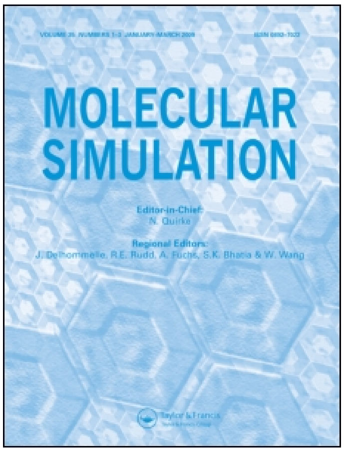


Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Molecular Dynamics Simulations of Calamitic and Discotic Liquid Crystals using a Hybrid Gay-Berne Luckhurst Romano Potential

M. P. Neal[a]; M. D. De Luca[b]; C. M. Care[c]
[a] School of Mathematics and Computing, University of Derby, UK [b] Division of Applied Physics, Sheffield Hallam University, UK [c] Materials Research Institute, Sheffield Hallam University, UK

To cite this Article Neal, M. P. , De Luca, M. D. and Care, C. M.(1995) 'Molecular Dynamics Simulations of Calamitic and Discotic Liquid Crystals using a Hybrid Gay-Berne Luckhurst Romano Potential', Molecular Simulation, 14: 4, 245 — 258
To link to this Article: DOI: 10.1080/08927029508022021
URL: http://dx.doi.org/10.1080/08927029508022021

Molecular Simulation, 1995, Vol. 14, pp. 245–258
Reprints available directly from the publisher
Photocopying permitted by license only

MOLECULAR DYNAMICS SIMULATIONS OF CALAMITIC AND DISCOTIC LIQUID CRYSTALS USING A HYBRID GAY-BERNE LUCKHURST ROMANO POTENTIAL

M.P. NEAL*[†], M.D. De LUCA** and C.M. CARE[§]

**School of Mathematics and Computing, University of Derby, UK*
***Division of Applied Physics, Sheffield Hallam University, UK*
[§]Materials Research Institute, Sheffield Hallam University, UK

(Received September 1993, accepted January 1995)

We report a molecular dynamics simulation study of a system of particles interacting via an anisotropic potential proposed by Luckhurst and Romano and modified by scaling with part of the well depth formalism employed by Gay-Berne. Parameters are selected to model calamitic mesogens and the system exhibits a variety of mesophases as the temperature is lowered. The phases are provisionally identified as isotropic, nematic, a highly ordered fluid with some smectic features and crystal. Comparison is made with a previous study with the same potential parameterised to model discotic mesogens.

KEY WORDS: Calmitic, discotic, liquid crystal, soft anisotropic potential

1 INTRODUCTION

Computer models of the liquid crystal phases of rod-like and disc-like molecules, calamitics and discotics, employing anisotropic potentials have led to an improved understanding of the way in which the intermolecular interactions between anisotropic molecules affect the observed liquid crystal phases.

Hard non-spherical molecules e.g. [1,2,3] have proved successful in simulating a variety of mesophases and are important as hard particle reference systems by comparison with theoretical studies [4]. A simulation [5] of a biaxial hard-ellipsoid fluid with three distinct semi-axes has been undertaken and found to be in semi-quantitative agreement with recent theories. A computer study of a calamitic mesogenic molecule has been undertaken [6] for three state points using realistic atom-atom potentials modelled by a standard empirical force field and building in realistic features such as molecular flexibility, complicated structural anisotropy and electrostatic forces. It provided predictions for phase behaviour and ordering that are in good agreement with experiment but suggested such simulations are currently beyond the range of modern computers.

[†] Author for correspondence

Single site phenomenological anisotropic potentials describing both short range repulsive and long rang attractive contributions to the potential have been developed in an attempt to provide computationally simple potentials for complex liquid crystal molecules and have proved valuable in simulating a variety of mesophases of calamitic and discotic mesogens [7, 8, 9] using adjustable parameters. Berne and Pechukas [10] proposed a gaussian overlap potential model to simulate liquid crystal behaviour. The original model suffered from several unrealistic features which would not be present in the pair potential between two liquid crystal mesogens and Gay and Berne [11] modified the potential by obtaining a function which gave the best fit to a linear array of four equi-distant Lennard-Jones centres. Real mesogenic molecules are biaxial and the Gay-Berne potential which is cylindrically symmetric provides an over- idealised model. Recently [12] a study has been undertaken of the Gay-Berne fluid using realistic molecule-molecule parameter values estimated for p-terphenyl from a total potential constructed from atom-atom terms with the biaxially projected out. The molecule p-terphenyl was chosen because of its rigidity and non-polar character.

Making the simplifying assumption of a rigid model we are in current work modelling p-terphenyl by a more realistic rigid biaxial three-site model in which the central site is twisted through an angle with respect to each to the end sites; each site interacts via an anisotropic potential which is a hybrid Gay-Berne Luckhurst- Romano potential (HGBLR).

Luckhurst and Romano [13] represented cylindrically symmetric particles by a Lennard-Jones 12–6 potential V_0 together with an additional anisotropic term V_a

$$V = V_0 + V_a \tag{1}$$

The Luckhurst Romano pair potential is scaled by part of the well depth formalism employed to fit the Gay-Berne so that the hybrid Gay-Berne Luckhurst-Romano potential becomes:

$$V = \varepsilon'(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})\{V_0 + V_a\} \tag{2}$$

where

$$V_0 = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} \tag{3}$$

and

$$V_a = -\lambda 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} + \left(\frac{\sigma}{r}\right)^{6}\right\} P_2(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2) \tag{4}$$

and

$$\varepsilon'(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \mathbf{r}) = 1 - \frac{\chi'}{2}\left[\frac{(\hat{\mathbf{r}}\cdot\hat{\mathbf{u}}_1 + \hat{\mathbf{r}}\cdot\hat{\mathbf{u}}_2)^2}{1 + \chi'\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2} + \frac{(\hat{\mathbf{r}}\cdot\hat{\mathbf{u}}_1 - \hat{\mathbf{u}}\cdot\hat{\mathbf{u}}_2)^2}{1 - \chi'\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2}\right] \tag{5}$$

The orientation of the molecules is specified by the unit vector $\hat{\mathbf{u}}$ and the intermolecular vector by the unit vector $\hat{\mathbf{r}}$. The parameter χ' determines the relative ratio of the end-to-end and side-to-side interactions and is given by

$$\chi' = (1 - \varepsilon_e/\varepsilon_s)/(1 + \varepsilon_e/\varepsilon_s) \tag{6}$$

where $\varepsilon_e/\varepsilon_s$ is the ratio of the end-to-end and side-to-side potential well depths. The parameters σ and ε are the usual Lennard-Jones parameters. The scalling factor λ takes the value 0.15 determined from preliminary calculations [13] and P_2 is the second Legendre polynomial.

The HGBLR potential is shown Figure 1 and as can be seen from equations (2) to (5) is characterised by a hard core which has spherical symmetry for a fixed orientation. The core is surrounded by an anisotropic attractive region. Such a potential allows us to study the effects of anisotropic dispersive forces upon the formation of liquid crystal phases by investigating the effect of ε' alone by varying $\varepsilon_e/\varepsilon_s$. Prior to undertaking a multi-site simulation the authors [14] have recently undertaken a molecular dynamics (MD) study of a single-site HGBLR potential parameterised in a disc-like form following previous work [9] so that $\varepsilon_e/\varepsilon_s$ takes the value 5.0 and favours the end-to-end interaction i.e. a discotic mesogen. We present here results for a single site HGBLR potential with $\varepsilon_e/\varepsilon_s$ set to 0.2 favouring the side-to-side interaction i.e. a calamitic mesogen.

2 MOLECULAR DYNAMICS SIMULATION

We have performed MD simulations for 256 and 500 particles in a cubic box with the usual periodic boundary conditions. No cut off was used as this did not aid vector-

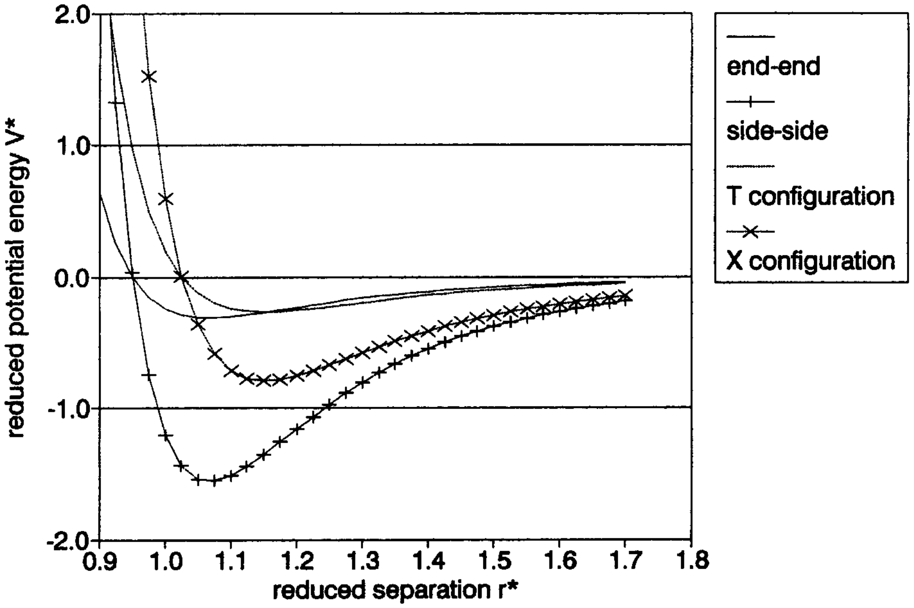


Figure 1 The distance dependence of the potential energy calculated from the hybrid Gay-Berne Luckhurst-Romano Potential for particular orientations of the particles with respect to one another and to the intermolecular vector. The parameterisation of the potential is that used in the molecular dynamics simulation, and described in the test.

isation. A more detailed description of the method is given in [14]. The results are presented for a reduced number density of $\rho^* = 1.1$ which enables equilibration of the system at low temperatures without cavity formation. The particles are axially symmetric about $\hat{\mathbf{u}}$ with a spherical repulsive core surrounded by a non-spherical attractive region equivalent to a rod. A reduced moment of inertia of $I^* = 1.00$, ($I^* = I/(m\sigma^2)$) was chosen to ensure a reasonable rate of equilibration between translational and rotational kinetic energy. The first simulation was started from an α-fcc crystal with kinetic energy such that the lattice method. The system was allowed to equilibrate over 15,000 steps, equipartition between translational and rotational energy being observed, and production runs of 15,000 steps were employed. The temperature was reduced by scaling the linear velocities and allowing the system to equilibrate for 15,000 steps between each production run. To provide acceptable energy conservation for each state point a value of reduced time step $\Delta t^* = (\varepsilon/m\sigma^2)^{1/2}\ \Delta t$ of 0.003 was employed and fluctuations of less than 1 part in 1000 of the total energy were observed for all state points except one just before the region identified as the isotropic-nematic transition in which the energy fluctuated by 1 part in 100. The following reduced quantities were calculated from the simulation: the pressure $P^* = P\sigma^3/\varepsilon$, temperature $T^* = Tk_B/\varepsilon$, the total internal energy per particle $E^* = E/\varepsilon$ the potential and kinetic energy per particle, V^* and K^*, the mean square displacement, $\langle |\mathbf{r}^*(t) - \mathbf{r}^*(0)|^2 \rangle$ and its components parallel and perpendicular to the director, the order parameter $\langle P_2 \rangle$ and the director of the phase $\hat{\mathbf{n}}$. The second rank order parameter $\langle P_2 \rangle$ was evaluated using the **Q** tensor defined by

$$Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^{N} \frac{3u_\alpha^i u_\beta^i - \delta_{\alpha\beta}}{2}$$

where u_α^i is the α-component of the unit vector along the symmetry axis of the molecule i. $\langle P_2 \rangle$ was defined as the ensemble average of the largest eigenvalue for the **Q** tensor, and the director as the corresponding eigenvector [15] and were calculated every 100 steps.

Additionally the second rank orientation correlation function $G_2(r^*) = \langle P_2(\hat{\mathbf{u}}_1 . \hat{\mathbf{u}}_2) \rangle$, the radial distribution function $g(\mathbf{r}^*)$ together with the longitudinal and transverse pair correlation functions $g_{\parallel}(r^*)$ and $g_{\perp}(r_{\perp}^*)$ were calculated.

3 RESULTS

The variations with temperatures of the second rank order parameter $\langle P_2 \rangle$ for the cooling runs for systems of 256 and 500 particles are shown in Figure 2. We see that the system is isotropic at reduced temperatures above $\langle T^* \rangle = 1.6$ although finite size fluctuations in evaluating the **Q** tensor lead to a small non-zero value for $\langle P_2 \rangle$. Cooling the system below $\langle T^* \rangle = 1.6$ causes the order parameter to rise rapidly to about 0.5. It then tends slowly to 1.0 as the system is cooled further. The internal energy also shows a transition at $\langle T^* \rangle = 1.65 \pm 0.05$ as shown in Figure 3; however there is a further significant decrease in internal energy at $\langle T^* \rangle = 0.88 \pm 0.03$ indicating the presence of a second phase transition between two highly ordered systems. The cooling runs were repeated for a system of 500 particles to investigate the effect of box size upon the phase

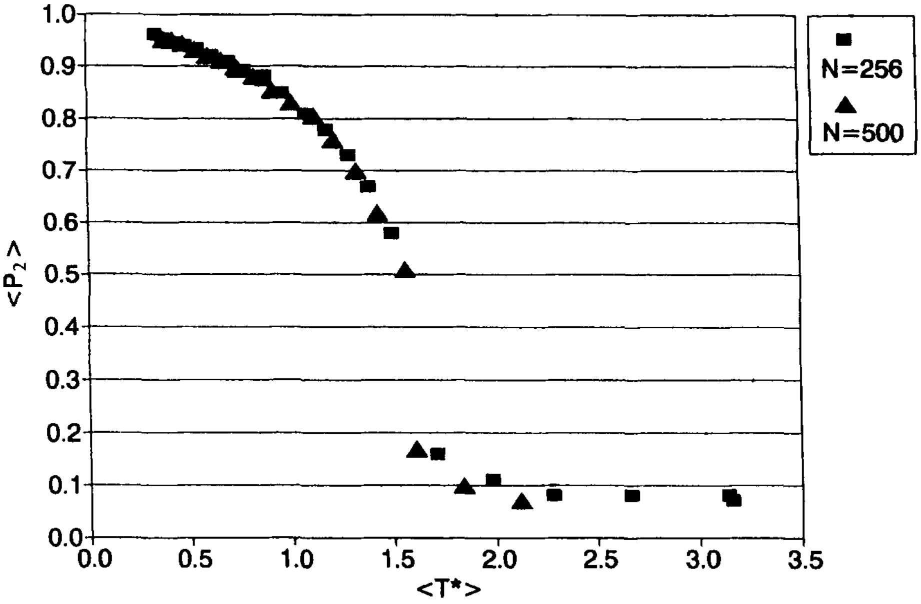


Figure 2 The variation of the second rank orientational order parameter $\langle P_2 \rangle$ as a function of temperature.

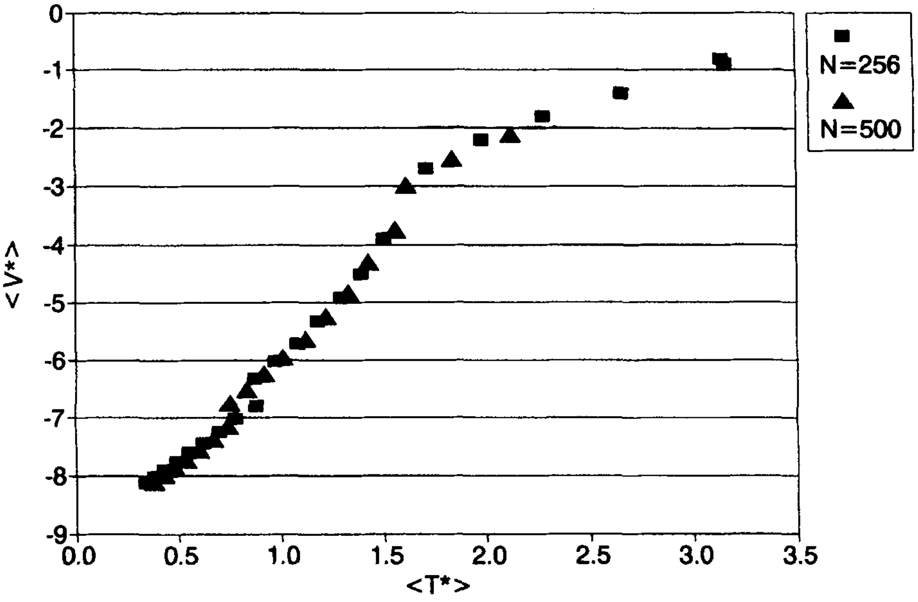


Figure 3 The variation of the potential energy $\langle V^* \rangle$ as a function of temperature.

diagram but no appreciable system size dependence was noted in the nematic region although the nematic isotropic transition region seemed somewhat affected by system size, as can be seen in Figures 2 and 3. Theentropy of transition $\Delta\langle V^*\rangle/\langle T^*\rangle$ was estimated to be 0.5 for each transition. The two mesophase transitions that were identified for the disc-like parameterisation [14] were relatively sharper with an estimated entropy of transition of 0.6.

Simulation runs near the transition at $\langle T^*\rangle = 1.6$ were extended to 60,000 steps and near the transition at $\langle T^*\rangle = 0.88$ were extended to 120,000 steps for the system of 256 particles. The diffusion coefficients D^* and its components $D_\parallel^*$ and $D_\perp^*$, parallel and perpendicular to the director were calculated from the Einstein relation valid at long times [16] by considering the final 30,000 and 35,000 steps of the simulation respectively as shown in Table 1.

Plots of the mean square displacement with time are shown in Figures 4(a), (b) and (c) for reduced temperatures of $\langle T^*\rangle = 1.57$, 0.93 and 0.84 respectively and are straight

Table 1 Reduced diffusion coefficients, mean order parameter and mean temperature for the system of 256 particles.

$\langle T^*\rangle$	D^*	$D_\parallel^*$	$D_\perp^*$	$\langle P_2\rangle$
1.98 ± 0.05	0.360	0.108	0.126	0.12 ± 0.05
1.72 ± 0.05	0.340	0.115	0.113	0.18 ± 0.17
1.57 ± 0.07	0.220	0.079	0.071	0.38 ± 0.08
0.93 ± 0.03	0.0156	0.0041	0.0057	0.861 ± 0.009
0.84 ± 0.02	0.0182	0.0067	0.0057	0.878 ± 0.009

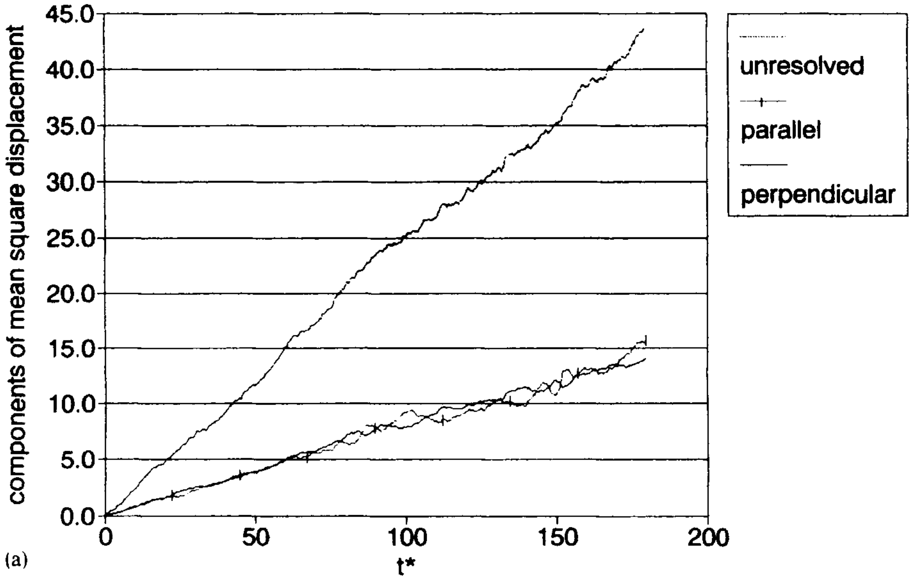
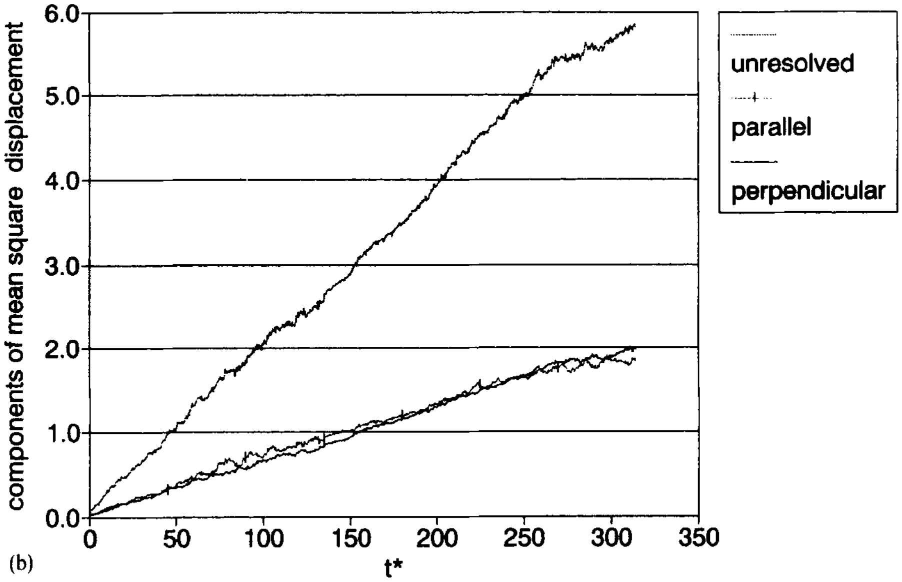


Figure 4 Mean square displacement versus time resolved with respect to the system director at reduced temperatures of (a) $\langle T^*\rangle = 1.57$ (b) $\langle T^*\rangle = 0.93$ and (c) $\langle T^*\rangle = 0.84$.



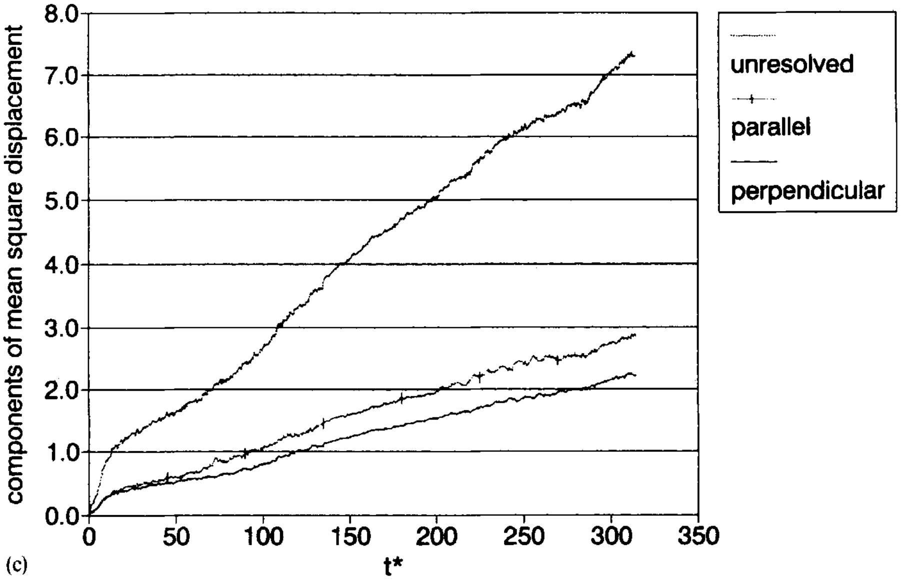


Figure 4 (*Continued*)

lines exhibiting liquid-like diffusion; below $\langle T^* \rangle \approx 0.8$ the diffusion virtually ceases indicating a solid phase. As Table 1 shows, the diffusion coefficient reduces as the temperature is lowered until $\langle T^* \rangle = 0.93$, and then shows an increase at $\langle T^* \rangle = 0.84$. This increase is due to an increase in diffusion parallel to the director, showing motion is less hindered parallel to the director although both values are very low at this temperature. This increase in diffusion parallel to the director is indicative of the onset of a smectic phase. We note however that at $\langle T^* \rangle = 0.93$ the diffusion coefficient is greater perpendicular to the director than parallel to it. Figures 5(a), 5(b), 5(c) and 5(d) show the radial distribution function $g(r^*)$ together with the longitudinal and transverse correlation functions $g_{\parallel}(r_{\parallel}^*)$ and $g_{\perp}(r_{\perp}^*)$ at temperatures of $\langle T^* \rangle = 1.57, 0.93, 0.88$

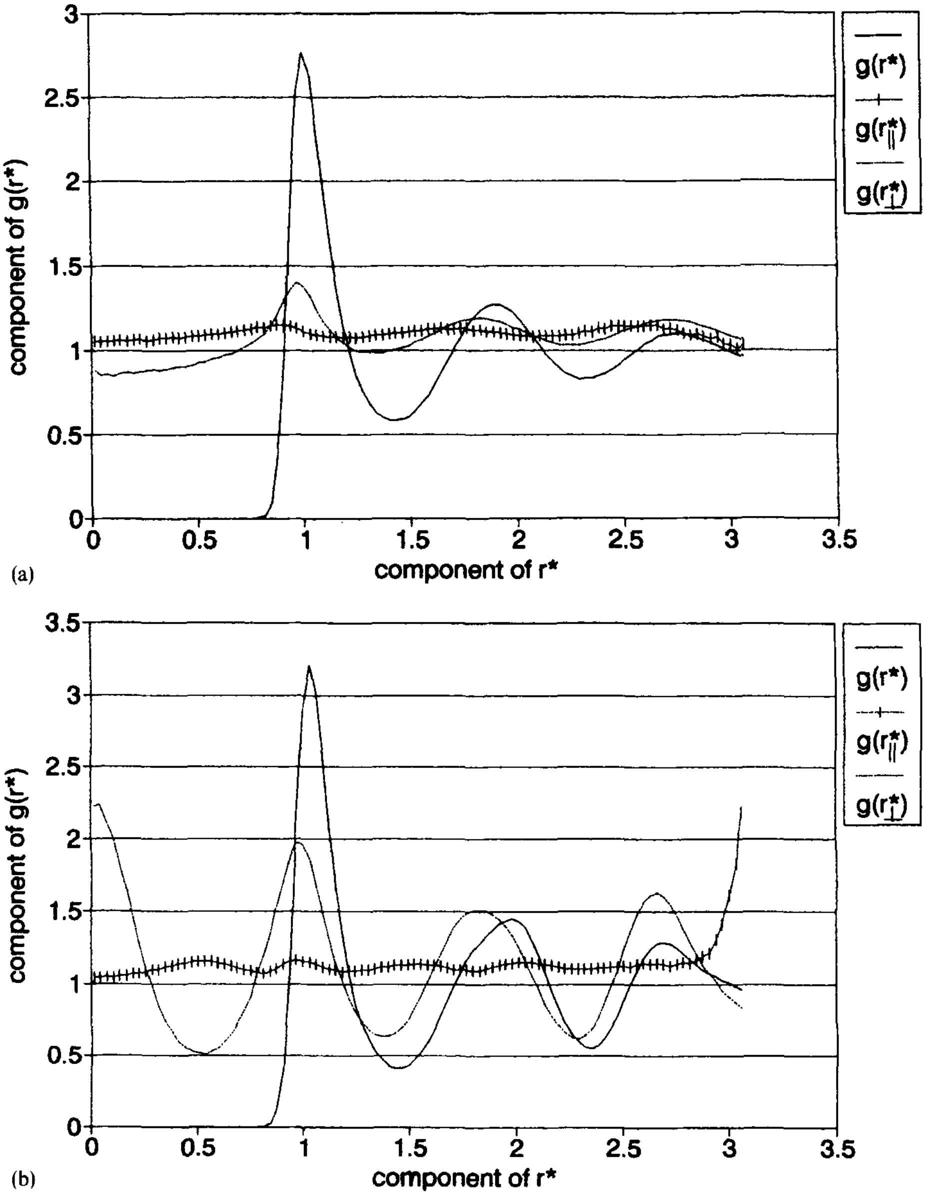


Figure 5 The radial distribution function $g(r^*)$ and the longitudinal and transverse pair correlation functions $g_{\parallel}(r_{\parallel}^*)$ and $g_{\perp}(r_{\perp}^*)$ resolved with respect to the system director as a function of scaled separation r^* simulated for the hybrid Gay-Berne Luckhurst-Romano potential at a series of reduced temperatures (a) $\langle T^* \rangle = 1.57$ (b) $\langle T^* \rangle = 0.93$ $\langle T^* \rangle = 0.84$ and (D) $\langle T^* \rangle = 0.34$.

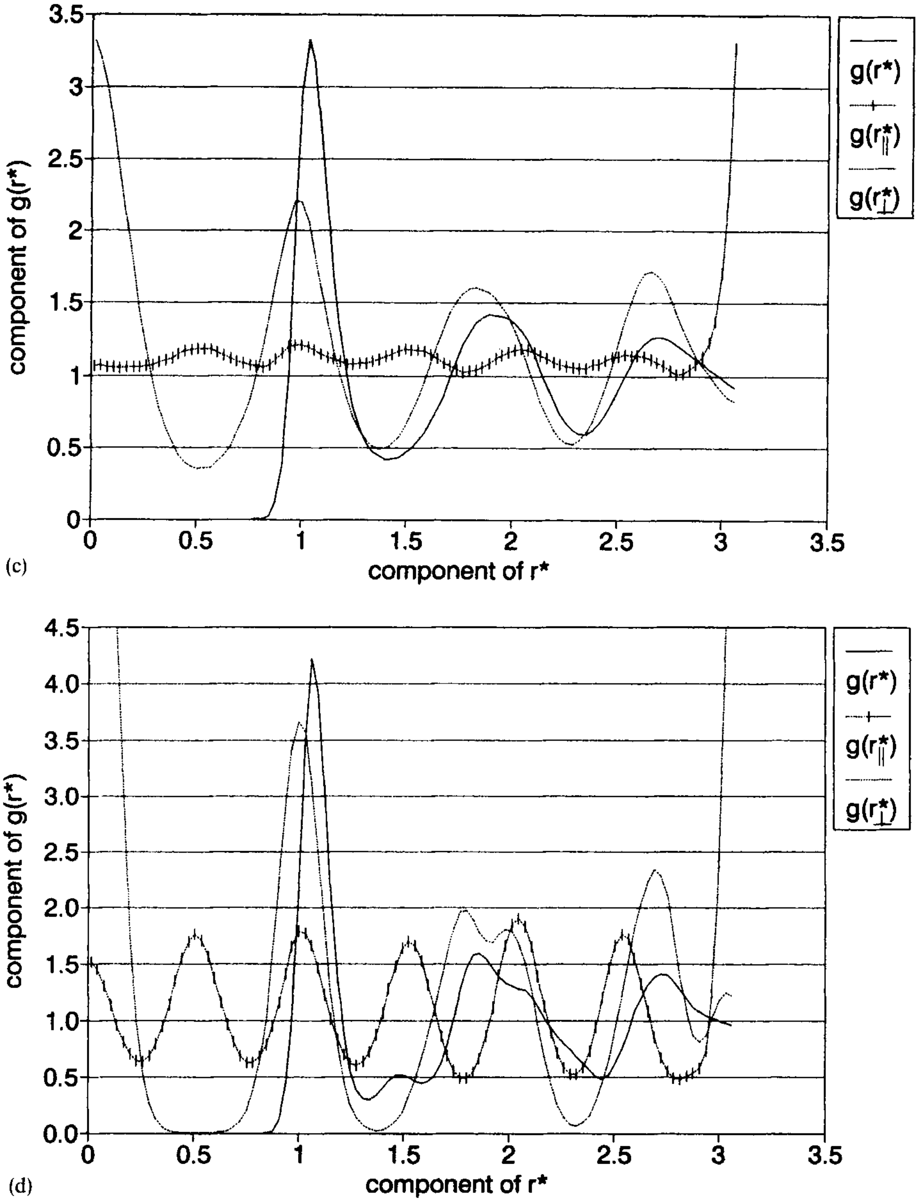


Figure 5 (*Continued*)

and 0.34 respectively. Figure 5(a) demonstrates that there is no discernible change from liquid-like behaviour at $\langle T^* \rangle = 1.57$ so that this phase is identified as nematic. Figure 5(b) exhibits a strong 1-dimensional oscillation in the pair correlation function perpendicular to the director and a weak oscillation in the pair correlation function parallel to the director. Figure 5(c) and 5(d) demonstrate that both these oscillations increase in magnitude progressively as the temperature is reduced to $\langle T^* \rangle = 0.84$ and to the solid phase at $\langle T^* \rangle = 0.34$. Figure 6 represents "snapshots" of sample configurations taken during runs at $\langle T^* \rangle = 1.29$, $\langle T^* \rangle = 0.88$ and $\langle T^* \rangle = 0.34$ corresponding to instantaneous values of the order parameter of $\langle P_2 \rangle = 0.71$, 0.90 and 0.96 respectively; the orientation of a particle is represented by a line pointing along the vector $\hat{\mathbf{u}}$ and the position of the centre of mass by a dot. In Figure 6(a) illustrating the nematic phase two views of the same configuration are presented perpendicular and parallel to the director. In Figure 6(c) two views are presented parallel to the director,

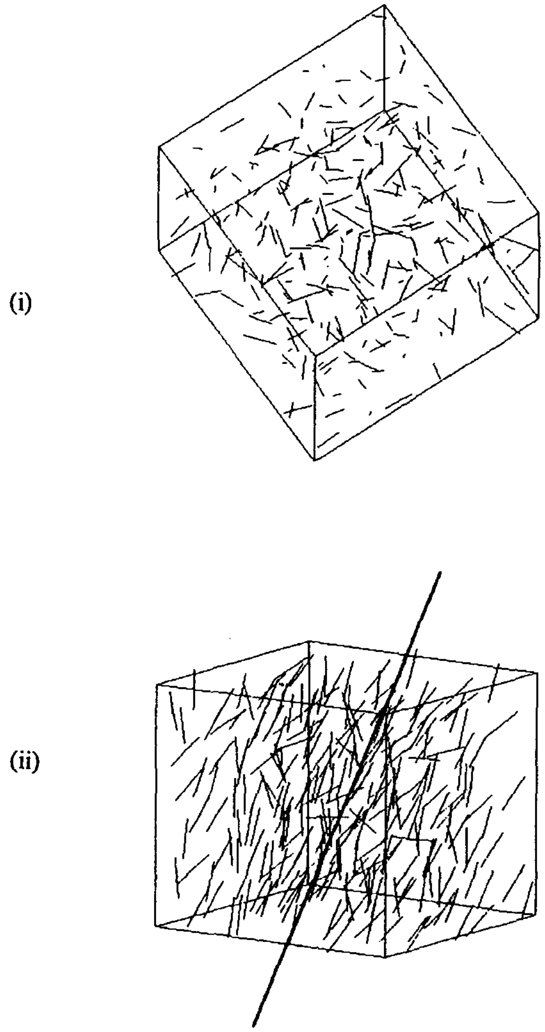


Figure 6a $<P_2> = 0.71$ $<T^*> = 1.29$

Figure 6 Three sets of snapshots from typical configurations at instantaneous values of the order parameter $\langle P_2 \rangle$ of (a) 0.71 (b) 0.90 and (c) 0.96.

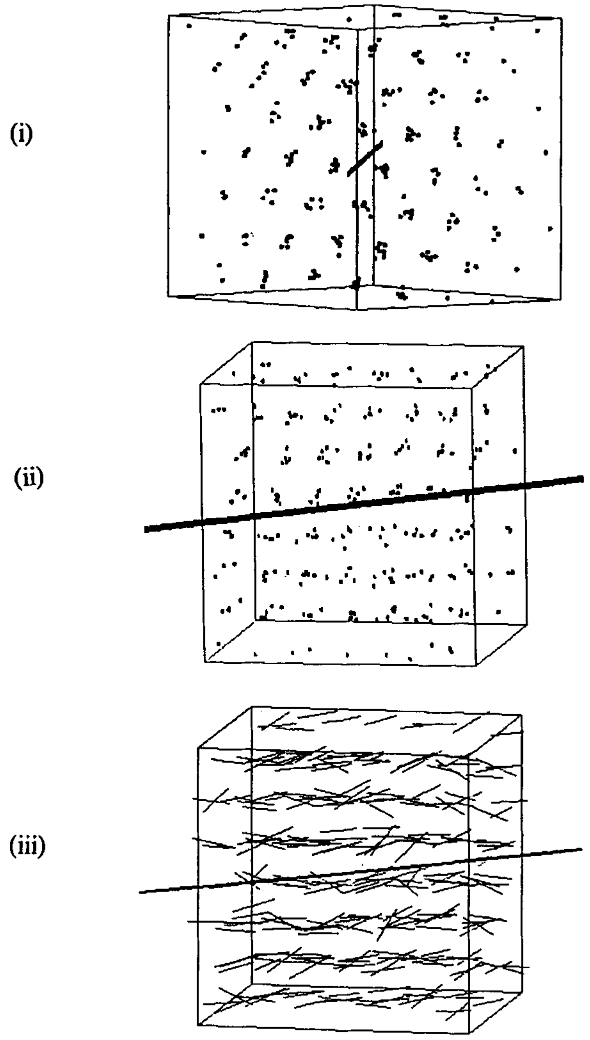


Figure 6b $\langle P_2 \rangle = 0.90$ $\langle T^* \rangle = 0.88$

Figure 6 (*Continued*)

and one perpendicular to the director; showing a structure with hexagonal symmetry, the intercalation of the rows accounting for the periodicity in of $g_{\parallel}(r_{\parallel}^*)$ in Figures 5(c) and (d). Figure 6(b) shows an ordered phase with more clearly delineated columns than rows indicated by the greater order shown in 6(i) than in 6(ii). Together with the larger diffusion coefficient perpendicular to the director at this temperature it appears the particles diffuse first into columns then into rows as temperature is reduced. Stroobants *et al.*

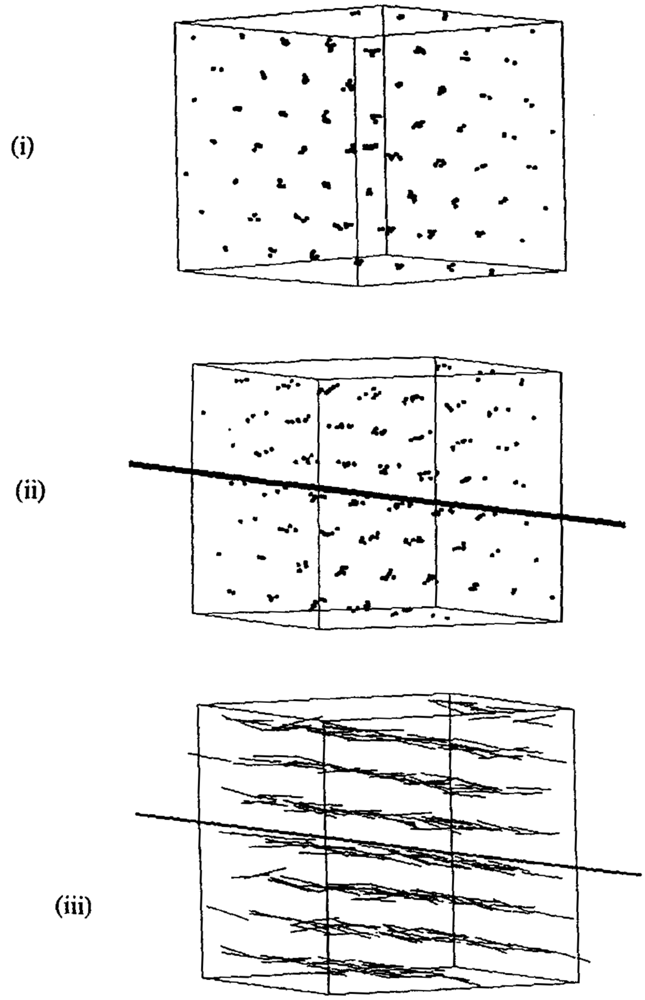


Figure 6c $<P_2> = 0.96$ $<T^*> = 0.34$

Figure 6 (*Continued*)

[17] observed a columnar phase at densities intermediate between the smectic and crystalline phases for a system of hard parallel spherocylinders with length to width ratios of greater than 3.

The second rank orientational correlation function $G_2(r^*)$ exhibited a peak close to a reduced separation of $r^* = 0.7$ in all cases. In the isotropic phase $G_2(r^*)$ quickly decayed to a limiting value close to zero, indicating the absence of any long range order. In the nematic and highly ordered phases $G_2(r^*)$ attains a limiting value of approximately $\langle P_2 \rangle^2$ indicative of the persistence of long range orientational order in this phases.

Performing MD simulations with the HGBLR potential parameterised as a disc we have obtained four distinct phases; isotropic liquid, discotic nematic, a highly ordered phase with some columnar characteristics and a crystal with honeycomb symmetry. The diffusion in a direction parallel and perpendicular to the director is approximately equal in the nematic phase but the diffusion coefficient perpendicular to the director is significantly greater in the columnar-type phase. In the highly ordered phase the plane of the discs is seen to be tilted with respect to the column axis. Columnar structures consisting of columns of tilted molecules have been observed experimentally [18], with a rectangular arrangement of columns.

4 CONCLUSIONS

We have used molecular dynamics simulations to simulate systems of rod-like particles interacting via an anisotropic potential proposed by Luckhurst and Romano and scaled by part of the well depth formalism employed by Gay-Berne. The potential has proved successful in simulating a wide variety of mesophases. We have identified a phase transition from an isotropic liquid to a nematic at a reduced temperature of $\langle T^* \rangle \approx 1.6$. The calamitic nematic phase is stable until the temperature is lowered to $\langle T^* \rangle \approx 0.88$ and subsequently undergoes a transition through a short-lived columnar phase to a smectic phase, before cooling to a crystal with hexagonal symmetry. The reduced cpu time required for the HGBLR potential will allow simulation studies of biaxial models of liquid crystals to be undertaken.

Acknowledgements

We are grateful to G.R. Luckhurst and P.S. Simmonds for a pre-print of their paper. We wish to acknowledge the award of a research studentship to MDD from the Science and Engineering Council (RS Quota Award ref. no. 9031742XO) plus a grant of CPU time on the Manchester Computer Centre VP1200 vector processor (SERC Award ref. GR/H55994).

References

[1] J.A.C. Veerman and D. Frenkel. Phase behaviour of disklike hard-core mesogens. *Phys. Rev. A.*, **45**, 5632–5648 (1992).
[2] H. Azzouz, J.M. Calliol, D. Levesque and J.J. Weiss. Phase behaviour of parallel cut spheres. Monte Carlo and integral equation results. *J. Chem. Phys.*, **96**, 4551–4558 (1992).
[3] D. Frenkel, B.M. Mulder and J.P. Mctague. Phase diagram of hard ellipsoids of revolution. *Mol. Cryst. Liq. Cryst.*, **123**, 119–128 (1985).
[4] D. Frenkel and R. Eppenga. Monte Carlo study of the isotropic-nematic transition in a fluid of thin hard discs. *Phys. Rev. Lets.*, **49**, 1089–1092 (1982).
[5] M.P. Allen. Computer simulation of biaxial liquid crystal. *Liq. Cryst.*, **8**, 499–511 (1990).
[6] M.R. Wilson and M.P. Allen. Computer simulations of mesogenic molecules using realistic atom–atom potentials. *Mol. Cryst. Liq. Cryst.*, **198**, 465–477 (1991).
[7] G.R. Luckhurst, R.A. Stephens and R.W. Phippen. Computer simulation of anisotropic systems. XIX Mesophases formed by the Gay-Berne model mesogen. *Liq. Crystal.*, **8**, 451–464 (1990).

[8] E. de Miguel, L.F. Rull, M.K. Challam and K.E. Gubbins. Liquid crystal phase diagram of the Gay-Berne fluid. *Mol. Phys.*, **74**, 405–424 (1991).

[9] A.P.J. Emerson. Molecular theories and computer simulations of liquid crystals PhD thesis,University of Southampton, UK (1991).

[10] B.J. Berne and P. Pechukas. Gaussian model potentials for molecular interactions. *J. Chem. Phys.*, **56**, 4213–4216 (1972).

[11] J.G. Gay and B.J. Berne. Modification of the overlap potential to mimic a linear site–site potential. *J. Chem. Phys.*, **74**, 3316–3319 (1981).

[12] G.R. Luckhurst and P.S.J. Simmonds. Computer simulation studies of anisotropic systems. XXI Parameterization of the Gay-Berne potential for model mesogens. *Molecular Physics* **80**, 233–252 (1993).

[13] G.R. Luckhurst and S. Romano. Computer simulation studies of anisotropic systems IV. The effect of translational freedom. *Proc. R. Soc. Lond. A.*, **373**, 111–130 (1981).

[14] M.D. De Luca, M.P. Neal and C.M. Care. Molecular dynamics simulations of discotic liquid crystals using a hybrid Gay-Berne Luckhurst-Romano potential. *Liq. Cryst.* **16** (1994), 257–266

[15] C. Zannoni, in The Molecular Physics of L iquid Crystals (ed. Luckhurst G.R. & Gray G.W.), Ch. 9., Academic Press, New York, USA (1979).

[16] D.J. Tildesley, in Molecular Liquids, Dynamics and Interactions, (ed. Barnes A.J., Orville Thomas W.J. and Yarwood J.) NATO ASI series Vol. 135, pp 519–560, Reidel, New York (1984).

[17] A. Stroobants, H.N.W. Lekkerkerker and D. Frenkel. Evidence for one-, two-, and three-dimensional order in a system of hard parallel spherocylinders. *Phys. Rev. A.*, **36**, 2929–2945 (1987).

[18] S. Chandrasekhar. Liquid crystals of disc-like molecules. *Phil. Trans. Roy. Soc., London*, **A309**, 93–103 (1983).