COMPUTER SIMULATIONS OF LIQUID CRYSTAL POLYMERS AND DENDRIMERS

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Abstract This article describes some of the progress made towards the simulation of liquid crystalline polymers and dendrimers within our laboratory. We describe the use of hybrid models, where a mixture of spherical and nonspherical potentials can be linked together to form model macromolecules. Results are presented for hybrid models of a side-chain and a main chain liquid crystal polymer, which have been studied by molecular dynamics simulation. Preliminary results are also presented from a modelling study of a third generation carbosilane liquid crystalline dendrimer. These involve molecular dynamics studies of single molecules in a solvent using a hybrid Gay-Berne/Lennard-Jones model; and studies of the bulk phases of the dendrimer using a coarse-grained hybrid spherocylinder/Lennard-Jones model. We also review briefly some of the progress made with other models for liquid crystals and polymers, point to the problems still faced and some of the current developments designed to overcome them.

Keywords: polymer, parallel, molecular dynamics, Monte Carlo

Introduction

There is considerable interest in the properties of new mesomorphic materials, which are composed of molecules with novel architectures. These include rod-coil molecules [Lee et al., 2001], polyphilic molecules [Pensec et al., 1995, Tschierske, 2001], block-copolymers [Stadler et al., 1995] and dendritic molecules [Percec et al., 2000]. In many of these systems microphase separation can be used to build new materials containing structures that are ordered on the nanoscale. Examples include the formation of spheres or rods within a uniform matrix of different chemical composition; or the self-assembly of a polyphilic system into lamellar layers. In these cases, microphase separation is induced by the presence of different types of chemical interactions within
different parts of the molecule. For example, a molecule could contain a number of segments that could be aliphatic, aromatic, fluoro, siloxane-based or hydrogen-bonding, all of which have very different types of interaction. In the case of AB diblock copolymers, the phase diagram is relatively easy to predict and depends on both composition and the difference in interaction energy between A and B [Leibler, 1980, Floudas et al., 2001]. However, the possibilities of building more complex molecular architectures from chemically distinct building blocks is limited only by the imagination of chemists.

At the current time, we have no way, other than chemical intuition, of predicting which bulk structures will be formed from novel molecular architectures. Here then is a major challenge for simulation; can we predict what phase, or sequence of phases, will be formed by complex multi-block oligomers, polymers, or dendritic molecules composed of several different groups? Can we predict the properties of these phases? Can we use simulation to “engineer” new materials, designing them from scratch to create the desired structure at the nanoscale?

The current answer to each of these questions is NO! Detailed atomistic simulation simply cannot handle the system sizes or the times-scales required to predict phase behaviour in such systems. It is of course possible to extend simulation to much longer lengths-scales and time-scales by simplifying potentials and coarse-graining. However, our current coarse-graining methods tend to be too crude to use simulation in this sort of predictive capacity. However, the prospect of solving some of these problems and using simulation to design the nanostructured materials of the future remains an intriguing one!

This article explores the possibilities of using simulation to predict the formation of complex structures for two relatively simple classes of mesomorphic materials: liquid crystal polymers and liquid crystal dendrimers (figure 1). In the first section of the article we discuss briefly some of the models available currently to the simulator. We then review some of our preliminary work in this area, developing hybrid models composed of a mixture of anisotropic and isotropic sites and using them to study liquid crystal polymers and dendrimers. We point also to some of the problems still faced in this area and some of the likely future developments designed to overcome them.

1. Simulation Models

Atomistic Models

Atomistic simulation is well-established as a tool for studying solids, liquids and gases. In brief, each atom within a molecule is represented by individual potential functions to model nonbonded interactions (van der Waals’s interactions and electrostatic interactions). The atoms are linked together by means of further multi-site potentials which model the intramolecular bond stretch-
Computer simulations of liquid crystal polymers and dendrimers

Figure 1. Schematic diagram illustrating the structures of two types of liquid crystal polymer and a liquid crystal dendrimer.

ing, bond bending and torsional interactions within molecules. Together all the potentials comprise a force field for the molecule, which can be used in molecular mechanics studies [Allinger et al., 1989] to find the lowest energy conformations of the molecule, or in molecular dynamics or Monte Carlo simulations to study the isolated molecule [Wilson, 1996] and the molecule within a bulk phase [Wilson and Allen, 1991, Wilson and Allen, 1992, McBride et al., 1998, Zannoni, 2003]. In the early days of simulation force fields were largely based on experimental data. However, increasingly they are being derived from good quality \textit{ab initio} quantum chemical calculations [Cheung et al., 2002].

In principle, atomistic studies with good quality force fields should be sufficient to represent liquid crystal phases or polymer melts to a high level of accuracy; and most material properties (order parameters, densities, viscosities elastic constants etc.) should be available from such simulations. In practise, this is rarely (if ever) the case. For example, using molecular dynamics, the computational cost of atomistic simulations is such that it is rarely possible to simulate for longer than a few tens of nanoseconds for (say) 10000 atoms. Even these modest times often require several months of CPU time on todays fastest processors. For low molecular weight liquid crystals, a few 10s of nanoseconds may be enough to see the growth of a nematic phase from an isotropic liquid [McBride et al., 1998]. (Elsewhere in this volume [Zannoni, 2003] Zannoni describes state-of-the-art calculations aimed at predicting the transition temperatures for three members of a homologous series of low molecular weight mesogens.) However, even a 100 ns can be a very short time in terms of relaxation mechanisms within a polymer of modest molecular weight. Moreover, the number of sites available in typical atomistic simulations, (30000 is still considered large by todays standards) severely restricts
the size of polymer and, for a liquid crystal, the type of phase that can be studied. In the case of liquid crystals a hundred molecules or more are required to see a reasonable nematic phase, a minimum of a few hundred molecules are required to see a smectic-A phase; and many thousands of molecules are required for exotic smectics such as the twist grain boundary phase [Allen et al., 1998]. Consequently, although atomistic simulation is well-established, it is rather limited as a tool for studying polymer liquid crystals and other complex materials.

**Simplified models for polymers and liquid crystals**

The need to push simulation to longer time scales and larger system sizes has led to the development of more coarse-grained models for both liquid crystals and polymers. Changing to a united atom model, in which a heavy atom and attached hydrogens are represented by a single site is of some help and can typically reduce the number of sites in a simulation by a factor of 3. However, more drastic coarse-graining is required if time and length scales are to be extended by several orders of magnitude.

In the area of liquid crystals, a popular coarse-graining approach involves the use of the Gay-Berne potential [Gay and Berne, 1981, de Miguel et al., 1996, Luckhurst et al., 1990, Berardi et al., 1993, Zannoni, 2001] (figure 2). Here, a liquid crystal molecule can be represented by a single anisotropic site with both anisotropic attraction and repulsion acting between molecules. From figure 2, the Gay-Berne can be seen to take a similar form to the well-known 12:6 Lennard-Jones potential. However, the energy at which the attractive and repulsive energies cancel, $\sigma$, and the depth of the attractive well, $\epsilon$, depend on the relative orientations, $\phi$, of the two particles, i.e. $U_{GB} = f(r_{ij}, \phi, \epsilon, \sigma)$. Four parameters, $\kappa, \kappa', \mu$ and $\nu$, control the form of the potential. The length/breadth ratio is given by the parameter $\kappa$ and the ratio of side-to-side/end-to-end well-depths is given by $\kappa'$. $\mu$ and $\nu$ can be used to vary the well-depths for molecules coming together in different relative orientations.

The Gay-Berne potential has successfully been used for many liquid crystal simulations, and (depending on the parameterisation used and the state points studied) can be used to simulate nematic, smectic-A and smectic-B phases. Variants of the GB potential have also been used to study the biaxial nematic phase (biaxial GB potential) [Berardi and Zannoni, 2000] and the smectic C phase (GB with quadrupole) [Neal and Parker, 1999]. The GB model has been used also to provide predictions for key material properties, such as elastic constants [Allen et al., 1996] and rotational viscosities [Cuetos et al., 2002], which have an important role in determining how a nematic liquid crystal responds in a liquid crystal display (LCD).
In the field of polymers, a common form of coarse-graining involves the use of bead-spring models (figure 3). Here the individual beads represent a small part of the polymer, with the degree of coarse-graining dependant on the system being studied. Often a cut and shifted Lennard-Jones potential is used for the beads; and this is combined with a FENE potential [Binder, 1995] for the springs. This potential is much softer than a normal bond stretching potential and therefore allows considerably longer time-steps to be employed in a molecular dynamics simulation than are possible for a model with an atomistic level of detail. An additional feature of the FENE is that an appropriate choice of parameters can practically forbid the crossing of chains if this is required. This, of course, is necessary if the effects of chain entanglements on dynamics are to be studied.

Lattice models have also been employed with great success for both liquid crystals and polymers. In liquid crystal simulation the earliest and most widely used model is that of Lebwohl and Lasher [Lebwohl and Lasher, 1972]. In this model each site on a cubic lattice contains a vector spin that represents a small region of liquid or liquid crystal. Neighbouring spins interact via a $P_2(\cos \theta)$ potential. The model, despite its simplicity, has been remarkably successful in representing many of the features of the bulk isotropic-nematic transition [Fabbri and Zannoni, 1986] and has been extended to look at liquid crystals in different geometries, such as a slab [Cleaver and Allen, 1993], cylindrical pores [Chiccoli et al., 1996] and spherical droplets [Chiccoli et al., 1992]; as well as being used as a way of studying model liquid crystal displays [Chiccoli
et al., 2001]. Variants of the Lebwohl-Lasher model have also been deployed successfully [Ilnytskyi et al., 1999].

Lattice models are also well-developed for polymers [Binder, 1995]. A popular model involves a self-avoiding walk (SAW) in which the polymer consists of a series of beads occupying sites on a simple cubic lattice. Bonds connecting two beads are represented by nearest neighbour links between occupied lattice sites. This model has been extensively used for problems involving both structure and dynamics [Sokal, 1995]. However, the most widely used lattice model for polymers is the bond fluctuation model [Carmesin and Kremer, 1988]. In this model each monomer occupies a cube of eight lattice sites, and the vector between two sites can take on a possible 108 different values. The model has all the advantages of speed associated with lattice models, but the large number of possible bonds that are available means that the model is far closer to an off-lattice model than the simple SAW on a cubic lattice.

Finally, an alternative level of coarse-graining involves the use of DPD (dissipative particle dynamics) models [Groot and Warren, 1997]. These have been used successfully in simulations of microphase separation for block copolymers [Groot and Madden, 1998, Groot et al., 1999] and in a number of other areas [Groot and Rabone, 2001, Groot, 2003]. Some of the recent progress in the field of liquid crystalline polymers is discussed by Clarke in this volume [Clarke, 2003]. This field is still in its infancy, and the best ways of coarse-graining to a DPD model from more atomistic descriptions are still open for discussion. None-the-less, the progress in this area is highly encouraging and these models show real promise in terms of solving the time and length scale problems that so often confront simulators in the areas of liquid crystals and polymers.
2. Hybrid Models

In recent years, my group in Durham has been looking at the use of simple coarse-grained models for the simulation of liquid crystalline macromolecules. These models combine anisotropic sites, such as the Gay-Berne potential (discussed above) and either bead-spring or simple united atom models for the polymer chains. A typical potential for such a system is represented by

\[
E = \sum_{bonds} \frac{k_{bond}}{2} (l - l_{eq})^2 + \sum_{angles} \frac{k_{angle}}{2} (\theta - \theta_{eq})^2 + \sum_{dihedrals} \left( a_{0,dih} + a_{1,dih} \cos \phi + a_{2,dih} \cos^2 \phi + a_{3,dih} \cos^3 \phi \right) + \sum_{i} \sum_{j<i} U_{atom}(r_{ij}) + \sum_{i} \sum_{j<i} U_{mesogen}(r_{ij}, e_i, e_j) + \sum_{i} \sum_{j} U_{mesogen/atom}(r_{ij}, e_j),
\]

where the intramolecular force field parameters for bond, angle and dihedral interactions \( k_{bond}, l_{eq}, k_{angle}, \theta_{eq}, a_{i,dih} \) are all tunable for the particular system under investigation. The nonbonded interactions energies, \( U_{atom}, U_{mesogen} \) can be represented by a combination of Lennard-Jones, Gay-Berne and extended Gay-Berne (for \( U_{mesogen/atom} \)) potentials [Wilson, 1997] or alternatively simpler potentials such as a combination of soft repulsive spheres and soft repulsive spherocylinders [Earl et al., 2001]. Further details of this hybrid approach are described for an early simulation of a liquid crystal dimer in reference [Wilson, 1997].

The advantage of such hybrid models is that complex macromolecules containing liquid crystal groups are still able to keep the essential characteristics of the molecular structure, while simplifying the structure considerably in comparison to a fully atomistic model. In addition, the development of two parallel molecular dynamics simulations codes, the replicated data program GBMOL, [Wilson, 2000] and the domain decomposition program GBMOL/DD, [Ilnytskyi and Wilson, 2001, Ilnytskyi and Wilson, 2002] means that it is now possible to use large parallel computer systems to push simulations to the longer times required to see the formation of liquid crystal mesophases.

In the following sections we review briefly some of the systems studied recently using the hybrid potential approach.

3. Side chain liquid crystalline polymers

A simple hybrid model for a siloxane side-chain liquid crystalline polymer is shown in figure 4. Here, the methylsiloxane backbone and the flexible alkyl
spacer of the real polymer have been replaced by a series of united atom potentials, and the mesogenic groups have been replaced by Gay-Berne [Gay and Berne, 1981] potentials.

Figure 4. Structure of the model side-chain siloxane polymer studied. The spheres represent united atom sites and the ellipsoid represents a Gay-Berne site.

The behaviour of the system can be understood by viewing snapshots of the system, as illustrated in figure 5 as the system is cooled down from a high temperature polymer melt. In figure 5 three separate quenches are considered. Two runs are carried out in the presence of an aligning potential of the form $E = -v P_2(\cos \theta)$, with $v = 2$ kJ mol$^{-1}$ and $v = 5$ kJ mol$^{-1}$ respectively, coupled to the mesogenic groups. The aligning potential mimics the effects of a magnetic field, and is applied because a strong magnetic field is usually required experimentally to produce uniformly aligned mesophases [Richardson et al., 1999a]. A further run is carried out in the absence of a magnetic field. The presence of the aligning potential leads to the formation of mesophases on cooling.

In the absence of the aligning potential, cooling induces microphase separation into mesogen-rich and polymer rich regions, as illustrated by the snapshot at 250 K. Within the mesogen-rich domains alignment of the Gay-Berne particles occurs to form a system containing small regions of liquid crystal separated by polymer. This can be seen quite clearly in figure 6, where the polymer
chains are removed to reveal the ordering of the mesogenic units. Despite the high degree of local order, the presence of polymer chains is sufficient to decouple the ordering of the mesogens in each region, resulting in a system with an overall order parameter that is close to a value of zero.

Figure 5. Cooling of a model side chain liquid crystalline polymer from an isotropic polymer melt. Top: absence of an aligning potential. Middle: in the presence of an external aligning potential with \( \epsilon = 0.2 \text{kJ mol}^{-1} \). Bottom: in the presence of an external aligning potential with \( \epsilon = 0.5 \text{kJ mol}^{-1} \).
Figure 6. Snapshots showing the structure of the model side chain liquid crystalline polymer at 350 K. Left: The polymer backbones are shown in dark grey, the flexible spacer are shown in grey and the mesogenic groups are shown in white. Right: positions of the mesogenic groups. Top: absence of an aligning potential. Middle: in the presence of an external aligning potential with $\epsilon = 0.2 \text{ kJ mol}^{-1}$. Bottom: in the presence of an external aligning potential with $\epsilon = 0.5 \text{ kJ mol}^{-1}$.

In contrast, under the application of an ordering potential, the onset of microphase separation is sufficient to induce the formation of a lamellar layers, corresponding to a smectic-A liquid crystal phase, as illustrated in the bottom two rows of figure 5. It is interesting to compare the behaviour for the two strengths of aligning potential. We note that for $v = 2 \text{ kJ mol}^{-1}$ at 350 K,
we see nematic order within the formed layers of liquid crystal (as illustrated in figure 6). At lower temperature this structure anneals to give smectic-A ordering within the individual crystalline layers. At $v = 5 \text{ kJ mol}^{-1}$, smectic-A ordering is already present at 350 K in well-formed layers. The left hand side of figure 6, allows different regions of the polymer to be viewed. In the unaligned system, the polymer backbone (shown in dark grey) forms a network separating the different mesogenic regions, and the flexible spacers seem to form a sheath around the polymer backbone. The sheath is also present in the two aligned systems, but here the polymer backbone is forced to lie mainly within the layers. Occasionally, the backbone is able to jump between layers, causing a small defect in the liquid crystalline regions as it transverses it. This has already been postulated as likely behaviour for the polymer backbone [Richardson et al., 1999a], but this is the first direct evidence from molecular simulation to support this. Further details of this polymer system will be published shortly [Stimson and Wilson, 2003].

4. Main chain liquid crystalline polymer

A similar hybrid model has also been used to study a series of main chain liquid crystalline polymers [Lyulin et al., 1998] (figure 7).

![Figure 7. General structure for the model main-chain polymers studied. The (CH)$_2$ groups are represented by united atom sites and the ellipsoid represents a Gay-Berne site. For the systems studied in reference [Lyulin et al., 1998], $m = 5, 8$ and $n = 10$.](image)

In this work, for the $m = 6$ system, spontaneous ordering of the polymer occurred on cooling from 500 K to 350 K to form a nematic phase, as shown in the snapshots of figure 8. To illustrate the ordering of individual chains, the periodic boundary conditions have not been applied to the snapshot in figure 8, and the polymer chains have been allowed to spill out of the simulation box. The change in order of individual chains on entering the nematic phase can clearly be seen with the chains stretching to lie parallel to the nematic director. Also, in the nematic phase, individual folds can be observed, which allow a stretched chain to double back on itself.

With a main chain polymer of this type, some odd-even effects would be expected to arise depending on the length of spacer separating the mesogenic groups. Some evidence for this is indeed observed from the simulations. For
Figure 8. Snapshots showing the structure of a model main chain liquid crystalline polymer for the model system with \( m = 6 \) and \( n = 10 \). Left: isotropic phase at 500 K. Right: the nematic phase at 350 K.

\( m = 6 \) in the nematic phase order parameters for even bonds are higher than those for odd bonds (counting bonds from the mesogenic unit). Limitations on simulation time did not allow for the growth of nematic phases for each system. However, evidence for odd-even effects in the system density plotted as a function of spacer length \( m \) were observed also.

5. Carbosilane liquid crystalline dendrimers

There has been much recent synthetic work in the area of liquid crystalline dendrimers and many different new materials have been made. It is possible that individual dendrimer molecules can be rod-like or disc-like in shape and form liquid crystalline phases. As an example, a stilbenoid dendrimer has been reported by Meier and Lehmann [Meier and Lehmann, 1998], where the whole dendrimer acts as a large discotic molecule. Alternatively, it is possible to design dendromesogens where mesogenic moieties are incorporated into the interior of the dendrimer [Issberner et al., 1994, Bauer et al., 1993, Percec et al., 1995], or to functionalise the surface of a dendrimer by mesogenic groups as illustrated in figure 1. An example of the latter is provided by carbosilane dendromesogens [Ponomarenko et al., 2000, Ponomarenko et al., 1996, Richardson et al., 1999b, Ponomarenko et al., 1999] the chemical structure of which is shown in figure 9 for a third generation dendrimer, and the overall molecular structure, including each branching point, is shown in figure 10.
In these carbosilane dendrimers the number of mesogens (and also approximately the number of atoms) doubles with generation number. The phase behaviour of these systems was initially studied by optical microscopy and differential scanning calorimetry, and subsequently by X-ray diffraction. For the first four generations of dendrimer, the systems are believed to exhibit smectic-C and smectic-A phases. Here, the suggestion is that the dendrimer structure, which appears spherical if a gas phase molecular model is constructed, deforms to give a rod and that the rods pack together to give smectic phases (shown schematically in figure 11). However, for the 5th generation dendrimers the series of phases was found to be different [Ponomarenko et al., 1999] and X-
Figure 10. Schematic diagram showing the branching structure within a carbosilane liquid crystalline dendrimer as the number of generations increases from 1 to 4.

Ray scattering suggests the formation of discotic $D_{nc}$ and $D_{hd}$ phases from discotic columns with ellipsoidal and circular columns respectively. Here the self-assembly pathway suggested is for the dendrimer to be squashed to form...
a disc and that such discs self-assemble to form columns, which in turn pack to form discotic columnar phases, as illustrated in figure 11.

In the work below we describe some initial attempts to understand the molecular ordering within these systems using simulation.

**Hybrid Gay-Berne/Lennard-Jones model**

In initial work we have looked at the behaviour of a hybrid Gay-Berne/Lennard-Jones model in the presence of a liquid crystal solvent [Wilson et al., 2003]. The structure of the molecule in the gas phase is shown in figure 12. Following the earlier LCP work, we have represented each heavy atom by a single Lennard-Jones site and each mesogenic group by a Gay-Berne potential and used molecular dynamics simulations to study the behaviour of the system. Within an isotropic solvent composed of Gay-Berne particles the arrangement of mesogenic groups remains random, though the radius of gyration increases slightly to accommodate solvent molecules, which are able to penetrate the outer layers of the dendrimer composed of mesogenic groups and the flexible chains. However, a remarkable structural change occurs when the dendrimer is immersed in a nematic solvent, as shown in figure 13. The dendrimer structure rearranges to form a rod-like shape with the order parameter of the mesogenic groups in the dendrimer rising so that the value is close to that of the nematic solvent. This rearrangement occurs over a period of around 4 ns and can be followed during the course of the simulations. It is mediated by conformational changes within the alkyl chains.

The structure of the different parts of the dendrimer can be mapped by distribution functions. These demonstrate that some backfolding of the chains is possible, and that they are able to fill spaces within the core. However, the degree of backfolding is quite small. As in the isotropic phase, the solvent is able to penetrate the region occupied by the chains and the mesogenic groups; but very little penetration of the solvent into the central core of the dendrimer is observed. The distribution functions show also that the structure of the dendrimer core does not change significantly with solvent. The anisotropy in structure within the nematic phase is attributed to the arrangement of chains alone.

When the dendrimer is immersed in a smectic solvent, the dendrimer structure changes again, so that the mesogens are able to lie in individual smectic layers, as shown in the snapshots of figure 14. As in the nematic phase, there is a lengthening of the dendrimer along the nematic director, which can be attributed to changes in the arrangement of chains around the dendrimer core. There are no significant changes in the structure of the core.

Recently, we have been looking at a number of structural variations for this model dendrimer. An obvious structural change to make is to bond the meso-
Figure 11. Schematic diagram showing the proposed self-assembly process for carbosilane dendrimers to form smectic and columnar phases.

genic groups laterally rather than terminally as shown in the left hand side of figure 15. There have been a number of recent synthetic studies than have experimented with lateral mesogen attachment, and such structural variations are
Figure 12. Picture of the model 3rd generation siloxane dendrimer. The ellipsoids represent Gay-Berne particles and the spheres represent Lennard-Jones particles.

Figure 13. Snapshot showing the molecular order of a third generation carbosilane dendrimer in a nematic phase.

Figure 14. Snapshots showing the molecular order of a third generation carbosilane dendrimer in a smectic-A solvent. Left: Solvated molecule with part of the solvent removed to show structure of the dendrimer. Right: Molecule with all solvent molecules removed.

now relatively easy to achieve. Interestingly, for the system with lateral attachment, the mesogens still align along the nematic director; but no longer gather at both ends of the molecule. Instead they are distributed over the surface of the dendrimer as shown in the right hand side of figure 15. This is because the chains can no longer stretch to lengthen the molecule along the nematic director and, at the same time, keep the mesogens aligned. Instead gauche
conformations in the chain are required to allow the mesogens to point parallel to the director and this causes the chains to curl more tightly round the core.

Figure 15. Snapshot showing the molecular order of a third generation carbosilane dendrimer with laterally bonded mesogenic substituents in a nematic solvent.

Coarse-grained model

In order to attempt to understand the structure of the bulk phases formed by the dendrimer, it is necessary to coarse-grain the model further to make it possible to simulate a reasonably large number of dendrimer molecules. With this in mind the simulations with the hybrid model provide a number of useful insights into the type of coarse-grained model than is required to capture the essential physics.

- Firstly, the dendritic core can seemingly be decoupled from the outer parts of the molecule.
- Secondly, the penetration of other molecules into the core can also be expected to be extremely small.
- Thirdly, flexible chains terminated in mesogenic units are clearly essential in any model.
- Finally, the degree of coarse-graining employed for the chains is probably not critical, but it is essential that chains should be able to wrap round the core and that they are able to change conformation easily to allow the mesogenic groups to order as they “want”.

With these factors in mind we have recently carried out studies of a number of coarse-grained models for the dendrimer. Here, we describe preliminary
results from two models. In the first model the central core of the dendrimer is coarse-grained to a single spherical site (as shown in figure 16); the chains are coarse-grained to three spheres each, and the mesogen is coarse-grained to a single spherocylinder. In our initial work, we used a purely repulsive potential in the form of soft repulsive spheres (represented by Lennard-Jones potentials that have been cut at the minimum in the potential well at $r = 2^{1/6} \sigma$ and shifted to go smoothly to zero at the cutoff) and soft repulsive spherocylinders of aspect ratio $L/D = 3.1$ to fit the mesogen. These are linked together by soft springs using an ultra-soft force constant and a repulsive potential of the form $E_{\text{bond}} = k_{\text{bond}} (l - l_0 g)^2$, which allows the coarse-grained sites to rattle between two repulsive walls and the time-step to be governed by the steepness of the soft repulsive potential between nonbonded sites. Hence a long-time step can be employed. A snapshot of a single dendrimer molecule is shown in figure 17.

The phase behaviour of the model system has been studied as a function of density. For this first model we have seen no evidence for spontaneous microphase separation or formation of mesophases prior to freezing. We have looked at the orientational order of the system when an aligning potential is coupled to the spherocylinders at densities close to the freezing transition. The influence of the aligning potential is shown in figure 18, where we see nematic ordering of the spherocylinders occurring within an isotropic melt. However, alignment does not induce microphase separation or lead to the formation of
Figure 17. Snapshot showing the structure of a single molecule for a coarse grained model of a third generation carbo silane dendrimer.

a smectic phase; and the orientational order relaxes once the potential is removed.

Figure 18. Response of a melt composed of coarse grained model dendrimer molecules under the application of an orientating potential, coupled to the spherocylinder units. The potential is applied for the first 750 ps of the simulation.

In a variant of this model we have reduced the size of the core, added an extra site to each chain to model the Si(Me)$_2$-O-Si(Me)$_2$ groups and extended the length of the spherocylinders used to give an aspect ratio of $L/D = 6$. For
this system, our preliminary results indicate that we do indeed see spontaneous microphase separation in the isotropic melt as illustrated in figure 19. In the presence of an aligning potential, the system forms a smectic-A mesophase as illustrated in the right-hand-side of figure 19. However, the liquid crystal phase only remains stable for densities just prior to freezing. So $L/D = 6$ spherocylinders seems to be right on the limit of the mesogens length required to see stable mesophases in this system.

The lack of attractive forces in this model mean that microphase separation is being induced mainly by entropic forces. Alignment of the spherocylinders increases their translational entropy. However, this is at the expense of both rotational entropy and entropy of mixing. As the density of the system increases, the translational entropy will eventually win out. However, at sufficiently high densities the system will freeze to form a glass. Increasingly the spherocylinder length simply pushes down the density at which alignment occurs. However, the fact that mesogens of $L/D = 6$ are required for microphase separation, suggests that in real systems anisotropic attractive forces must play an essential role in the formation of mesophases.

Preliminary results from these simple soft repulsive models are being used to improve our coarse-grained descriptions of these complex molecules.

Figure 19. Top: snapshot of the modified dendrimer model using spherocylinders with $L/D$ ratios of 6:1 and 4 spheres per dendrimer arm. Left: spontaneous microphase separation occurs as the liquid melt is compressed. Right: formation of a smectic-A phase as an orientating potential is applied to the spherocylinders.
6. Summary

This article has reviewed some of the progress made in simulating liquid crystalline macromolecules. After a brief review of the types of model available for both polymers and liquid crystals, we have concentrated on hybrid models. These facilitate a moderate degree of coarse-graining while retaining many elements of structure of the real macromolecules. Such models allow the combination of spherical and nonspherical potentials that can be used to coarse-grain polymer chains and rigid mesogenic groups. This approach has been successfully applied in Durham to simulate flexible macromolecules such as side-chain and main-chain liquid crystalline polymers and liquid crystalline dendrimers. We demonstrate, that simulations can show the presence of liquid crystalline phases in such systems; and can be used to provide an insight into the molecular order within these phases.

This area of study is one where it is difficult to make rapid progress. Simulation is hampered strongly by the need to use large systems sizes and employ extremely long simulation times to achieve equilibrium. In fact the work presented here, is amongst the first simulation work to appear in the literature. However, we hope that hybrid models, of the type we discuss, combined with state-of-the-art coarse-graining techniques (which are starting to appear) will stimulate further work. Ultimately, we are hopeful that improvement in coarse-graining, will allow us to take the results from fully atomistic simulations of single molecules, and use them to design simple hybrid models that will be able to predict the behaviour of bulk systems. Work in this area is already underway in our laboratory.

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Computer simulations of liquid crystal polymers and dendrimers


