

Here we give the expressions for the orientational dependence of the contact separation and well depth appearing in the Gay–Berne potential for cylindrically symmetric particles. The contact separation $\sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}})$ has its origins in the gaussian overlap model developed by Berne and Pechukas [19] and is

$$\sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}) = \sigma_o \times \left\{ 1 - \chi \left[\frac{(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{r}})^2 + (\hat{\mathbf{u}}_j \cdot \hat{\mathbf{r}})^2 - 2\chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{r}})(\hat{\mathbf{u}}_j \cdot \hat{\mathbf{r}})(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)}{1 - x^2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)^2} \right] \right\}^{-1/2}. \tag{A1}$$

In this expression, σ_o is the contact separation when the symmetry axes of the particles are orthogonal to the interparticle vector. The parameter χ controls the shape anisotropy and is defined by

$$\chi = \frac{(\sigma_f/\sigma_e)^2 - 1}{(\sigma_f/\sigma_e)^2 + 1} \tag{A2}$$

where σ_f and $\sigma_e (= \sigma_o)$ are the contact separations when the particles are in the face-to-face and edge-to-edge arrangements, respectively. The orientational dependence of the well depth has evolved in an *ad hoc* manner from that developed originally from the gaussian overlap model; it is

$$\varepsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}) = \varepsilon_0 \varepsilon^{\nu}(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) \varepsilon'^{\mu}(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}). \tag{A3}$$

In this expression

$$\varepsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = [1 - \chi^2(\hat{\mathbf{u}}_i\ \hat{\mathbf{u}}_j)^2]^{-1/2} \tag{A4}$$

which comes from the original analysis, and

$$\varepsilon'(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}) = 1 - \chi' \times \left(\frac{(\hat{\mathbf{u}}_i\ \hat{\mathbf{r}})^2 + (\hat{\mathbf{u}}_j\ \hat{\mathbf{r}})^2 - 2\chi'(\hat{\mathbf{u}}_i\ \hat{\mathbf{r}})(\hat{\mathbf{u}}_j\ \hat{\mathbf{r}})(\hat{\mathbf{u}}_i\ \hat{\mathbf{u}}_j)}{1 - \chi'^2(\hat{\mathbf{u}}_i\ \mathbf{u}_j)^2} \right) \tag{A5}$$

which is a correction introduced to allow for the dependence of the well depth on the orientation of the particles with respect to the interparticle vector. The parameter ε_0 is the well depth when the symmetry axes of the particles are orthogonal to each other and to the interparticle vector. The orientational dependence of $\varepsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}})$ is determined by the anisotropy parameter χ' which by analogy with χ is defined by

$$\chi' = \frac{(\varepsilon_e/\varepsilon_f)^{1/\mu} - 1}{(\varepsilon_e/\varepsilon_f)^{1/\mu} + 1} \tag{A6}$$

in terms of the well depths for the face-to-face and edge-to-edge arrangements.

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