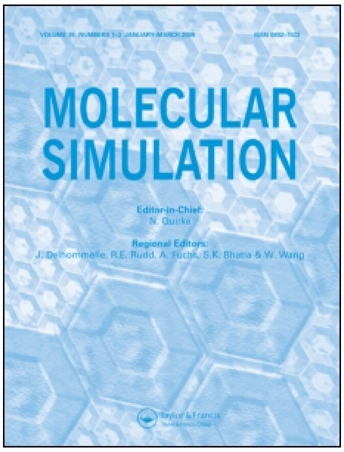

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Molecular Graphics and the Computer Simulation of Liquid Crystals

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MOLECULAR GRAPHICS AND THE COMPUTER SIMULATION OF LIQUID CRYSTALS

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Molecular dynamics simulations of systems of hard ellipsoids of revolution have been carried out. Using configurations generated in these simulations, it is shown how molecular graphics can be used to examine the structure within the nematic liquid crystal phase, and close to the isotropic-nematic phase transition. A way of visualizing the degree of orientational order in these systems is presented.

KEY WORDS: Molecular graphics, Liquid crystals, structure, nematic phase, orientational order

1 INTRODUCTION

In collaboration with Dr. D. Frenkel (Amsterdam) I have been conducting molecular dynamics simulations of molecules represented by hard ellipsoids of revolution. For suitable values of length a (of the symmetry axis) to width b, these systems have been shown to have a thermodynamically stable nematic liquid crystal phase (N) in between the isotropic liquid (I) and the solid [1]. We have published details of reorientational time correlation functions for this system, and have observed critical slowing down of collective rotation near the I–N transition [2]. We have also carried out the first calculation of Frank elastic constants *via* simulation [3]. These quantities are of great interest, for example, in device technology. The general conclusion of this type of work [4] is that, just as in the case of isotropic liquids, hard particles are physically reasonable reference systems for more realistic models of liquid crystals. Few other models known to exhibit liquid crystalline phases exist [5].

The purpose of the present work is to show how molecular graphics can assist in the understanding of structure and dynamics in liquid crystal phases.

2 SIMULATIONS

The technical details of our molecular dynamics simulation algorithm have been reported informally [6] and will appear in the primary literature elsewhere [7]. Suffice it to say here that we solve the proper hard-body equations of motion, with free flight between elastic collisions which obey the usual dynamical conservation laws. In the work reported here we used prolate ellipsoids of axial ratio $a/b = 3$ and a system size of $N = 144$ molecules, enclosed in a cuboidal box with periodic boundary conditions applied. We have also conducted simulations on larger systems (up to $N = 1000$) and employed a truncated octahedral box, in an effort to investigate system-size effects. For the smaller systems studied here, the program generates roughly 10^6 collisions per cpu hour on a CYBER-205.

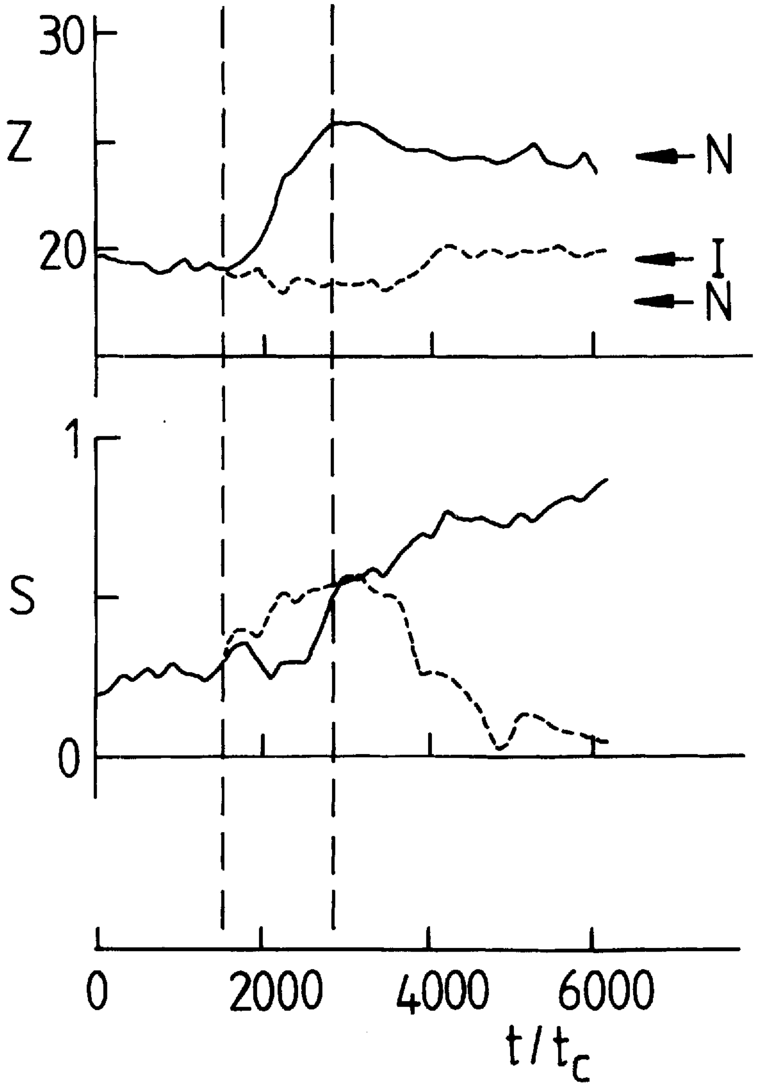

Figure 1 We plot the equation of state $Z = PV/Nk_BT - 1$ and the order parameter S as functions of time, for a run at $\varrho/\varrho_{cp} = 0.70$ (dashed line) and for a run being compressed to $\varrho/\varrho_{cp} = 0.75$ (solid line). The period of compression is delimited by vertical dashed lines. The horizontal arrows indicate values of Z obtained by Monte Carlo simulation [1] on both branches of the equation of state at the lower density, and on the nematic branch (the isotropic liquid being unstable) at the higher density.

Our runs are rather long: after equilibration, a system in or near the nematic phase region is studied for about 50000–75000 t_c where t_c is the mean time between collisions per particle. For these systems, this means that a typical production run is 5×10^6 collisions.

In this work, we concentrate on two densities, $\varrho/\varrho_{cp} = 0.70, 0.75$, where ϱ_{cp} is the close-packed density. $\varrho/\varrho_{cp} = 0.75$ is well within the nematic region, while $\varrho/\varrho_{cp} = 0.70$ is close to the I–N transition: in fact, based on a determination of free energies [1] it should be just on the nematic side of the coexistence range.

Moving from one state point to another is achieved by steady uniform expansion or compression. It is of particular interest to observe this close to the I–N transition. The $\varrho/\varrho_{cp} = 0.70$ density was obtained by compressing the isotropic liquid. The system was allowed to equilibrate for several thousand t_c, and both the non-ideal contribution to the equation of state, $Z = PV/Nk_BT - 1$, and the nematic order parameter S (see later) were monitored. Large, slow fluctuations between an essentially isotropic phase and a nematic one were observed (see Figure 1). This behaviour continued throughout the production run of length 50000 t_c. At a certain point in this simulation, further compression to $\varrho/\varrho_{cp} = 0.75$ was undertaken. The results are compared with the unperturbed run in Figure 1. As can be seen, the equation of state responded quite quickly to the change in density. The order parameter was much more slow to respond, but eventually settled down to a value $S \approx 0.7$ characteristic of the nematic phase. It should be emphasized that no external fields were applied to induce ordering. It is also worth noting that, in this case, the director became aligned with one of the simulation box axes, indicating that periodic boundaries play some role in the pre-transitional orientational fluctuations. However, we have also observed cases in which this alignment with the box does not occur, indicating that perhaps this effect is not too great. The degree of ordering remained stable (within about 20%) and the director orientation remained almost fixed, throughout the production run of 75000 t_c which followed.

3 MOLECULAR GRAPHICS AND ORIENTATIONAL ORDER

Figures 2 and 3 show snapshots of configurations generated in the course of these simulations. They were produced on a 32 × 32 mini-DAP with direct video output, by John Quinn; his molecular graphics program was originally based on the work of Hubbard and Fincham [8].

It may be of some interest to describe how the ellipsoids were represented. The

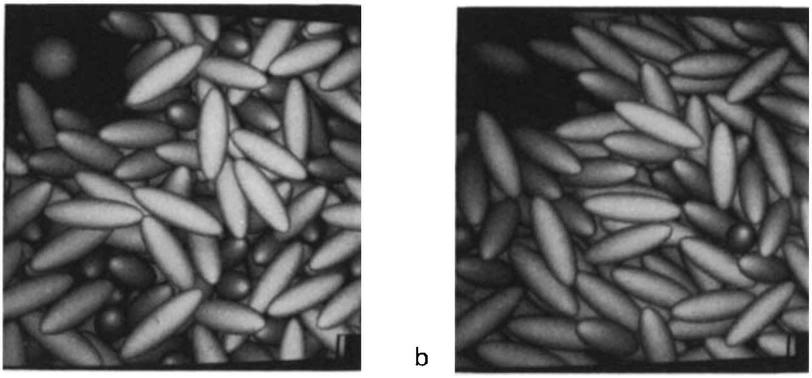

Figure 2 We show two snapshots of configurations at $\varrho/\varrho_{cp} = 0.70$. The ordering spheroid is depicted in the corner. (See colour plate II.)

surface of an ellipsoid with its centre at position $\mathbf{r}_c$, and having a unit vector $\mathbf{e}$ pointing along the symmetry axis, is defined by the equation

$$(\mathbf{r}-\mathbf{r}_c)\cdot \mathbf{A}^{-1}\cdot(\mathbf{r}-\mathbf{r}_c) = 1. \tag{1}$$

Here $\mathbf{r} = (x, y, z)$ and $\mathbf{A}^{-1}$ is the inverse of the dyadic matrix

$$\mathbf{A} = b^2\mathbf{1} + (a^2-b^2)\mathbf{ee}. \tag{2}$$

Suppose that we are viewing along the z-axis; then each pixel on the raster screen corresponds to a pair of values (x, y). To determine the corresponding z coordinate we simply have to solve the above quadratic equation. On the mini-DAP, 1024 pixels are treated in this way in parallel. The 512 × 512 screen is treated as a succession of 32 × 32 squares. The surface of each ellipsoid is logically added into the picture in a straightforward way. Each point on the surface is shaded by an amount depending upon the z-component of the surface normal, and additional shading is used to indicate depth in the field of view.

The DAP is well-suited to many of the logical and pixel-based operations involved in generating these pictures. Each frame took ≈ 10 seconds to draw. The program runs somewhat more slowly for a configuration of ellipsoids than for, say, atomic spheres, since the latter require fewer floating-point operations. Nonetheless, the operation has proved sufficiently fast to allow the making of a movie film, and Figures 2 and 3 are still shots taken during the filming.

The pictures also show a visual way of representing the degree, and direction, of orientational ordering in such systems. The symmetric, second-rank, traceless orientation tensor is defined

$$Q_{\alpha\beta} = \frac{1}{N}\left(\sum_{i=1}^{N}\frac{3}{2}e_{i\alpha}e_{i\beta} - \frac{1}{2}\delta_{\alpha\beta}\right) \tag{3}$$

with $\alpha, \beta = x, y, z$ and $e_{i\alpha}$, $e_{i\beta}$ being components of the unit vector $\mathbf{e}_i$ along the axis of molecule i. $\delta_{\alpha\beta}$ is the Kronecker delta. In a well-ordered, uniaxial, nematic, the three eigenvalues of Q, namely λ_+, λ_0, λ_- in decreasing order, are all related to the usual

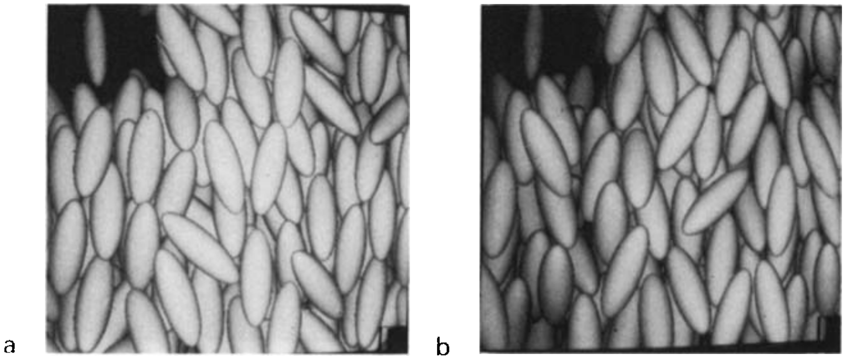

Figure 3 We show two snapshots of configurations at $\varrho/\varrho_{cp} = 0.75$. The ordering spheroid is depicted in the corner. (See colour plate III.)

'scalar' order parameter S which takes values in the range $0 \leqslant S \leqslant 1$:

$$\begin{aligned} \lambda_+ &\approx S \\ \lambda_0 &\approx -\frac{1}{2}S \\ \lambda_- &\approx -\frac{1}{2}S \end{aligned} \tag{4}$$

Arguments have been made in favour of computing S from λ_0 rather than from λ_+ [9] and we use the former definition in Figure 1. The eigenvector corresponding to λ_+ is associated with the director, although the ordering should not really be thought of as a vector quantity: it is second-rank in nature [10]. Here, we use the ordering tensor to define a spheroidal body which correctly represents the degree and direction of ordering. Firstly, it is most convenient not to make the tensor traceless, but instead to define

$$Q'_{\alpha\beta} = \frac{1}{N}\left(\sum_{i=1}^{N}\frac{3}{2}e_{i\alpha}e_{i\beta}\right). \tag{5}$$

The equation

$$\mathbf{r}\cdot\mathbf{Q}'^{-1}\cdot\mathbf{r} = 1 \tag{6}$$

now defines the surface of a general spheroid, the principal axes of which are determined, in magnitude, by the eigenvalues and, in direction, by the eigenvectors of $\mathbf{Q}'$. The spheroid may be represented in molecular graphics just as easily as are the ellipsoidal molecules: again a quadratic equation is to be solved for each pixel. It is shown in the corner of Figures 2 and 3. The shape and orientation of the spheroid tell us about the type and degree of ordering in the liquid. For an isotropic liquid, the spheroid becomes near-spherical in shape. For a very strongly-ordered nematic phase, it becomes long and thin, with the long axis aligned with the director.

In Figure 2, we see two configurations taken from the run at $\varrho/\varrho_{cp} = 0.70$: one is nearly isotropic, and the other corresponds to nematic ordering with $S \approx 0.5$. In the movie, it is easy to see the fluctuations from one state to the other reflected in this changing shape. In Figure 3, the spheroid is rather more elongated, corresponding to the higher value of S, and it does not change greatly in appearance as the simulation proceeds: the movie reveals only a slight 'wobble'. By contrast, the individual molecules are seen to be in relatively rapid diffusive motion at both state points.

4 CONCLUSIONS

The ability to produce molecular graphics pictures of the kind shown here, especially at a rate which enables a movie to be made, is extremely useful in visualizing the structure, and the evolution of collective dynamics, in liquid crystals. This approach will become widespread as the necessary computer hardware becomes available to individual research groups at reasonable cost.

Acknowledgements

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