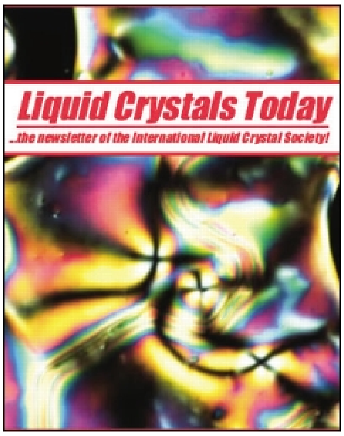

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What creates liquid crystal phases?

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What creates liquid crystal phases?

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Introduction

Molecular anisotropy is clearly responsible for the long range orientational order of thermotropic liquid crystals, be they formed from rod- or disc-like molecules. However, for many years it was not clear what were the roles played by anisotropic repulsive and attractive forces in determining liquid crystal behaviour [1]. Thus the success of the Maier-Saupe theory of nematics seemed to suggest that it is the attractive forces which are dominant, but less successful hard particle theories have also contributed to our understanding of liquid crystals. This apparent contradiction and resulting controversy as to the driving force for liquid crystal formation must stem in part from the uncertain reliability of the statistical mechanical approximations employed in the various theories. Such uncertainty can be removed by the use of computer simulation techniques. As an important step in this approach Frenkel [2] and others have investigated the phase behaviour of hard particles. Of particular interest is the study of hard ellipsoids which revealed that for both rods and discs the system will exhibit nematic behaviour provided the shape anisotropy is sufficiently large. The inability of hard ellipsoids to form smectic or columnar phases is of special importance, but it should be noted that systems of other hard objects have been found to form such translationally ordered phases [2]. At Southampton our work has focused on ellipsoidal particles which may prove to be a realistic shape for mesogenic molecules, and the incorporation of anisotropic forces in the potential is relatively straightforward. We have probed the addition of these forces because they should result in the creation of thermally driven transitions as well as the formation of smectic and columnar phases in keeping with real systems.

The Gay-Berne Potential

Berne and his colleagues have been concerned with the development of single site or Corner potentials with which to represent the interaction of cylindrically symmetric particles. Building on earlier work involving gaussian overlap models Gay and Berne have proposed a shifted 12-6 potential which seems well suited for the investigation of anisotropic attractive and repulsive interactions in liquid crystal formation [3]. The functional form of the potential is somewhat forbidding and so instead of giving this we show in **Figure 1** the distance dependence of the potential for various orientations of the particles with respect to each other and to the intermolecular vector. The variation of the potential with orientation clearly reveals the anisotropy in the repulsive forces (via the distance of closest approach) and the attractive forces (via the well depth). The particles have an ellipsoidal shape although it should be remembered that the ellipsoidal core is not totally hard but has a softer R^{-12} dependence. The large well depth when the molecules are side-by-side as opposed to end-to-end should be noted. It is this anisotropy in the attractive forces which leads to translational ordering for both rods and discs.

Rod-like Molecules

We have shown that the Gay-Berne potential for rod-like particles is capable of forming nematic, smectic A and smectic B phases [4]. However the potential contains four adjustable parameters whose values had been selected by Gay and Berne to model the interaction between two molecules composed of just four Lennard-Jones centres. Such a structure is clearly not typical of mesogenic molecules, which often contain several aromatic rings e.g. p-terphenyl. We have therefore calculated the atom-atom potential for two molecules of p-terphenyl and mapped it onto the Gay-Berne potential [5]. Our parameters differ from those proposed by Gay and Berne, especially for the anisotropy in the well depth which is considerably enhanced. To see the influence on the phase behaviour we used the new parameters in a simulation of the Gay-Berne mesogen, and found the system exhibits both nematic and smectic A phases. The relatively weak translational order of the smectic is revealed by the density wave along the director shown in **Figure 2**. This may be far smaller than is often pictured for real systems. We have also used this model to investigate the role of the anisotropy in the well depth to stabilise the smectic A phase. We have considered ratios for the well depth for the side-by-side to the end-to-end configurations from about 40 to 4, and still find that the smectic A phase is formed, but as soon as the ratio is reduced below 4 the smectic A phase vanishes.

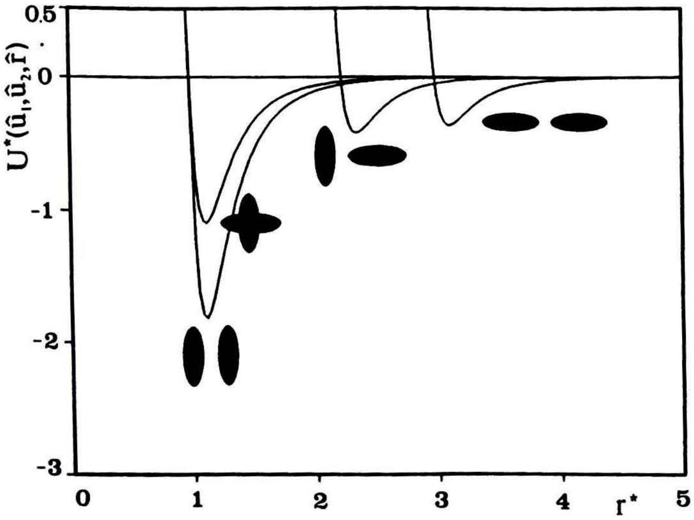

Figure 1. *The distance dependence of the Gay-Berne potential for particular orientations of the molecules with respect to each other and the intermolecular vector.*

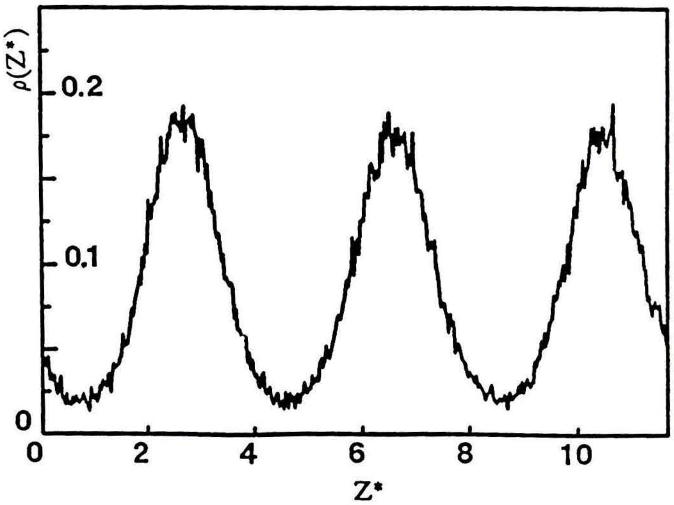

Figure 2. *The dependence of the number density along the director in the smectic A phase formed by the Gay-Berne mesogen.*

The molecular dynamics simulations of the Gay-Berne model potential have been performed at constant volume. This constraint on the volume of the system may have important implications for the structure of the phases, especially for those with high order. This situation obtains because the periodic nature of, say, the smectic B phase within the simulation box may not be commensurate with the periodicity of the images that surround it. In the extreme case the incompatibility of the two could result in a distortion of the layer spacing [4]. For example the layer spacing in the smectic B phase is 0.87 times the molecular length , which represents significant interdigitation; this may have resulted from extreme constraints on the structure. One way to overcome such problems is to perform the simulations at constant pressure; this allows the size and shape of the box to change so that the periodic images are indeed commensurate with the particles in the simulation box. We have performed constant pressure Monte Carlo simulations at temperatures and pressures for which the smectic B phase is stable [6]. Here the dimensions of the box were changed independently during the Monte Carlo cycle although the box was kept orthogonal. We found that the layer spacing was essentially the same as that found in the constant volume studies, so the periodic images do not appear to influence this important feature of the phase structure.

We were also able to investigate the molecular organisation within the layers and both the in-plane radial distribution function as well as the instantaneous configuration of the centres of mass confirm the hexagonal arrangement of the particles but with incomplete order, see **Figure 3**. In contrast, the projection of all the centres of mass onto a common plane is devoid of any structure, and suggests that the system does indeed form a smectic B rather than crystal B phase. Of particular significance for the structure of this smectic B is that the smectic layers exhibit a pronounced ripple as can be seen for the layers shown in **Figure 4**. We have no simple explanation for this ripple structure although it is certainly known to exist in real liquid crystals.

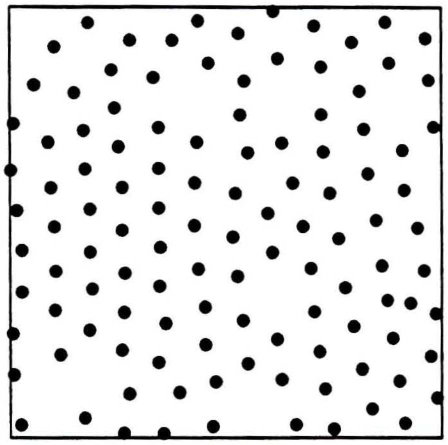

***Figure 3** The distribution of the molecular centres of mass within a single layer of the Gay-Berne smectic B phase obtained at constant pressure.*

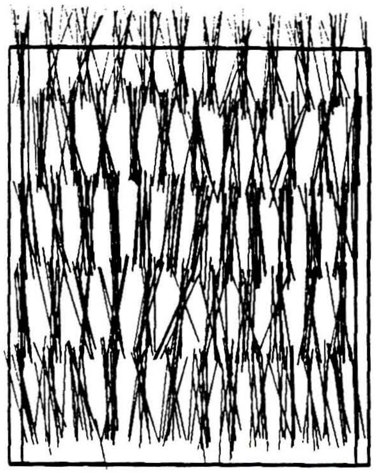

***Figure 4.** The interdigitated structure of the smectic B phase of the Gay Berne mesogen at constant pressure, showing the ripple in the layers.*

Disc-like Molecules

In 1977 Chandrasekhar and his colleagues reported that disc-like molecules are capable of forming liquid crystal phases. Since this seminal observation, many such materials have been synthesised, and a rich polymorphism of discotic systems has been revealed. In addition to the nematic phase, discotics also exhibit columnar phases in which the columns can be arranged both hexagonally and rectangularly [7]. Our understanding of discotic phases is less advanced than for those formed from rod-like molecules and so we have initiated a computer simulation study of the phases formed by Gay-Berne discs [8]. The parameters in the potential were chosen to reflect those expected of disc-like materials, but our aim was to understand the roles of anisotropic attractive and repulsive forces in a whole class of materials. A discotic nematic phase was certainly observed; indeed the nematic-isotropic transition was found to be first order with a high value of the nematic orientational order parameter. This behaviour contrasts with that for rod-like Gay-Berne particles where the entropy of transition is vanishingly small. Such differences may result from the relatively low energy of interaction for the T-configuration which then leads to higher orientational order in the nematic phase [4].

Below the nematic phase there is another first order transition to a columnar phase and the molecular organisation in this is shown in **Figure 5**, where the translational order within the columns is high. The structure reveals that there is a strong correlation between discs in neighbouring columns, with molecules in one column fitting into the grooves of a neighbour. These grooves result from the elliptical cross-section of the particles. The extent of this interdigitation of molecules in neighbouring columns also means that it is not possible to obtain hexagonal packing of the columns; instead they have a four-fold coordination. Such a structure is quite unusual but has been observed for a lyotropic columnar mesophase. We suppose, therefore, that in the system we have studied, the anisotropic attractive forces lead to self assembly into columns; these columns then self-organise to give the square coordination. The structure of the phase seems to result from the repulsive interactions between the columns.

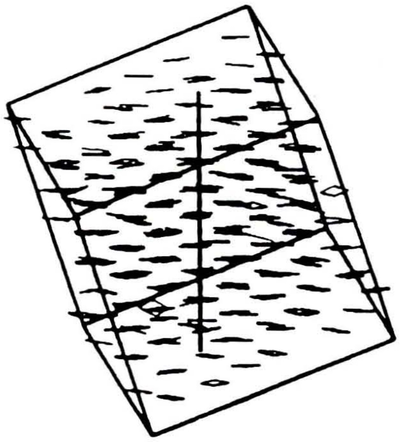

***Figure 5.** Molecular organisation in the columnar phase formed by the Gay-Berne discs.*

Flexible Gay-Berne Mesogens

One of the features of virtually all mesogenic molecules is some degree of non-rigidity; this is often achieved by the inclusion of alkyl chains within the structure [1]. This feature is usually included in the material to lower its melting point, but flexibility can also have a major influence on the liquid crystal properties themselves. This is especially true when a flexible spacer links two anisometric groups [9]. The simplest example of such a link is a dimethylene group, and materials with this flexible spacer find wide application in electrooptic display devices. We have therefore extended the Gay-Berne model to include such an ethane link between two rod-like particles [10].

This system is found to exhibit both nematic and smectic A phases. Of particular interest in these studies is the ability to monitor the change in the conformational distribution as the orientational order in the system varies. This synergy between conformational and orientational order has often been invoked to understand the behaviour of real mesogens. However, the experiments never give one distribution separate from the other, and so it is necessary to invoke a model in order to achieve this *separation*. The beauty of the simulation experiments is that we can determine the conformational distribution function uniquely. The results for this are shown in **Figure 6**, where it is clearly apparent that the probability of the *trans* conformer increases dramatically with the extent of the orientational order. Indeed within the smectic A phase at T* of 0.9 the dimer exists almost entirely in the *trans* conformation. This behaviour is in keeping with the model analysis as well as the fact that the *gauche* conformer is more bent than the *trans*.

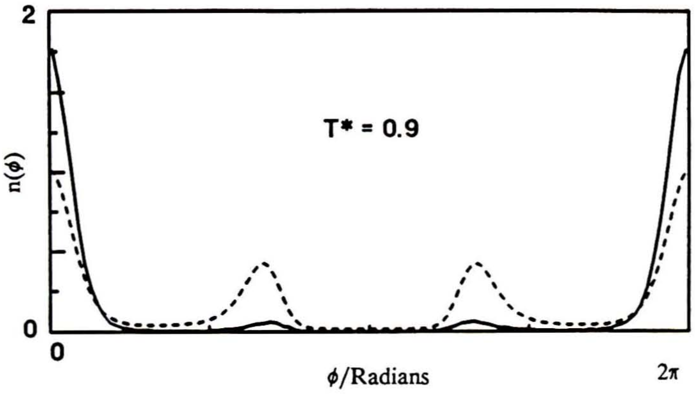

Figure 6. *The conformational distribution for the flexible Gay-Berne dimer in the smectic A phase. The dashed line shows the distribution calculated in the absence of orientational ordering.*

The smectic A phase exhibited by this flexible dimer is found to have an unusual structure. Thus the layer spacing is observed to be just half the molecular length. In other words the structure is intercalated with no correlation in the structure of the ethane link between the mesogenic groups along the director. The molecular organisation in this intercalated smectic A phase is shown in **Figure 7** and resembles that proposed for non-symmetric liquid dimers in which the flexible spacer joins two different mesogenic groups [11].

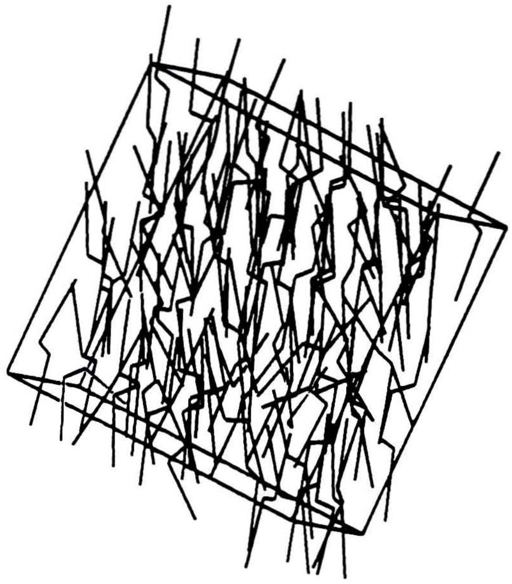

Figure 7. *Molecular organisation within the intercalated smectic A phase formed by the flexible Gay-Berne dimer.*

The model we have developed also allows us to investigate the importance of the torsional potential in influencing liquid crystal behaviour. Thus, as the energy difference between the *trans* and *gauche* conformers grows, so the material should become more mesogenic. Conversely as this difference decreases so the tendency to form a liquid crystal is reduced. This is indeed what we observe, and in the limit of free rotation about the ethane bond both the nematic and smectic A phases vanish completely, at least for temperatures at which the smectic A phase was stable when the torsional potential was included. This very strong dependence of liquid crystallinity on the torsional potential is surprising and may well have implications for the design of mesogenic molecules. ■

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