
Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: M. P. Neal & A. J. Parker (1999): Computer Simulations using a Quadrupolar Gay-Berne Model, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 330:1, 565-572

To link to this article: http://dx.doi.org/10.1080/10587259908025635

*Mol. Cryst. Liq. Cryst.*, 1999, Vol. 330, pp. 565-572
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# Computer Simulations using a Quadrupolar Gay-Berne Model

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Systems of Gay-Berne particles with longitudinal and transverse linear quadrupoles are studied by molecular dynamics simulations. Attention is paid to the characterisation of the smectic phase as a function of the quadrupole magnitude and direction. It is found that the longitudinal quadrupole destabilises the formation of the smectic phase whereas the transverse quadrupolar Gay-Beme system demonstrates a greatly extended smectic A region. The smectic phase is found to be sensitive to the magnitude of the longitudinal quadrupole with smectic A, B and C phases observed. A simulated annealing method for characterising a smectic C phase is described.

*Keywords:* smectic C; quadrupole; Gay-Berne; simulated annealing

## 1. INTRODUCTION

Computer simulation offers the opportunity to study the interaction of different asymmetries, such as electric or steric, that characterise the complex molecules which form liquid crystal mesophases. This paper reports briefly on a set of molecular dynamics simulation studies in the *NPT* ensemble which examine a range of electric quadrupolar Gay-Berne models with a view to relating molecular structure to phase behaviour and properties. In these *NPT* studies the dimensions of the simulation box were

allowed to vary. This enabled structures formed within the box to adjust so that they were commensurate with their boundary conditions and were not artefacts of the boundary conditions. The interaction between the molecules was modelled by a uniaxial potential comprising an anisotropic Gay-Berne [1] potential together with a longitudinal or transverse point quadrupole [2, 3], located at the centre of the prolate ellipsoid, and takes the form :

$$U^*(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) = U^*_{GB}(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) + U^*_{QQ}(\hat{\mathbf{v}}_i, \hat{\mathbf{v}}_j, \hat{\mathbf{r}}_{ij}) \tag{1}$$

where

$$U^*_{GB}(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) = 4\varepsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij})\left[\left(\frac{\sigma_0}{r - \sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) + \sigma_0}\right)^{12} - \left(\frac{\sigma_0}{r - \sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) + \sigma_0}\right)^{6}\right] \tag{2}$$

and

$$U^*_{QQ}(\hat{\mathbf{v}}_i, \hat{\mathbf{v}}_j, \hat{\mathbf{r}}_{ij}) = \frac{3Q_i^* Q_j^*}{4r^5}[1 + 2(\hat{\mathbf{v}}_i \cdot \hat{\mathbf{v}}_j)^2 - 5(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{v}}_i)^2 - 5(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{v}}_j)^2 - 20(\hat{\mathbf{v}}_i \cdot \hat{\mathbf{v}}_j)(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{v}}_i)((\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{v}}_j) + 35(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{v}}_i)^2(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{v}}_j)^2] \tag{3}$$

Here $\mathbf{r}_{ij}$ is the vector linking the centres of mass of the two molecules, the unit vectors $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_j$ represent the orientation of the molecules and $\hat{\mathbf{v}}_i$ and $\hat{\mathbf{v}}_j$ represent the orientation of the electric quadrupoles $Q_i^*$ and $Q_j^*$ of molecules $i$ and $j$, where $Q_i^* (= Q_i / (4\pi\varepsilon_0 \epsilon_0 \sigma_0^5)^{1/2})$ is the dimensionless moment and $\epsilon_0$ is the permittivity of free space. The strength $\varepsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij})$ and range $\sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij})$ anisotropy functions of the Gay-Berne potential are defined as in reference [1].

## 2. MOLECULAR SHAPE AND PHASE BEHAVIOUR

The Gay-Berne potential has recently been examined systematically to determine the effects of varying the parameters for the energy anisotropy [4] $\varepsilon_e / \varepsilon_s$ and the shape anisotropy [5] $\sigma_e / \sigma_s$. The exponents were assigned the fixed values $\mu = 2$, $\upsilon = 1$ and those values were used in the studies reported here. A region of stability for the smectic A phase was found [5] for $\sigma_e / \sigma_s >$ 3.4 with $\varepsilon_e / \varepsilon_s$ set equal to 0.2. In the simulations reported here $\sigma_e / \sigma_s$ was assigned the value 4 to allow for the possible occurrence of a smectic A to C transition and the same value of $\varepsilon_e / \varepsilon_s$ was used.

We have studied quadrupolar Gay-Berne systems with transverse and longitudinal point quadrupoles so that $\hat{\mathbf{v}}_i$ is respectively perpendicular and parallel to $\hat{\mathbf{u}}_i$. The Gay-Berne particle plus a longitudinal quadrupole is a uniaxial molecule whereas the addition of a transverse quadrupole forms a biaxial molecule. The shape of the molecules, corresponding to the zero potential energy contour for parallel molecules interacting via the potential, demonstrates two minima in the side-to-side configuration as $Q^*$ is increased [6] for the longitudinal quadrupole. The addition of the transverse quadrupole leads to the formation of three possible transverse configurations, one of which shows two minima with the other two demonstrating an increase in the side-to-side attractive wells [6].

For the longitudinal quadrupolar Gay-Berne system we have studied [6] the smectic phase was shown to be sensitive to the magnitude of $Q^*$ with a

variety of smectic phases formed, including smectic A, smectic C, and smectic B, with the eventual formation of a crystal. The maximum magnitude of the tilt observed was 17.2°, comparable with experimentally observed magnitudes. The results are reported more fully [7] elsewhere with details of the identification of the smectic C region discussed below.

The temperature dependence of the phases was investigated for fixed $Q^*$ of 1.0 and $P^*$ of 2.0. In the longitudinal quadrupolar fluid the smectic phase disappeared for all temperatures studied. In comparison with this an extended smectic A region was observed for a transverse quadrupolar Gay-Berne fluid. The temperature of onset of the smectic region was found to be raised in comparison with the system with no quadrupole. Full details of these simulations will be given in later publications.

In studying these smectic and nematic phases system sizes of 500 particles were typically used with $N = 1000$ employed for state points of particular interest such as the smectic C or tilted B systems. Between 5 and 7 layers were typically formed in a smectic phase in the cubic or cuboid box respectively. It was necessary to use extremely long simulation runs of 4 - 12 X $10^5$ molecular dynamics time steps in order to allow metastable states to equilibrate. Analysis of the orientational structure was undertaken by use of the second rank order parameters [8,9] $Q_{20}^2$ and $Q_{22}^2$ where $Q_{20}^2$ was defined as the largest eigenvalue of the **Q** tensor,

$$Q_{\alpha\beta} = \frac{1}{N}\sum_{i=1}^{N}\frac{3u_i^\alpha u_i^\beta - \delta_{\alpha\beta}}{2} \qquad (4)$$

Here $u_i^\alpha$ is the α-component of the unit vector along the symmetry axis of

the molecule *i*. The director of the system is then the corresponding eigenvector $\hat{\mathbf{e}}$. The orientationally averaged pair distribution function $g(r^*)$ and the longitudinal pair distribution function $g_{\|}(r_{\|}^*)$ were also calculated.

## 3. THE LONGITUDINAL PAIR CORRELATION FUNCTION AND THE SMECTIC A-C TRANSITION

The onset of a smectic phase was identified by the onset of oscillations in the longitudinal pair distribution function $g_{\|}(r_{\|}^*)$ parallel to the system director $\hat{\mathbf{e}}$. However in a tilted system these oscillation will become less sharp, eventually disappearing at a large enough angle of tilt. It is necessary to identify the normal $\hat{\mathbf{n}}$ to the planes and determine the longitudinal pair distribution function $g_{\|}(r_{\|}^*)$ parallel to this normal to confirm the presence of a tilted smectic region. The method chosen for calculation of the normal $\hat{\mathbf{n}}$ to the planes was simulated annealing[10]. It has proved robust in problems with multiple close minima such as this. Here the integrity of the layer must be also be defined in systems such as smectic C which are not perfectly ordered. A smectic layer made of *m* particles was considered where $\{(x_i, y_i, z_i), i = 1,....,m\}$ are the sets of co-ordinates defining the centres of mass of the particles in the layer. The system was divided into *n* layers so that the problem is to find the normal $\hat{\mathbf{n}}$ to the layers. Writing the equation of the plane formed by a smectic layer as $Ax + By + Cz - d = 0$ where *A*, *B* and *C*, are the direction cosines of the normal to plane $\hat{\mathbf{n}}$, the method of

simulated annealing was utilised to minimise the objective function,

$$\chi^2 = \sum_{n\ layers} \sum_{i=1}^{m} (Ax_i + By_i + Cz_i - < d_j >)^2 \qquad (5)$$

for a given step $j$ in the simulation.

The method was applied using the following algorithm:

(i) The particles were separated into planes using the director of the system as a first approximation to the normal to the planes. The projection $r^*_{\|}$ of the position vector $r^*$ of the centre of mass onto the system director $\hat{\mathbf{e}}$ was calculated and the particles were arranged in ascending order. A plane was defined as the set of $m$ particles, $k = 1,....,m$, for which:

$$\left\{ \begin{matrix} m \geq 10 \\ r_{\|}^{k} - r_{\|}^{k-1} \leq 0.1 \end{matrix} \right\}$$

The appropriate value to define separation between layers, $r_{\|}^{k} - r_{\|}^{k-1}$, was determined by experimentation until the number of layers calculated matched those seen in the graphics. Using this method some particles were not assigned to layers although the total proportion was 5% or less and the integrity of the layers was maintained.

(ii) The direction cosines, $A$, $B$ and $C$, of the normal to plane $\hat{\mathbf{n}}$ were randomly varied for a number of trials, 50,000 in this case. The random change in the direction cosines was accepted for a given trial $l$ with a probability $p = \exp[-(\chi_l^2 - \chi_{l-1}^2)/T^*]$ except where $\chi_l^2 - \chi_{l-1}^2 < 0$ when it was always accepted.

(iii) The normal determined by (ii) was used to divide the particles into layers in the next step in the simulation.

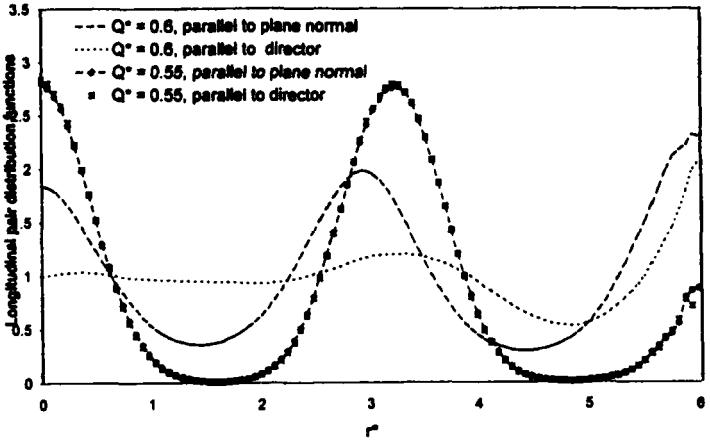


FIGURE 1 Longitudinal pair distribution functions resolved both parallel to the director and parallel to the plane normal for $Q^* = 0.6$ and $Q^* = 0.55$.

(iv) An appropriate annealing schedule was found by experimentation so that a normal to the planes was determined which could not be significantly improved upon. The annealing schedule used was a linear scale dependent on the step number so that $T = T^*/(\text{step number} / 30)$.

(v) The angle of tilt of the production run was calculated as $\alpha = < \cos^{-1} (\hat{\mathbf{e}}.\hat{\mathbf{n}}) >$ for the production run.

Figure 1 shows the results for the longitudinal quadrupolar Gay-Berne fluid with $Q^* = 0.6$ and $Q^* = 0.55$ at $T^* = 1.75$ and $P^* = 2.0$. The system shows no tilt for $Q^* = 0.55$ since the longitudinal pair distribution function $g_{\parallel}(r_{\parallel}^*)$ parallel to the director and the plane normal are identical. For $Q^* = 0.6$ the system is in a tilted phase with a large tilt angle calculated to be 17.2°. The longitudinal pair distribution function parallel to the plane

normal is sharply oscillating and demonstrates a closer layer spacing than at $Q^* = 0.55$, indicating the presence of the tilted phase. The longitudinal pair distribution function parallel to the director is almost flat in comparison indicating a large angle of tilt, in this case.

The method produced similar results for systems of $N = 500$ and $N = 1000$ particles and differentiated between layered systems with and without a tilt.

## ACKNOWLEDGEMENTS

We are grateful for the support of the Engineering and Physical Sciences Research Council awards, GR/l04948 and GR/K4224, and that of the Defence and Evaluation Research Agency, Malvern

## *References*

[1] J.G. Gay, and B.J. Berne, *J. Chem. Phys.*, **74**, 3316 (1981).
[2] A.D. Buckingham. *Adv. Chem. Phys.*, **12**, 107 (1978).
[3] S.L. Price, A.J. Stone, and A. Alderton, *Mol. Phys*, **52**, 987 (1984).
[4] E. De Miguel, E. Martin Del Rio, J.T. Brown, and M.P. Allen, *J. Chem. Phys.*, **105**, 4234 (1996).
[5] J.T Brown, M.P. Allen, E. Martin Del Rio, and E. de Miguel, *Phys. Rev. E*, **57**, 6685 (1998).
[6] M.P. Neal, and A.J. Parker, in preparation.
[7] M.P. Neal and A.J. Parker, *Chem. Phys. Lett.*, **294**, 277 (1998).
[8] C. Zannoni, in *The Molecular Physics of Liquid Crystals*, Edited by G.R. Luckhurst and G.W. Gray, (New York Academic Press, 1979) Chapter 3.
[9] M.P. Allen, *Liq. Cryst.*, **8**, 499 (1990).
[10] W.H. Press, S.A. Teukolsky, W.T. Vetterling and B.P. Flannery, Numerical recipes in Fortran, 2nd Ed., (Cambridge University press, 1986).