

Liquid Crystal Simulation

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Introduction

CCP5 sponsors a collaboration in the area of liquid crystal simulation. This enables several UK research groups to get together from time to time, exchange recent results and, especially, concentrate on the major technical challenges to progress in modelling these phases. The most recent meeting was held in Bristol on Friday 26 March 1993. It was attended by: Mike Allen, Carl Mason, Mark Warren (Bristol, Physics), George Jackson, Dave Williamson, Alejandro Gil (Sheffield, Chemistry), Geoffrey Luckhurst, Doug Cleaver (Southampton, Chemistry), Andrew Masters (Manchester, Chemistry) and Mark Wilson (Lancaster, Physics/Materials). These groups currently use models at all levels of complexity, from lattice spins to fully-realistic atom-atom potentials, but most of the discussion related to hard nonspherical particles and to the Gay-Berne, soft attractive ellipsoidal potential. This article is an account of the discussions that took place at that meeting.

Hard particle simulation

George Jackson described a systematic programme of Monte Carlo simulations of hard spherocylinders and hard-sphere chains, in progress at Sheffield. Simulations of spherocylinders with $L/D = 3,5$ (i.e. length-to-width = 4,6) are initially intended to check earlier work by Stroobants, Frenkel and Veerman, as a reference system prior to studying the same system with added point dipoles. For both elongations, the isotropic phase pressure-density curves agree well with previous results, and also are well represented by Boublik's equation of state. Further work is necessary on the nematic, smectic and solid phases. There was some discussion of the value of constant-pressure simulations, especially near the phase transitions, and the need to adjust box dimensions independently for some of these phases. The next phase is to add a point dipole at the centre, both along the symmetry axis and in a transverse direction, and to put a dipole in an off-centre position giving a chiral molecule.

The group has studied the whole range of N -atom linear rigid chains of tangential hard spheres, from $N = 2$ to $N = 6$, by Monte Carlo, with simulations of $N = 7$ now in progress. These simulations are quite expensive, with a month of cpu time required per state point for the longer chains. Configuration evolution is sluggish, with the (very knobbly) molecules tending to get locked with each other. The group had greatly improved the situation by using reptation Monte Carlo moves, in which an atom is transferred from one end of the chain to the other. No nematic phase had been seen for $N \leq 6$; the equation

of state for the isotropic phase is well represented by the BHS (bonded hard sphere) theory originally due to Wertheim.

Dave Williamson gave further details of the Sheffield simulations, and described the application of Onsager theory, based on the second virial coefficient with a Parsons-type resummation of higher virials, to these systems. There are significant differences between hard-sphere chains and spherocylinders of the same overall dimensions. In minimizing the free energy as a function of the orientational distribution function $f(\Omega)$, the group uses a tabulated function and a Monte Carlo simulated annealing approach, rather than the traditional method based on trial functions of specified form.

At Lancaster, Mark Wilson has been conducting molecular dynamics simulations of hard-sphere chains for some time. In these systems the degree of flexibility is adjustable, via a set of maximum and minimum constraints on interatomic distances. For a nearly-rigid model, molecular dynamics runs up to 20 times faster than a program written for an equivalent fully-rigid system. A constant-pressure ensemble is studied: standard constant- P Monte Carlo box scalings are carried out in between periods of normal dynamics. This assists equilibration. There was some early study of a 5-atom chain, but this did not yield any oriented fluid phases; subsequent work concentrated on the $N = 7$ case.

For the most rigid 7-atom chain molecule studied, isotropic, nematic and smectic phases have been observed. The isotropic phase equations of state agree well with the BHS form. On relaxing the molecular rigidity somewhat, the smectic phase is lost, the isotropic-nematic phase transition is pushed to higher density, but there are indications that the solid may also be destabilized, so the nematic range is extended. For the fully flexible chain (a model of the kind studied before by Rapaport) there is no liquid crystal. These systems can show long periods of quasi-stability in the order parameter, which can be misleading. There was some interest in the change of molecular shape with density. The flexible systems tend to contract (radius of gyration becomes smaller) on increasing the density. The semi-rigid systems become longer and thinner in the nematic phase as the order parameter goes up with density. Similar effects are seen in ‘realistic’ simulations and in experiment. Another interesting point is that, in the nematic phase, the average value of the order parameter $\langle P_4(\cos \theta) \rangle$ is always positive, and the distribution function $f(\cos \theta)$ is always peaked along the director, contrary to many Raman (and other optical) measurements.

At Bristol, hard ellipsoids of revolution are being studied in a variety of ways. Mike Allen described a new system of twisted periodic boundary conditions, which permits the simulation of a uniformly twisted nematic liquid crystal, with a prescribed helix pitch. This has already been used to calculate the Frank twist elastic constant in a direct way. Most recently, it has proved possible to calculate the helical twisting power β for a chiral dopant molecule dissolved in a nematic phase. This is the coefficient of proportionality between the concentration of right-handed (or left-handed) molecules (assumed dilute) and

the wavenumber of the helical structure induced by these molecules. The relation may be manipulated to relate β to the chemical potential difference between mirror image forms of the molecule in the artificially twisted solvent. Preliminary results have been obtained for a particular choice of dopant molecule (an ellipsoidal dimer, in a scissors arrangement) and it is hoped to extend the method to treat more general cases.

Carl Mason described three further projects currently under way at Bristol. Firstly, extensive simulations of highly nonspherical ellipsoids have been carried out, to compare equations of state and phase transition points with the predictions of an Onsager/Parsons type of theory due to Evans and Samborski. Secondly, a detailed study of the $e = 3$ ellipsoid system is in progress. Some doubt has been shed on the stability of the nematic phase here; the original studies were by Frenkel and Mulder, but more recent work of the Orsay group suggests that, as the system size increases, the phase is squeezed out between isotropic liquid and solid. This is being checked in some detail. To date, spontaneous formation of nematic (at a density in the middle of Frenkel and Mulder's range) from isotropic has been seen for $N = 108, 256$ and 512 , using Monte Carlo and molecular dynamics. MD is significantly more cost effective: the nematic forms within days rather than weeks of running. More work is needed before any firm conclusions can be reached: formation of nematic from solid is being attempted, using constant-pressure MD, and free energy calculations are needed. Lastly, studies of the distribution of director orientations within the simulation box are being carried out for relatively small system sizes, but with very long runs (several million MC sweeps), for systems well within the nematic region. The aim is to start quantifying finite size effects, an area which has always been of concern (especially for the calculation of Frank elastic constants). Very preliminary results suggest that the effect may be significant, and that cubic boxes behave differently from truncated octahedral boxes. In the cubic case, the director prefers to align along the cube axes, with the body diagonal very disfavoured, while for TO boundaries alignment nearly (but not exactly) along the diagonal seems preferred. It should be possible to associated a free energy with this effect; more work using special windowing and non-Boltzmann sampling techniques is needed.

Gay-Berne potentials

Geoffrey Luckhurst described the work being undertaken at Southampton to develop a strategy for choosing the parameters of the Gay-Berne potential, based on a knowledge of the types of molecules we wish to model. It is necessary to choose a shape anisotropy parameter, which is relatively easy, a well-depth anisotropy, which is slightly more difficult, and a pair of exponents μ and ν which determine the way the well depth varies with changing orientation of the molecules and the vector between their centres. Different groups have tinkered with the values of these exponents, and the growing variety of different

versions of the potential is unfortunate in some ways. The original fit was to a molecule of 4 fused Lennard-Jones spheres. Best fits to systems of 4–9 LJ atoms give varying choices of μ and ν . Such a fitting procedure, applied to realistic models of mesogens, can at least be used to choose the exponents in a rational way.

There was some discussion of the observation that in simulations of smectic B phases using the Gay-Berne potential, the director (and layer normal) invariably seemed to point along the body diagonal of the simulation box. A layer spacing less than the molecular length pointed to some interdigitation, and the possibility that translational constraints imposed by the periodic boundary conditions were having an effect on the overall orientation. For the smectic B, a rippling of the molecular layers had been observed, and the preferred position for each molecule seemed to be above the midpoint of a line between two molecules in the layer below, rather than above the centre of a triangle of molecules in the layer below.

Simulations using disk-like molecules, constructed in the Gay-Berne fashion, were also in progress. Here the face-to-face energy parameter was chosen to be five times the edge-to-edge value. A state point in the discotic-nematic region of the phase diagram was chosen by referring to the hard-ellipsoid results of Frenkel and Mulder. The Gay-Berne model also forms a columnar phase, in which the columns of disks are interdigitated and, probably as a consequence, are packed in a tetragonal or square arrangement at certain densities; on lowering the density the more common hexagonal structure is seen. Finally, lyotropic systems formed from disk-like micelles are under investigation, using a model in which the edge-to-edge attraction is larger than the face-to-face value. Here the disks form lamellae, which are stacked in a (possibly incommensurate) layered fashion.

Mark Warren described his initial progress on a project started last autumn at Bristol, using the Gay-Berne potential. A molecular dynamics program has been written, in which the director of the nematic phase is precisely constrained by Lagrange multipliers. An initial application is to calculate the Frank elastic constants, where it is convenient to fix the director so that wavevectors consistent with the box axis vectors are also stationary in the director frame. A second application is to examine the distribution of the director within the simulation box (as discussed above) by directly integrating the constraint force with respect to orientation to find the associated free energy function. There are several more potential applications of the technique. The programs have been written in parallel form to run on the DAP at Bristol and the Intel at Daresbury, in collaboration with Bill Smith.

Doug Cleaver described a series of Monte Carlo simulations of the Gay-Berne system in the nematic phase, carried out with Andy Emerson, at Southampton. In this work, the director is constrained to lie within a cone of prescribed angle (typically 5 degrees) of the z axis, by rejecting Monte Carlo moves that would take it outside this range. The aim (just as at Bristol) is to facilitate the calculation of Frank elastic constants. Prelimi-

nary results had already been achieved for one state point, and they seemed to be of the expected magnitudes. There was some discussion of the equivalence, or non-equivalence, of applied orienting fields (which ‘quench’ the orientational fluctuations), Monte Carlo biasing functions, and windowing functions.

Other work

Mike Allen described a recent advance in our understanding of diffusional processes in the nematic phase, due to Tang and Evans (Oregon). By formulating the kinetic theory of hard nonspherical bodies in a way that accounted for the different directions of molecular motion, molecular symmetry axis and (for the nematic) the director, they had obtained excellent agreement with the diffusion coefficients of ellipsoids (parallel and perpendicular to the director), including the interesting dependence on density that had been observed on the high-density side of the isotropic-nematic transition. Moreover, the two-exponential decay of the velocity autocorrelation function was also reproduced with impressive accuracy, by a theory with no adjustable parameters, which simply required the collision rate and order parameter as input. Andrew Masters described his own kinetic theory (Boltzmann equation) analysis of ellipsoid diffusion coefficients (which should be essentially equivalent to that of Evans). An interesting feature of the simulation results was the accuracy with which the particular combination $\mathcal{R} \equiv (D_{\parallel} - D_{\perp})/(D_{\parallel} + 2D_{\perp})$ fitted the ‘affine transformation’ prediction of Hess, over a wide range of order parameter and molecular elongation. Hess’ theory relates the ellipsoidal system to a perfectly aligned system of ellipsoids, and hence to hard spheres. For perfectly aligned ellipsoids the Boltzmann analysis can be taken through to a final form for \mathcal{R} which looks much more complicated than the Hess expression, but which is numerically very close indeed over most of the range of elongations. For imperfectly aligned ellipsoids \mathcal{R} must be obtained numerically, but again it is very close to the Hess prediction. The separate diffusion coefficients $D_{\parallel}/D_{\text{hard sphere}}$ and $D_{\perp}/D_{\text{hard sphere}}$, however, differ significantly from Hess’ theory.

Geoffrey Luckhurst described simulations of rod-plate mixtures using a lattice system, using $\pm\epsilon P_2(\cos\beta_{ij})$ interactions with a positive or negative sign to represent unfavourable or favourable terms. The aim here is to look for biaxial nematic phases for the mixture, which would be competing against the phase separation predicted by a theory of Dunmur’s. The tricky problem of identifying elements of the ordering tensor, and averaging them in an appropriate manner to obtain uniaxial and biaxial order parameters, was discussed.

There was no time to discuss realistic liquid crystal simulations in detail, but Doug Cleaver mentioned that a model of the cyanobiphenyls had been developed at Southampton, and was being used to simulate layers of these molecules on graphite for comparison with atomic force microscope experiments. Mark Wilson is developing a code to simulate a realistic model of a mesogen in a non-mesogenic solvent (e.g. carbon tetrachloride) to

study the effects of varying concentration, and certain specific chiral interactions.

Conclusions

Recurring themes in the discussion were the need to conduct runs of the order of several millions of MC sweeps or MD timesteps, in order to properly equilibrate systems near phase transitions, and properly sample order parameter distributions. Also, the long-standing questions regarding system-size effects, and the influence of the box on orientational ordering, have come to the fore once more; some groups are seeking to quantify this and/or control the director more closely in simulations. This is particularly critical, in that it may affect directly some of the properties of most interest, namely the elastic constants. Finally, many groups are paying attention to the various ingredients of molecular interactions that may influence liquid crystal behaviour: shape and size, flexibility, long-range electrostatics, and the general shape and range of the attractive well.