

Report on CCP5-Sponsored Meeting of Liquid Crystal Simulators
Sheffield Hallam University
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This meeting of a loose consortium of liquid crystal / complex fluid simulators was held at Sheffield Hallam University, and attracted representatives from Bristol (Mike Allen), Derby (Maureen Neal), Lancaster (John Wheeler), Manchester (Andy Masters), Sheffield (George Jackson and group), Sheffield Hallam (Chris Care and group; Doug Cleaver) and Southampton (Andy Emerson). As on previous occasions, the main purpose of the meeting was to disseminate recent results and discuss the work in progress in the various groups.

Following announcements regarding the conferences to be held at Manchester in July and Sheffield in September, the meeting got underway with a description from Mike Allen of the history and progress of the T3D project. He explained that SERC had, at short notice, sought proposals from the CCP's to cover the first year of the machine's use. The CCP5 steering committee had decided that its main bid should be based on the DL_POLY routines, with an emphasis on the modelling of biomolecular systems. A second bid based on liquid crystals / complex fluids was also deemed suitable, however, and so Mike had coordinated a joint proposal put forward by the consortium as a whole. This bid had detailed five systems suitable for simulation on this scale, namely: a chiral smectic; a disclination defect (in a large system); the biaxial nematic phase; a polymer liquid crystal; and various surfactant phases. A brief discussion followed regarding the options available for any future bids for this facility.

Following this, there were four short presentations of work based on lattice model systems. Chris Care described a microcanonical MC technique which enables efficient calculation of the density of states through the measurement of a transition matrix. This technique was shown to compare favourably with the multiple histogram techniques when applied to the 2-d Ising model. More extensive comparisons of the two methods were being planned, involving larger system sizes and models with continuous energy spectra. Leila Ayat (SHU) then described how she had applied Chris' microcanonical technique to the Lebwohl-Lasher liquid crystal model. She showed energy distribution functions, specific heat curves and the roots of the partition function for different system sizes. The transition temperatures given by these three indicators all extrapolated to a common value in the infinite system limit. The results were in excellent agreement with those of previous studies of the model, and appeared to indicate the first order nature of the transition at smaller system sizes than did other techniques.

Next, Doug Cleaver described an initial study he had been performing on a variant of the Lebwohl-Lasher model which incorporates random anisotropy. This model is thought to simulate

the behaviour of a liquid crystal confined in a randomly interconnected porous network (systems which have generated recent experimental interest). The simulation results showed that the first order nematic-isotropic transition is suppressed by the anisotropy, the specific heat peak being broadened and shifted to lower temperatures. Also, the orientational correlation function was shown to take a qualitatively different form from that of the Lebwohl-Lasher model: it decayed algebraically rather than exponentially, indicating that there is no long ranged order (i.e. no nematic phase) in the infinite system limit. Finally, in this section, Jean Desplat (SHU) described the extensions he is making to a lattice model of surfactant behaviour. This model, originally developed by Chris Care and David Brindle, uses short, fully flexible chain molecules composed of ‘head’ and ‘tail’ sites arranged on a simple cubic lattice and moved using reptation. With the 3-d version of this model, micellar, cylindrical, bicontinuous and lamellar phases have been observed. The planned extensions will involve increasing the coordination number of the underlying lattice, incorporating a term into the Hamiltonian to take account of chain bending energies and implementing the configurational bias technique for performing moves. The model will then be used to investigate the properties of non-ionic surfactants and mixtures thereof.

The afternoon session was dedicated to discussion of off-lattice simulations. First to speak was Maureen Neal. She described work being performed as part of a collaboration between Derby, SHU and Hull, in which a simple model is being sought for triphenylene. This molecule, whilst not being a mesogen itself, does form the core of a wide range of discotic and calamitic liquid crystals. The development of this model is seen, therefore, as a step towards the simulation of more ambitious and complicated systems. The model was developed in a two step process. First, the actual molecule was compared with a model involving 30 Lennard-Jones sites and 3 quadrupoles. A 4-site arrangement of hybrid Gay-Berne Luckhurst-Romano (HGBLR) potentials was then mapped onto this intermediate model through comparison of the interaction between pairs of molecules at seven different relative orientations. MD simulations of 256 and 108 of these 4-site molecules have shown no indication of any thermodynamic singularities. Diffusion measurements suggest that there may be a sharp change in the dynamical behaviour, although the radial distribution function is virtually identical on both sides of this change.

Dominic De Luca (SHU) described how a similar approach had been used to investigate the molecule p-terphenyl by taking it to consist of two coplanar end rings with a central ring rotated by 39° about the para axis. In this case, the intermediate model used was one of 32 Lennard-Jones sites and the final one was a 3-site HGBLR arrangement. Simulations were performed with this three site model both with and without the 39° twist. In both cases, an ordered low temperature phase was formed with a director *perpendicular* to the molecular long axes. This indicated that the dominant ordering field was that between the constituent rings rather than that due to the molecular shape anisotropy. When quadrupoles were incorporated into the intermediate model, the intermolecular potential was found to alter considerably. Incorporation of quadrupoles into the three site model was not a viable option, so instead a modification was made to the well depth ratio of the three HGBLR sites. MD runs on this system have indicated no ordered phases to date.

Mike Allen discussed three different pieces of work being performed in his group. The first of these concerned measurements of the Frank elastic constants of the Gay-Berne nematogen. This is being attempted in his group using a constrained director MD technique, and at Southampton/SHU using a similar (but different) MC approach. Both groups are attempting to extract the elastic constants from measurements of fluctuations in the ordering matrix elements. A third measurement of one of the elastic constants by use of twisted boundary conditions is also being performed at Bristol. Mike also reported the findings of his group's shear viscosity measurements in systems of anisotropic hard bodies in the isotropic phase. Previous measurements of this quantity had been found to disagree with Glenn Evans' kinetic theory. These more recent simulations, using extremely long run times, have vindicated the theoretical predictions however; the failure of previous simulations appears to be explained by the long relaxation times required for the orientations of the elongated molecules to equilibrate. Finally, Mike spoke briefly about some even longer runs currently being performed on rather small systems ($\simeq 100$ particles) in order to investigate the free energy associated with the orientation of the director with respect to the simulation box. Analysis of the measured distribution functions is planned for the near future.

Next came two contributions describing the simulation of biaxial molecules using a kinked dimer to represent each molecule. The first of these came from Andy Emerson, who described an initial study of the behaviour of Gay-Berne dimers. His MC simulations have used two 3:1 rod-like monomers per molecule, the monomers being joined end to end at an angle α . Thus far, using angles $\alpha = 109^\circ$ and 150° , no evidence of nematic ordering has been seen for these systems. Andy Masters described a similar project he has been performing in collaboration with Mike Allen using dimers of hard spherocylinders. In most of this work, monomers with $l/d = 2$ were used, the simulations been executed using constant pressure MC. The results indicated stable nematic phases for $\alpha \geq 150^\circ$ but no ordering for $\alpha = 120^\circ$. Once in the nematic phase, little variation was seen in the equation of state with variation of α , the results being in reasonable agreement with Frenkel's for $l/d = 5$ spherocylinders. These systems proved very prone to log-jams, however, and no spontaneous isotropic to nematic transitions were observed. Plans to study this model using theory were also described. In the isotropic phase it is hoped that Wertheim theory can be extended by relating the dimer fluid to the equivalent monomer fluid. Attempts to measure the required distribution function by simulation have proved unsuccessful, however.

The final contribution to the meeting came from George Jackson, and concerned both theory and simulation of hard body systems. The first project he described was based on simulations of linear chains of m tangential hard spheres using the reptation algorithm. This is a long running project which has progressed from $m = 2$ up to (most recently) $m = 7$. For $3 \leq m \leq 6$, these systems have been found to progress from solid to liquid with no intermediate phases (apart from glasses in which the molecules get trapped by the cusps between the constituent spheres). For $m = 7$, a stable nematic *has* now been observed. Comparison of these results with the 'easy' nematic phase formation shown by Mark Wilson's MD on semi-flexible chains with $m = 7$, leads to the conclusion that flexibility aids orientational ordering. A further project described by George

is based on large system (1000+) simulations of hard spherocylinders, the aim being to examine the earlier results of Frenkel. For $l/d = 3$, these new results have shown that no smectic phase is formed (Frenkel found one but doubted its validity). For $l/d = 5$, the new results have confirmed the phases seen by Frenkel although slight shifts are apparent.

The first piece of theoretical work described by George concerned a MC annealing technique which can be used to minimise the free energy with respect to the singlet orientational distribution function. Good agreement has been found between the results of this theory and simulations. A specific model which is being studied using theory is that of hard spherocylinders with 'sticky ends'. Here, results predict orientational order even at small l/d as the molecules dimerise to effectively double in length. Reentrant phenomena were predicted to result from this dimerisation. Future work will focus on systems of dipolar hard spherocylinders, using longitudinal, transverse and off-centre transverse dipoles. Again this should lead to dimerisation (though this time it will be side to side rather than end to end) and, again, reentrant behaviour is expected to result.