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Computer simulation studies of the dependence on density of the orientational order in nematic liquid crystals

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Simulations of the temperature dependence of the nematic orientational order parameter, $\bar{P}_2$, at different densities have been made using the Gay–Berne potential. The results are used to calculate $\Gamma = -(\partial \ln T/\partial \ln V)_{\bar{P}_2}$, which is a measure of the relative sensitivity of $\bar{P}_2$ to temperature and density. Previous experimental measurements of Γ have obtained values in the range 2–6 for real nematogens, whilst the present simulations yield $\Gamma = 8 \pm 1$. Changing the Gay–Berne potential by increasing the steepness of the repulsive term increases the calculated value of Γ, whilst changing the relative well depths for side-by-side compared to end-to-end arrangements of Gay–Berne particles leaves Γ virtually unchanged. These exploratory calculations suggest that Γ is a useful parameter for testing the parametrizations of model potentials.

1. Introduction

The molecules in a liquid crystal phase have long range orientational order, such that for a unit vector, $\hat{\mathbf{u}}$, fixed in a rigid sub-unit of the mesogen, $\bar{P}_L$, the averages of the Legendre polynomials $P_L(\hat{\mathbf{u}} \cdot \hat{\mathbf{n}})$ are non-zero for L even. The unit vector $\hat{\mathbf{n}}$, known as the director, specifies the average orientation of the vectors $\hat{\mathbf{u}}$ at any point in the sample. For simplicity we shall consider molecules which are rigid and cylindrically symmetric, in which case only one vector $\hat{\mathbf{u}}$, coinciding with the symmetry axis, is necessary for describing the orientational ordering of the whole molecule. The second-rank order parameter, $\bar{P}_2$, can be measured by a variety of methods [1], and our discussions will be confined to this member of the set $\bar{P}_L$. The dependence of $\bar{P}_2$ on temperature and pressure has been studied experimentally [2–9], and from this data it is possible to obtain the dependence on density, ρ, (or molar volume, V) of $\bar{P}_2$. The procedure is straightforward if the equation of state for the nematic phase is known, and there have been a limited number of studies of this kind [3–7, 9]. A convenient way of expressing the relative importance of temperature and density in determining $\bar{P}_2$ is the thermodynamic parameter, Γ, introduced by McColl [4],

$$\Gamma = -(\partial \ln T/\partial \ln V)_{\bar{P}_2}. \qquad (1)$$

The values of Γ obtained from experimental data cover the range 2–6. Attempts to relate the value of Γ to the nature of the forces contributing to the anisotropic potential energy of the molecules have often relied on the molecular field approximation. In the

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simplest version of this model the potential of mean torque $U(\beta)$ for a rigid, cylindrically symmetric molecule in the average potential field of all other molecules in the sample can be written as,

$$U(\beta) = -\varepsilon V^{-\gamma}\bar{P}_2 P_2(\cos\beta), \tag{2}$$

where β is the angle between $\hat{\mathbf{n}}$ and the molecular symmetry axis, and ε is a constant. This can be regarded as a phenomenological potential with γ as an adjustable parameter with which to fit experimental data, and in this case γ can be identified with Γ. However, Cotter [10] has pointed out that if equation (2) is derived from a pair potential, then statistical mechanical consistency dictates that $\gamma = 1$. This implies that although equation (2) is a possible approximate form for $U(\beta)$, the molecular significance of the value of γ is obscure. Thus, if dispersion forces, which depend on r_{ij}^{-6}, where r_{ij} is the intermolecular separation, dominate $U(\beta)$, then γ and Γ might be expected to be close to a value of 2 [11]. However, γ also depends on the density dependence of the radial distribution function, and this is unknown. Probably the only practical way to interpret experimental values of Γ in terms of the forces contributing to $U(\beta)$ is to determine the density dependence of the orientational order by a numerical simulation based on a model for the pair potential. If such an approach is possible, then Γ could be used to optimise the parameters in the model potentials. With this aim in mind we have carried out simulations of the density dependence of orientational order using a model potential introduced by Gay and Berne [12], which has been shown to give stable nematic and smectic phases [13–15].

2. The model potential

Nematogens are composed of quite large molecules, with even the smallest containing 27 atoms. To solve the equations of motion for a sample of N such molecules interacting via an atom–atom potential, and to repeat the calculations until thermal equilibrium is established, imposes a practical limit on N with presently available computing power of about 128 molecules [16]. Repeating such calculations for the sample at different temperatures and densities imposes an added practical limitation. For these reasons we chose to use the simpler Gay–Berne potential, which attempts to model the potential between pairs of cylindrically symmetric particles. It is based on the single-site potential introduced first by Corner [17], which has range σ, and strength ε, parameters which depend on the orientations of the two particles,

$$U(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) = \varepsilon_0 \varepsilon_1^{\nu}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)\varepsilon_2^{\mu}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})(R^{-12} - R^{-6}). \tag{3}$$

$\hat{\mathbf{u}}_1$ and $\hat{\mathbf{u}}_2$ are unit vectors along the symmetry axes of the particles, and $\mathbf{r}$ is the vector between the centres of mass of two Gay–Berne particles, with $\hat{\mathbf{r}}$ as the associated unit vector. The function ε_1 is

$$\varepsilon_1(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = [1 - \chi^2(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)^2]^{-1/2}, \tag{4}$$

where

$$\chi = \{(\sigma_{\|}/\sigma_{\perp})^2 - 1)\}/\{(\sigma_{\|}/\sigma_{\perp})^2 + 1)\}. \tag{5}$$

The function ε_2 is

$$\varepsilon_2(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) = 1 - \tfrac{1}{2}\chi'\{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_1 + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_2)^2/(1 + \chi'(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)) + (\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_1 - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_2)^2/(1 - \chi'(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2))\}, \tag{6}$$

where

$$\chi' = \{(\varepsilon_{\perp}/\varepsilon_{\|})^{1/\mu} - 1\}/\{(\varepsilon_{\perp}/\varepsilon_{\|})^{1/\mu} + 1\}. \tag{7}$$

The labels ∥ and ⊥ refer to the orientations of the particles axes relative to the inter-particle vector, **r**. The reduced and shifted distance parameter R is defined as

$$R=\{r-\sigma(\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2,\hat{\mathbf{r}})+\sigma_0\}/\sigma_0, \tag{8}$$

with

$$\sigma_0=\sigma_\perp \tag{9}$$

and

$$\sigma(\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2,\hat{\mathbf{r}})=\sigma_0\{1-\tfrac{1}{2}\chi[(\hat{\mathbf{r}}\cdot\hat{\mathbf{u}}_1+\hat{\mathbf{r}}\cdot\hat{\mathbf{u}}_2)^2/(1+\chi(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2))+(\hat{\mathbf{r}}\cdot\hat{\mathbf{u}}_1-\hat{\mathbf{r}}\cdot\hat{\mathbf{u}}_2)^2/(1-\chi(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2))]\}^{-1/2}. \tag{10}$$

The parameters in this relatively complicated potential were chosen by Gay and Berne to mimic the potential between molecules comprising four centres equally spaced on a line at intervals of $2\sigma_0/3$ and interacting via a 12-6 Lennard–Jones potential. Thus, the ratio $\sigma_\parallel/\sigma_\perp$ is set equal to 3, ν to 1, μ to 2, and $\varepsilon_\parallel/\varepsilon_\perp$, the ratio of the well depths when the particles are either parallel or perpendicular to the inter-particle vector, is given the value of 1/5. With these values χ is 0·8 and χ' is 0·382.

The scaled moment of inertia about an axis perpendicular to the molecular symmetry axis, $I_\perp^*=I_\perp/m\sigma_0^2$ was assigned the value of 4, which is the same as in previous studies of the liquid crystal phases with this potential [13, 14]. This was chosen to ensure that the optimum time steps for the orientational and translational motions were approximately the same.

3. The calculations

A modified version of the Gay–Berne simulation program written by Adams *et al.* [13] and described more fully by Luckhurst *et al.* [14], was used, and the calculations were carried out on an IBM 3090-150VF. The system consisted of 256 particles for most of the simulations. The intermolecular potential was truncated at a cut-off of 0·45 of the box length ($4{\cdot}27\sigma_0$ at $\rho^*=N\sigma_0^3/V=0{\cdot}30$). On average about 100 neighbours were included in the calculations of the forces acting on, and the energy of, each particle. A scaled time step $\Delta t^*=\Delta t(\varepsilon_0/m\sigma_0^2)^{1/2}$ of 0·005 was used for most of the calculations, but was decreased for some of the higher temperatures with the hybrid potential in order to insure the conservation of energy (the hybrid potential is defined in equation (18)). Energy fluctuations were kept below one part in 10^4 over the whole of the simulation with this time step. For typical values of the parameters for the Gay–Berne particles the time step is about 10^{-14} s. This value was obtained by taking σ_0 to be 4 Å, which is typical of rod-like mesogenic molecules. The energy parameter ε_0 was obtained from the scaled nematic–isotropic transition temperature, T_{NI}^*, ($T^*=k_\mathrm{B}T/\varepsilon_0$) of 2·0 and equating it with a typical transition temperature of 400 K, giving $\varepsilon_0/k_\mathrm{B}=200$ K. The mass of the Gay–Berne particles was taken to correspond to the mass of 12 carbon atoms. Run lengths varied according to the ease of equilibration, and the importance of the particular temperature in calculating Γ. For those points near the nematic to isotropic transition, from 50*k* to 100*k* or more, time steps were followed.

The order parameter $\bar{P}_2$ was calculated by forming the Q tensor with elements

$$Q_{\alpha\beta}=(2N)^{-1}\sum_i(3l_{\alpha i}l_{\beta i}-\delta_{\alpha\beta}),$$

where $l_{\alpha i}$ is the direction cosine of the ith particle and the αth box axis. Diagonalizing **Q** gives $\bar{P}_2$ as the largest eigenvalue and the director is the corresponding eigenvector.

Preliminary simulations were done to establish that the runs were of sufficient length, that equilibrium had been reached, and that the values obtained for $\bar{P}_2$ were independent of the initial configuration. To test the latter point two separate simulations were made, each corresponding to a scaled density of 0·35, and a scaled temperature $T^* = 3{\cdot}0$. One simulation started from an equilibrated sample at $T^* = 2{\cdot}75$, and the other from $T^* = 3{\cdot}25$, and the results are shown in figure 1. This shows values of $\bar{P}_2$ calculated at intervals of 500 time steps after changing the temperature to $T^* = 3{\cdot}0$. After about 2×10^4 time steps the instantaneous values of $\bar{P}_2$ are independent of the starting configuration, but there is a considerable fluctuation about the time and ensemble average, $\bar{P}_2$, as expected.

Two methods of calculating Γ were explored: one which directly mimics the experimental method, which we shall refer to as the direct method, and the other which is analogous to that used to calculate heat capacities, and which yields Γ from a single simulation at a fixed temperature and density. We shall refer to this as the fluctuation method. In the direct method, the temperature dependence of $\bar{P}_2$ is calculated at constant density from a number of simulations of the nematic phase. Repeating the calculations for at least one more density enables the partial derivatives in equation (1) to be estimated at constant $\bar{P}_2$. One disadvantage of this method is that it requires a very large amount of computer time. This is because characterization of the temperature dependence of $\bar{P}_2$ requires exploratory calculations to locate the nematic–isotropic phase transition temperature, T_{NI}, followed by sufficient calculations corresponding to different temperatures in the nematic phase so that comparisons at constant $\bar{P}_2$ can be made for samples at different densities. This extensive set of calculations is analogous to the large number of NMR experiments that have to be made, for precisely the same reasons, in order to obtain Γ. It should be noted, however, that is rather easier to set the temperature or pressure in an NMR experiment than to obtain an ensemble at a desired temperature and density in the simulations.

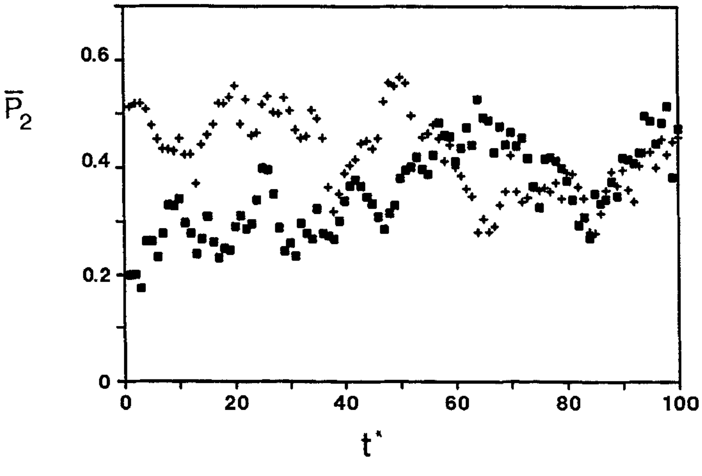

Figure 1. Dependence of $\bar{P}_2$ on time, t^*, in units of thousands of scaled time steps Δt^*, for two different starting configurations of 256 particles interacting via the Gay–Berne potential. The temperature T^* is 3·0, and the density $\rho^* = 0{\cdot}35$. The values of $\bar{P}_2$ were calculated at intervals in t^* of 500 steps. One set of calculations started from an ensemble equilibrated at $T^* = 2{\cdot}75$(+), whilst the other started from $T^* = 3{\cdot}25$ (■).

The fluctuation method for obtaining Γ is based on re-expressing this parameter as,

$$\Gamma=(V/T)\,(\partial \bar{P}_2/\partial V)_T/(\partial \bar{P}_2/\partial T)_V \tag{11}$$

and noting that, as shown in the Appendix, for the canonical ensemble

$$T(\partial \bar{P}_2/\partial T)_V=[\overline{P_2(\cos\beta)U}-\bar{P}_2\bar{U}]/(k_B T), \tag{12}$$

whilst

$$V(\partial \bar{P}_2/\partial V)_T=[\bar{P}_2\bar{W}-\overline{P_2(\cos\beta)W}]/(k_B T). \tag{13}$$

The bar denotes an ensemble average. The function W, which is related to the virial, is given by

$$W=(1/3)\sum_i\sum_{j<i} r_{ij}(\partial U/\partial r_{ij})_{\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j} \tag{14}$$

with r_{ij} the magnitude of a particular inter-pair separation, and

$$U=\sum_i\sum_{j<i} U(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\mathbf{r})$$

is the total potential energy of a configuration. Note the similarity of these expressions to that for $C_V=(\partial U/\partial T)_V$, the specific heat at constant volume,

$$C_V=[\overline{U^2}-\bar{U}^2]/(k_B T^2). \tag{15}$$

These fluctuation formulae are based on averages in the canonical ensemble, and they must be modified, as discussed by Allen and Tildesley [18], for use in the microcanonical ensemble explored by the standard molecular dynamics simulation. The modifications are given in the Appendix.

4. Results and discussions

4.1. *Calculations on static arrays*

We addressed first the question of what range of densities should be used. We were guided by the knowledge that Adams *et al.* [13] had established that a nematic phase exists when ρ^* is 0·32, which is in accord with the phase diagram obtained by Frenkel *et al.* [19] for a system of hard ellipsoids. It remained to investigate the value ρ^* has for a solid sample of particles interacting with the Gay–Berne potential at 0 K. To do this a study was made of the most stable arrangements of Gay–Berne particles in the solid phase at 0 K. This did not aim to explore all possible lattices, since this would have been too time consuming, but rather to examine the relative energies of the most probable arrangements in order to establish a range of densities which would be close to those of real systems. The quantity of interest is U_{array}, the potential energy per particle for a particular lattice. The geometry of the unit cell was varied to obtain the minimum U_{array} for different lattices. The system size for these calculations was increased until U_{array} was independent of N. This was achieved with N equal to about 4000. Originally single layers were studied, and the minimum energy structure was hexagonal packing with the particle long axes parallel to the layer normal. Tilting one or all of the molecules raises the energy.

Calculations on three dimensional layers showed that hexagonal layers with an ABAB layer arrangement is slightly more stable than an ABCABC stacking pattern. If an AAA stacking is adopted, the energy is a minimum when the particles are tilted to point into the holes in the neighbouring layers, and the energy is well above that of the non-tilted ABAB or ABCABC patterns. The ratio of the side-by-side separation of the particles within a layer to the interlayer separation in the optimised ABAB structure is 2·226, compared with a value of 3 if the particles are stacked end-to-end. Clearly, therefore, there is considerable interdigitation of the layers. A similar layer interdigitation has been found for the crystal smectic B phase formed by a sample interacting with the Gay–Berne potential [20]; in this case the ratio was found to be 2·6 for ABAB packing.

The density ρ^* is 0·3776 for both ABAB and ABCABC optimized packing for the solid. Changes in the density on melting for real mesogens are typically 10 per cent, and so densities in the range 0·30–0·35 were used in our simulations on the liquid phases. After our simulations were completed a study was published of the phase diagram of particles interacting with a Gay–Berne potential, which showed that in their simulations the nematic phase is stable over the narrow range of approximately $\rho^*=0{\cdot}30$–$0{\cdot}36$ [15].

4.2. *Calculations of* Γ *from the temperature and density dependence of* $\bar{P}_2$

Figure 2 shows the dependence of $\bar{P}_2$ on scaled temperature, T^*, for values of ρ^* of 0·30, 0·32 and 0·35. To obtain Γ requires choosing points on the three curves corresponding to constant values of $\bar{P}_2$. Fluctuations in time of the instantaneous values of $\bar{P}_2$ are large, as shown in figure 1, and so picking a value of T^* at which $\bar{P}_2$ has a particular value is necessarily imprecise. This problem was alleviated by fitting the simulation data to a smooth curve. We chose as an appropriate functional form

$$\begin{aligned} \bar{P}_2 &= 0{\cdot}9(1-T^*/T^*_{\mathrm{NI}})^\beta + 0{\cdot}1 \qquad \text{for } T^* < T^*_{\mathrm{NI}} \\ \text{and} \qquad & \\ \bar{P}_2 &= 0{\cdot}1 \qquad \text{for } T^* > T^*_{\mathrm{NI}}. \end{aligned} \tag{16}$$

This is similar to that used to fit experimental data [21], with the important difference that $\bar{P}_2$ is observed to be zero in a real isotropic phase, whereas in the simulations a non-zero value is obtained, even at very high temperatures. It has been argued [22] that in simulations the value of $\bar{P}_2$ calculated from the Q tensor should tend to a value of $N^{-1/2}$ in the isotropic phase, and this accords with the value of 0·1 used in the present calculations. Values of β and T^*_{NI} were found which give best fits to the data at each of the three densities, and these are given in the table; the function is drawn as the solid lines in figure 2. A separate evaluation of Γ is obtained from each pair of $\bar{P}_2(T^*)$ curves at two different densities. The most accurate values of Γ are obtained by choosing a value for $\bar{P}_2$ in the region where it is changing most rapidly with temperature, and hence the values in the table were obtained for $\bar{P}_2=0{\cdot}4$, but the resulting Γ is not sensitive to the particular value chosen for $\bar{P}_2$.

The molecular field potential given in equation (1), with $\gamma=\Gamma$, leads to the relationship,

$$T^*_{\mathrm{NI}} \propto V^{*-\Gamma}. \tag{17}$$

Values of Γ obtained from the three pairs of T^*_{NI} values are shown in the table, and are virtually identical with those obtained by the direct method. The values of Γ determined by these methods have an average of 8 ± 1, which is just beyond the top of the range found experimentally. This suggests that the Gay–Berne potential should be modified in order to accord more closely to real liquid crystals.

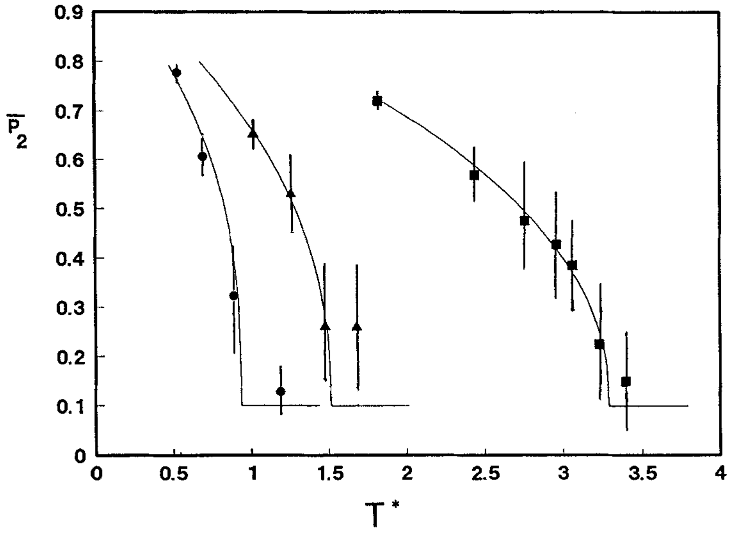

Figure 2. Dependence of $\bar{P}_2$ on scaled temperature, T^*, for scaled densities, $\rho^* = 0{\cdot}30$ (●), 0·32 (▲), and 0·35 (■), calculated for the standard Gay–Berne potential. The continuous lines are the best fits to equation (16).

Values of the nematic–isotropic transition temperature, T^*_{NI}, for different densities, ρ^*. The values of β are those which give the best fits of the data to equation (16). The values of Γ are those calculated from pairs of values of T^*_{NI} using equation (17), and also obtained by the direct method with $\bar{P}_2$ constant at 0·4. U_{GB} is the standard Gay–Berne potential, U_{HB} is the hybrid version, and $U_{\varepsilon=7}$ that with $\varepsilon_{\perp}/\varepsilon_{\parallel} = 7$.

				Γ	
Potential	ρ^*	β	T^*_{NI}	From T^*_{NI}	Direct method
U_{GB}	0·30	0·37	0·94	7·3	(0·30, 0·32)† 7·3
	0·32	0·43	1·51	8·7	(0·32, 0·35) 8·3
	0·35	0·45	3·29	8·1	(0·30, 0·35) 7·9
U_{HB}	0·32	0·56	5·86	10·5	(0·32, 0·35) 10·4
	0·35	0·58	15·02		
$U_{\varepsilon=7}$	0·32	0·29	1·31	8·7	(0·32, 0·35) 8·4
	0·35	0·37	2·87		

† The pairs of densities from which Γ is calculated.

4.3. *Calculations of* Γ *from fluctuations*

Calculations of Γ from equations (11)–(13) gave 8 ± 4 for $\rho^* = 0{\cdot}35$ and $T^* = 2{\cdot}74$, in excellent agreement with the values obtained by the direct method. The lower precision obtained by this method is a consequence of the comparable magnitudes of the two terms on the right-hand side of equations (12) and (13), so that in each case the differences are small with large errors. The advantage of calculating Γ in this way is that it can be done from the results of a single simulation at fixed temperature and density.

4.4. *Calculations of* Γ *with modified potentials*

Returning to calculations of Γ by the direct method, we have made some exploratory calculations with modified Gay–Berne potentials in an attempt to determine the sensitivity of calculated values of Γ to the form of the potential. The Gay–Berne potential contains several parameters whose values might affect Γ, and changing the functional form would also, in principle, change the calculated density dependence of the orientational order.

We chose to investigate first the effect of changing the steepness of the potential at inter-particle separations less than that for which $U(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \mathbf{r})$ is a minimum. However, this cannot be done in a simple way without changing other features of the potential. Thus, changing the repulsive part of $U(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \mathbf{r})$ by replacing R^{-12} by some higher power, say R^{-18}, alters the potential in several respects. Figure 3 compares a 12-6 with an 18-6 Lennard-Jones potential. Note that the minimum in the 12-6 potential is shifted inwards and lowered relative to the 18-6 curve, and the area of the negative region is increased. We wished to change only the steepness of the Gay–Berne potential at short R, hence simply replacing R^{-12} by R^{-18} did not seem appropriate. Multiplying the 18-6 potential by a constant so as to give an equal well-depth as the 12-6 potential also raises the attractive part and makes the potential tend to zero more quickly as R increases. A compromise choice was to use the 18-6 form from $R=0$ to the position where $U(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \mathbf{r})$ is a minimum, and then to switch to the 12-6 form for the rest of the range of R. This was achieved by shifting the minimum of the 18-6 form outward in R and upwards in energy, in such a way that the 12-6 and 18-6 potentials coincide at the minimum. The resulting hybrid potential, U_{HB}, is continuous and has a continuous first derivative, and looks like a 12-6 potential with a steeper repulsive wall. It has the functional form (cf. equation (3))

$$\begin{aligned} U_{\mathrm{HB}} &= C(R^{-12} - R^{-6}) && R > 2^{1/6} \\ &= C[(R-R_s)^{-18} - (R-R_s)^{-6} + E_s], && R < 2^{1/6} \end{aligned} \qquad (18)$$

where the shift parameters are

$$R_s = 2^{1/6} - 3^{1/12}$$

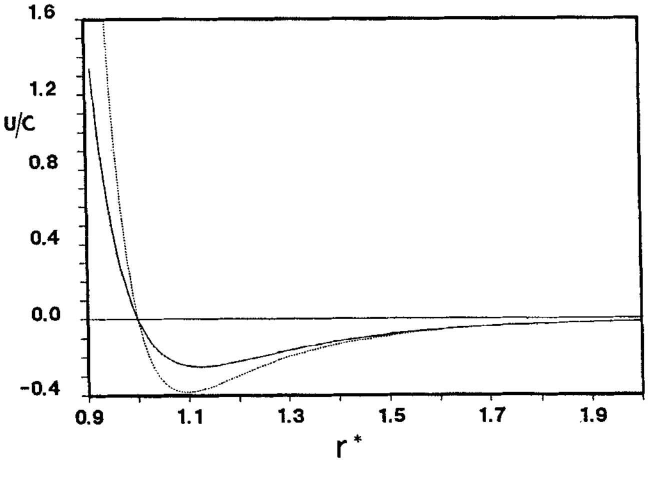

Figure 3. The distance dependence, in scaled units of $r^* = (r/\sigma_0)$, of a Lennard-Jones 12-6 potential (full line), and an 18-6 potential (dotted line).

and

$$E_s = -3^{-3/2} + 3^{-1/2} + 2^{-2} - 2^{-1}.$$

Simulations with U_{HB} were performed with $\rho* = 0{\cdot}32$ and $0{\cdot}35$, and calculated variations of $\bar{P}_2$ with T^* are shown in figure 4.

The largest effect produced in changing from the Gay–Berne to the hybrid potentials is that T^*_{NI} is increased, for example by a factor of 4 at $\rho^* = 0{\cdot}32$. This corresponds to a ratio of absolute transition temperatures, so that if ε_0 is chosen to make $T_{NI} = 400$ K for $\rho^* = 0{\cdot}32$ and the Gay–Berne potential, which is a typical value for a nematic–isotropic transition temperature, then T_{NI} for the hybrid potential is 1552 K.

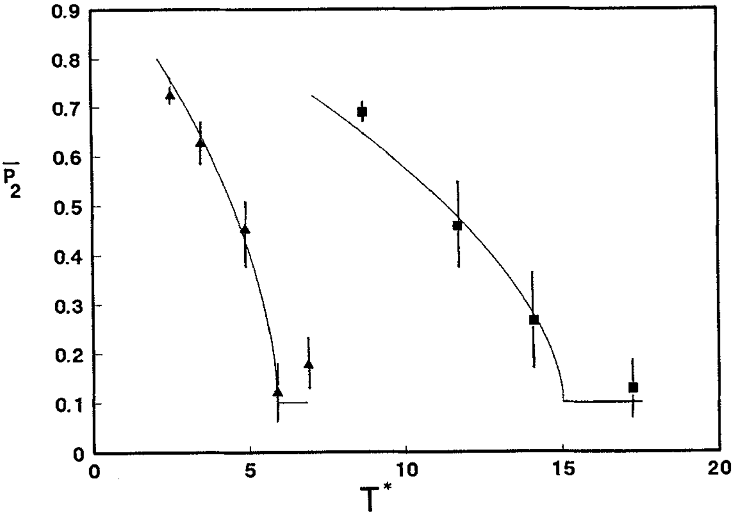

Figure 4. Dependence of $\bar{P}_2$ on T^* calculated with the hybrid potential, U_{HB}, for scaled densities of 0·32 (▲), and 0·35 (■). The continuous lines are the best fits to equation (16).

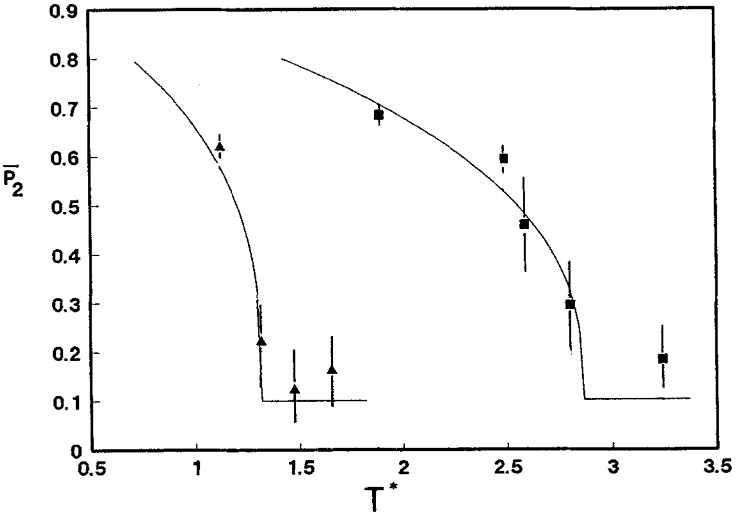

Figure 5. Dependence of $\bar{P}_2$ on T^* calculated with the Gay–Berne potential with $\varepsilon_\perp/\varepsilon_\parallel = 7$, $U_{\varepsilon=7}$, for scaled densities of 0·32 (▲) and 0·35 (■). The continuous lines are the best fits to equation (16).

The value of Γ, obtained either by the direct method, or from values of T^*_{NI}, increases from 8 ± 1 to $10{\cdot}5 \pm 1{\cdot}0$, demonstrating that the magnitude of this parameter does reflect the steepness of the repulsive part of the potential, albeit with a rather low sensitivity for these two potentials.

We have also investigated the effect of changing the value of $\varepsilon_\perp/\varepsilon_\parallel$ to 7 compared with 5 for the Gay–Berne potential. This increases the well depth of the end-to-end relative to the side-by-side molecular arrangements, but has barely any effect on Γ, as shown by the data given in the table. The dependence of $\bar{P}_2$ on T^* obtained with this potential is shown in figure 5. The transition temperatures for $\rho^* = 0{\cdot}32$ and $0{\cdot}35$ reduce with this value of $\varepsilon_\perp/\varepsilon_\parallel$ but only by a ratio of 0·9.

5. Conclusion

We have shown that the Gay–Berne potential leads to a nematic phase in which the order parameter $\bar{P}_2$ has a dependence on density which is in qualitative agreement with experimental measurements. The values calculated for the parameter Γ of about 8 are close to the experimental values which range between 2 to 6. Support was found for the view that the value of Γ obtained experimentally does reflect the nature of the potential, rather than being independent of the form of the pair potential and taking the value of unity, as required for molecular field potentials which are derived by averaging pair potentials. Thus increasing the steepness of the repulsive part of the potential in the simulations leads to an increased value for Γ. It should be possible, therefore, to use a comparison between observed and calculated values of Γ to adjust the balance between repulsive and attractive parts of a model potential. This is not a simple task for the Gay–Berne potential since it is difficult to discern with any precision how the many parameters in this potential influence the value of Γ. However, we do know that for hard rods Γ is necessarily infinite, and in contrast to this, computer simulations have shown that for particles interacting via a scalar Lennard-Jones potential with an embedded anisotropic attractive term Γ is approximately unity [23]. These observations suggest therefore that it is the relative contributions of the anisotropic repulsive and attractive forces which determines Γ and to decrease this quantity the relative importance of the anisotropic attractive term should be increased. In other words, for the Gay–Berne potential the variation of $\sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})$ with the molecular orientation should be reduced, or the angular variation of the well depth, $\varepsilon_0 \varepsilon_1^\nu(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) \varepsilon_2^\mu(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})$ should be increased. The anisotropy in $\sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})$ is controlled by the single parameter χ; this takes values from zero for spheres to unity for infinitely long rods. In principle, therefore, we could reduce the importance of the anisotropy in the repulsive forces by reducing χ. In practice, however, decreasing χ will also reduce the anisotropy in the attractive contribution to the potential because $\varepsilon_1(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)$ is also controlled by χ (see equation (4)). A further complication with the existing Gay–Berne potential is that even in the limit that χ goes to zero some anisotropy in the well depth remains because of the other contribution, $\varepsilon_2(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})$, which was introduced to allow for the dependence of the attractive term on the molecular orientation with respect to the intermolecular vector (see equation (6)). Nonetheless it is clear that to be able to vary the relative contribution of the attractive and repulsive forces to the Gay–Berne potential the quantity χ in equations (4) and (10) should be allowed to take different values. This necessarily introduces a new parameter χ'' into the equation for $\varepsilon_1(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)$ which is determined by the change in energy when the molecules pass from being parallel to being perpendicular to each other. The behaviour of particles interacting with such a modified Gay–Berne potential remains to be explored.

Appendix

We outline here the derivation of equations (11)–(13) which are the basis for the calculation of Γ from fluctuations. Beginning with the definition of $\bar{P}_2$,

$$\bar{P}_2 = Z^{-1}\int P_2(\cos\beta_1)\exp(-U/k_\mathrm{B}T)\,d\tau_1\ldots d\tau_N, \tag{A 1}$$

with

$$Z=\int\exp(-U/k_\mathrm{B}T)\,d\tau_1\ldots d\tau_N,$$

and τ_i represents the position, $\mathbf{r}_i$, and orientation, Ω_i, of molecule i. Differentiating with respect to T gives equation (12),

$$T(\partial\bar{P}_2(1)/\partial T)_V = [\langle P_2(1)U\rangle - \bar{P}_2(1)\langle U\rangle]/k_\mathrm{B}T. \tag{A 2}$$

Note that we are using $\langle\ \rangle$ to denote an average in the canonical ensemble, whilst retaining the bar notation for $\bar{P}_2$. This is to be able to denote the kind of ensemble over which the average is performed, and keeping the widely accepted notation for the order parameter. In order to differentiate equation (A 1) with respect to volume, a transformation to dimensionless coordinates is useful [24], so that $\mathbf{r}_i$ is replaced by $V^{1/3}\mathbf{R}_i$, and

$$V d\mathbf{R}_i = d\mathbf{r}_i.$$

The pair potential $U(V^{1/3}R_{ij}, \Omega_1, \Omega_2)$ can now be differentiated with respect to V, and a transformation back to the original coordinates gives equation (13),

$$V(\partial\bar{P}_2(1)/\partial V)_T = [\bar{P}_2(1)\langle W\rangle - \langle P_2(1)W\rangle]/k_\mathrm{B}T. \tag{A 3}$$

Because these quantities depend upon fluctuations, they are not independent of the ensemble used for their calculation. Thus, the derivation is based on equation (A 1), which requires a constant NVT ensemble. The molecular dynamics simulations are carried out on an ensemble at constant NVE, so correction terms for the change of ensemble must be included. The general expression for this change is [18],

$$\langle\delta A\delta B\rangle_E = \langle\delta A\delta B\rangle - (\partial\langle A\rangle/\partial T)(\partial\langle B\rangle/\partial T)/C_V, \tag{A 4}$$

where

$$\begin{aligned}\langle\delta A\delta B\rangle &= \langle(A-\langle A\rangle)(B-\langle B\rangle)\rangle\\ &= \langle AB\rangle - \langle A\rangle\langle B\rangle.\end{aligned}$$

Application of equation (A 4) to equations (A 2) and (A 3) then gives

$$\Gamma = -(5Nk_\mathrm{B})\langle\delta P_2\delta W\rangle_E/\{(2C_V)\langle\delta P_2\delta U\rangle_E\} - 2\langle\delta W\delta U\rangle_E/(5Nk_\mathrm{B}^2T^2). \tag{A 5}$$

$\langle\ \rangle_E$ represents an average in the microcanonical ensemble and the factors of 5/2 in this final expression arise from the equipartition of kinetic energy in the 5 degrees of freedom of each Gay–Berne particle.

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