Molecular simulation of liquid crystals: progress towards a better understanding of bulk structure and the prediction of material properties

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This *tutorial review* covers recent progress in the field of computer simulation of liquid crystals. The development of the main "molecular-based" models for liquid crystals is described. These include lattice models, coarse-grained single site models based on hard and soft interaction potentials, atomistic models and multi-site coarse-grained models. A brief historical review is followed by an assessment of some of the new areas in this field, with an emphasis on understanding of molecular structure in liquid crystal phases and the prediction of bulk material properties. The article also looks to link the field of liquid crystal simulation with important developments in areas such as polymer simulation, lyotropic liquid crystals and model membranes.

1. Introduction

In recent years rapid advances in the speed of computers has led to the increased use of molecular simulation as a tool to understand complex chemical systems. In the case of self-organising materials, such as liquid crystals, simulation is often difficult, with subtle changes in intermolecular forces leading to changes in phase behaviour. Moreover, in the case of liquid crystals many properties of interest arise from specific ordering of molecules (or parts of molecules) in the bulk; and so can only be studied by simulation of many molecules. Despite these difficulties the progress in molecular simulation has been rapid.[1,2] In particular, simulation has led to a much better understanding of bulk structure in many liquid crystals, from low molecular weight nematics to complex macromolecular systems, and simulation is now being used as a way of predicting material properties.

Liquid crystals have much in common with other areas of soft matter chemistry. As a result the same techniques used for simulation of liquid crystals are of interest for other self-organising materials. For example, recent advances in coarse-grained simulations of liquid crystals have counterparts in polymer simulation, simulation of bilayers and model membranes, simulation of micelles, and the study of structure in peptides and proteins.

2. Types of simulation model

A number of different types of simulation model have been developed for modelling liquid crystal systems. Possibly the simplest model is based on the spin-models of classical physics. Here, vectors (spins) are situated at sites on a lattice (see Fig. 1). These can be used to represent a molecule (or cluster of molecules), which interact with neighbouring vectors through a simple interaction potential. The simplest realisation of this, is a pair potential of the form

$$U_{ij} = -\varepsilon P_2(\cos\theta_{ij}) = -\varepsilon\left(\frac{3}{2}\cos^2\theta_{ij} - \frac{1}{2}\right), \quad (1)$$

where the angle θ_{ij} is the angle between two vectors. The phase behaviour of the model can be simulated using the Monte Carlo method using random changes to the orientations of the individual spins and accepting or rejecting these "trial moves" based on a Metropolis acceptance/rejection criterion.[3] This ensures that, for a given temperature, individual configurations occur with the correct Boltzmann weight. The degree of liquid crystal order (in this case simply orientational order) for a set of the vector spins, **u**, is measured *via* an order parameter

$$S_2 = \langle P_2(\mathbf{n.u})\rangle, \quad (2)$$

measured relative to the preferred direction of order in the system. The latter is given by the vector, **n**, termed the liquid

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crystal director. Here, the angular brackets in the formula refer to an ensemble average. A value of 1 measures perfect order and a value of zero corresponds to what is expected for a random arrangements of orientations, as would be found in a liquid of elongated molecules.

This lattice model, was originally developed by Lebwohl and Lasher in the 1970s as the first simulation model for a nematic,[3] and has proved highly successful. It shows a first order phase transition between ordered and disordered states as a function of temperature, has a small enthalpy change associated with the phase transition (as with real liquid crystals) and with suitable boundary conditions, can be adopted to simulate a liquid crystal display.[4] Lattice models are highly configurable, and by careful choice of the inter-site potential it has been possible to adapt the basic model of Lebwohl and Lasher to make it suitable for the simulation of biaxial liquid crystals,[5] liquid crystal mixtures, a cubatic phase, liquid crystal dimers, chiral liquid crystals and for studying liquid crystal ordering in aerogels.

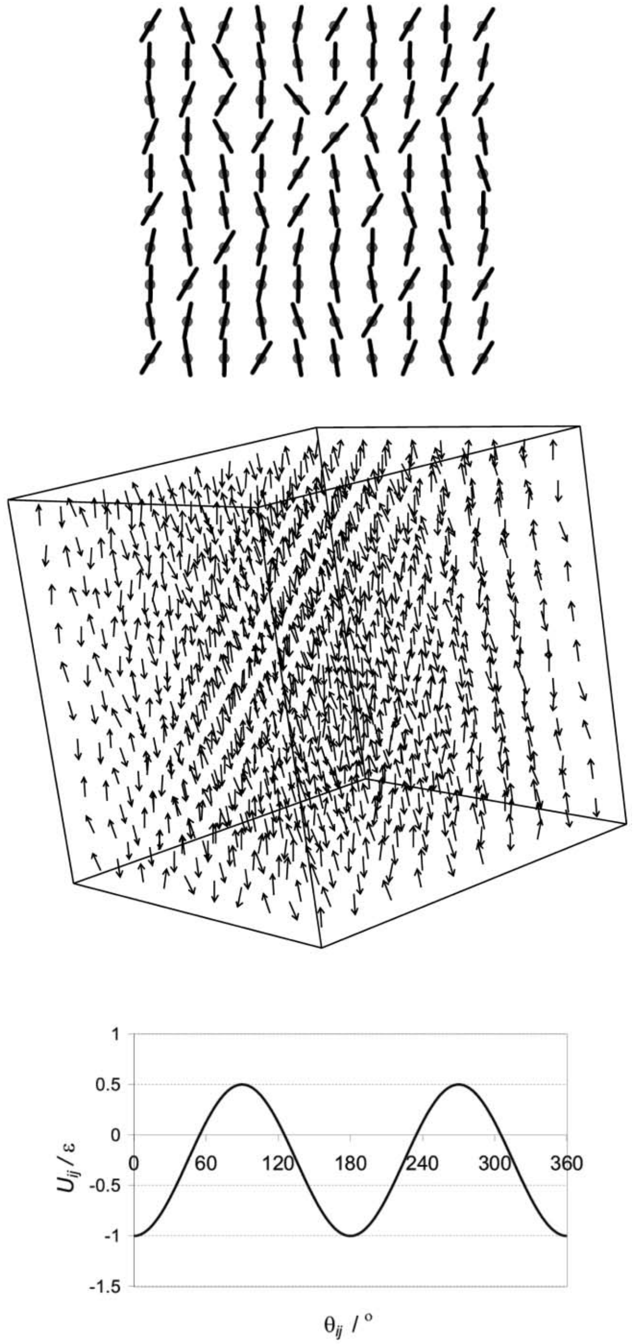

Fig. 1 Schematic representation of a liquid crystal lattice model. Top: molecules (or groups of molecules) are represented by vector spins which are free to rotate on a lattice. Here a 3d lattice is shown from the side in 2d. Middle: a 3d representation of a nematic phase within the Lebwohl–Lasher lattice model. Bottom: the potential used in the original lattice model of Lebwohl and Lasher.

A second class of models that has historically been extremely useful are those based on single site off-lattice potentials, some of which are shown in Fig. 2. Collectively these could be termed "single-site-coarse-grained molecular models". Here, the potential is based on either a hard wall (hard anisotropic potential) or has an attractive part (soft anisotropic potential). In the same way that hard spheres and soft Lennard-Jones particles were useful in providing the first reference models for molecular liquids in the 1960 and 1970s, single site anisotropic potentials have proved immensely useful in providing reference models for understanding the properties of liquid crystal phases and developing methods for the prediction of material properties. Common single site hard particle models are hard spheroids[6] which can form nematic phases, hard cut-spheres[7] which can form a nematic discotic phase, a columnar phase and the rather exotic cubatic phase (which has so far not been seen experimentally) and hard spherocylinders[8] which can form a smectic-A and smectic-B phase in addition to the nematic phase (see Fig. 2). For hard particles, temperature does not influence phase behaviour. Consequently phases

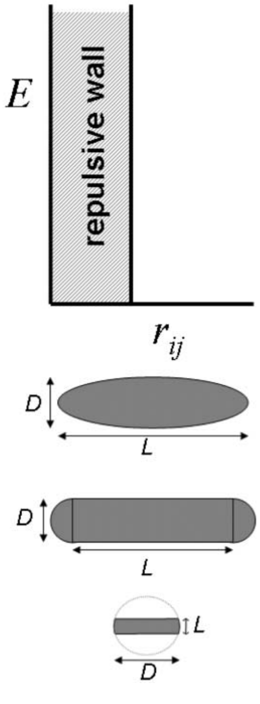

Fig. 2 Single-site hard particle models for liquid crystal molecules. From top to bottom: the hard wall interaction potential, a prolate ellipsoid, a spherocylinder and a cut sphere.

change as a function of system density. Such models are therefore excellent reference models for colloidal systems.

Most hard particle work uses Monte Carlo simulation to sample phase space. Here, the interaction potential is either zero or infinity, so the Metropolis acceptance criterion is particularly simple: all overlapping configurations are rejected, all non-overlapping configurations are accepted. For some models it is possible to carry out molecular dynamics,[9] with careful choice of an appropriate algorithm to predict the next collision in the system and implement the collision dynamics.

While hard particle models also provide reference models for thermotropic systems in terms of the ordering of molecules, it is arguably more appropriate to model thermotropic systems by using a soft potential in which phase behaviour will explicitly depend on temperature. By far the most successful soft particle model, has been Gay–Berne potential (Fig. 3)[10]

$$U_{ij} = 4\varepsilon_o \left[\varepsilon\left(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j\right)\right]^{\nu}\left[\varepsilon'\left(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}}_{ij}\right)\right]^{\mu} \\ \mathrm{x}\left[\left(\frac{\sigma_o}{r_{ij}-\sigma\left(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}}_{ij}\right)+\sigma_o}\right)^{12} - \left(\frac{\sigma_o}{r_{ij}-\sigma\left(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}}_{ij}\right)+\sigma_o}\right)^{6}\right] \tag{3}$$

This model is essentially a soft ellipsoid model, in which the repulsion ($\sim 1/r^{12}$) and attraction ($\sim 1/r^{6}$) mimic the behaviour of a Lennard-Jones potential, with the added feature that both depend on the relative orientation of the two sites i and j (given by the unit vectors $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_j$) in addition to their separation, r_{ij} along the unit vector $\hat{\mathbf{r}}_{ij}$. A nice feature of the Gay–Berne model is that it is easy to change the relative well-depths and distance of separations of the attractive wells, shown (for fixed particle orientations) in Fig. 3, by adjusting the constants ν and μ and adjusting parameters which contribute to ε and σ. This provides the possibility of an infinite number of Gay–Berne models, which can be tuned to mimic different molecular potentials. As with the lattice models mentioned above, it is possible to adapt the interaction potential to simulate disc-shaped molecules[11] (leading to discotic and columnar mesophases) and the potential can be generalized to handle biaxial and non-centrosymmetric molecules also.[12] Suitable tuning of the molecular shape and interactions for such models have led to the formation of a thermotropic biaxial nematic phase, and to a polar nematic.

Monte Carlo in the constant-*NpT* (isothermal–isobaric) and the constant-*NVT* (canonical) ensembles has proved to be the preferred simulation method for the Gay–Berne and other single site potentials. However, for any soft continuous potential, it is possible to write down expressions for the forces and torques between a pair of molecules. Once these are known it is possible to implement *molecular dynamics* methods to integrate the equations of motion for the anisotropic particles in an appropriate thermodynamic ensemble.

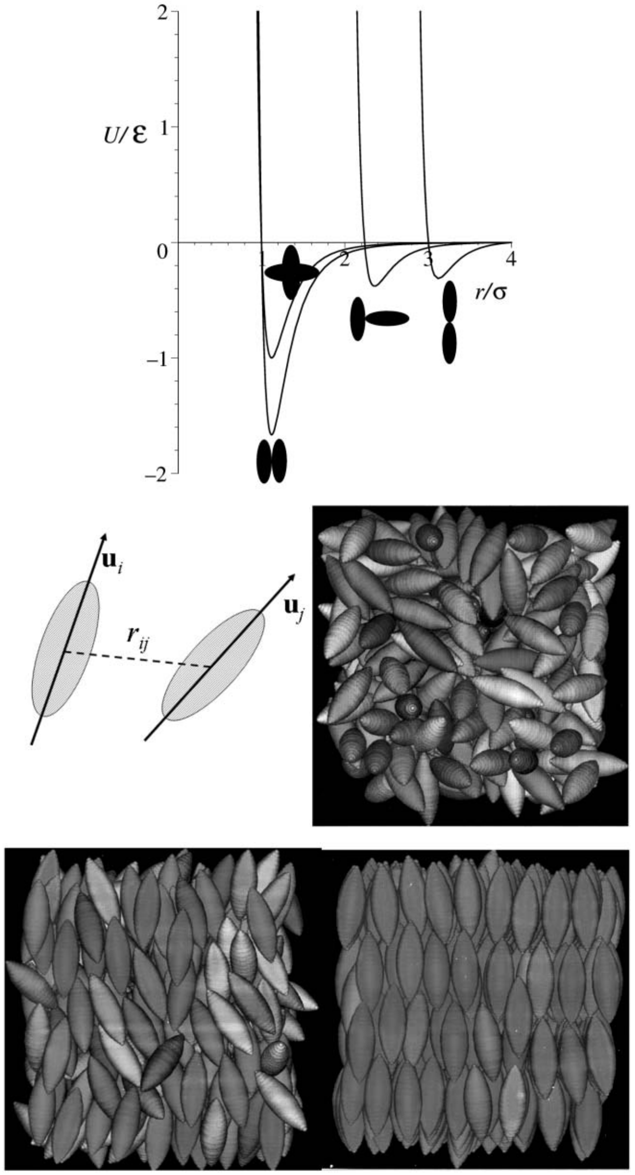

Fig. 3 Interaction potential for a Gay–Berne mesogen and snapshots of phases. The potential is plotted as function of distance, r_{ij}, for four fixed relative orientations defined by the vectors $\mathbf{u}_i$ and $\mathbf{u}_j$ (middle, left). One parameterisation only is shown from an infinite number of possible Gay–Berne potentials. Snapshots are shown for a Gay–Berne system, which exhibits liquid (middle, right), nematic (bottom, left) and smectic-A phases (bottom, right).

For the single site models mentioned above, it is relatively easy to add point dipoles or quadrupoles to the model potential. Doing so leads to rich phase behaviour. For example, the addition of a longitudinal quadrupole moment at the centre of a Gay–Berne induces the formation of a tilted smectic phase (SmC).[13] Tilted phases may also be formed from Gay-Berne particles with two suitably orientated outboard dipoles. In general the addition of a single dipole along the long axis will stabilize nematic behaviour if the dipole is towards the end of the molecule but will stabilize smectic behaviour if the dipole is in the centre of the molecule. An interesting striped smectic A phase (SmÃ phase) can also appear for molecules with the dipole at the end of the Gay–Berne particle.[12] Here there is strong correlation between neighbouring smectic layers. Increasing dipole strength can lead to a strongly interdigitated partial bilayer (smectic A_d) phase.

Beyond single site potentials two types of model have been developed which attempt to make a closer link with the structure of real liquid crystals: atomistic models and multi-site coarse-grained models.

Atomistic models use molecular mechanics potentials of the general form

$$E = \sum_{bonds} E_{\mathrm{bond}} + \sum_{angles} E_{\mathrm{angle}} + \sum_{dihedrals} E_{\mathrm{torsion}} + \sum_{i} \sum_{j>i} E_{\mathrm{nonbonded}} \quad (4)$$

in which the interaction energy is composed of intramolecular parts representing the bond stretching, bending and torsional energy; and intermolecular parts representing the nonbonded interactions. The latter usually involve electrostatic interactions modelled *via* a Coloumb potential and steric/van der Waals interactions modelled *via* a Lennard-Jones 12:6 potential. In *all-atom* models,[14] which are typical of modern force fields, nonbonded interactions run over all nonbonded pairs of atoms in the system, with each atom represented explicitly. In *united atom* models,[15] hydrogens attached to carbon are usually combined to provide a single *united atom* site. Although Monte Carlo procedures are possible, the simulation method of choice is *molecular dynamics*. Naturally, the computational expense of these models depends on the number of nonbonded pair interactions in the system. Typically a few hundred molecules would correspond to the current limits of the sizes of system that are possible today. This is a reasonably sized system for studying nematic behaviour but is rather small for other mesophases. So although atomistic models have the advantage of providing a detailed description of molecular interactions, including molecular flexibility, they have clear limitations.

Multi-site coarse-grained models, are designed as a way of retaining information about chemical structure (present in atomistic models), while limiting computational expense.[16] Atom-based potentials are typically replaced by a series of spherical or nonspherical sites (Gay–Berne particles or spherocylinders), which may be linked together with a series of potentials to model internal structure. Usually, these potentials are softer than those found in atomistic force fields, enabling simulation methods, such as molecular dynamics, to move through phase space more quickly. Often the coarse-grained sites can be chosen to mimic the different types of structural features in a real liquid crystal molecule, *i.e.* different types of molecular interaction (aromatic or aliphatic) and rigid or flexible molecular segments. There is however no consensus on the best technique to develop a coarse-grained model; methods vary considerably between research groups.

The real advantage of multi-site coarse-grained models is in the ability to look at complex macromolecular liquid crystals, such as liquid crystal polymers (LCPs) and dendrimers (LCDr). These cannot be simulated by other molecular based models, so the information provided on molecular structure in a liquid crystal phase, or dynamical processes or phenomena such as microphase separation, is invaluable.

3. Modelling across time and length scales

The models discussed above should be seen as covering a wide-range of lengths and time-scales. While bond motion happens rapidly on a femtosecond time scale and Ångstrom length scale, formation of smectic phases occurs on a minimum time scale of 10–100 ns for systems with hundreds or thousands of molecules. Some phenomena, such as the interaction of defects in nematics, are almost at the limit of what can be achieved with a molecular based model, and switching in liquid crystal displays is normally considered in terms of the motion of a liquid crystal director, rather than molecules. Two sets of successful "none molecular" modelling approaches are widely used for studying mesoscopic phenomena: these are nemato-hydrodynamics approaches and continuum modelling.[2]

In common with most forms of modelling, in liquid crystals there is a clear trade off between complexity of the potential and the desire to reach longer times and/or access larger length scales. This has been discussed in more detail in two recent reviews.[1,2] There is also a difficulty in modelling across the time and length scales in a coherent way. A real challenge for the next generation of liquid crystal simulations is how to transfer information between each level of modelling; and effectively link the different descriptions together.

The sections below discuss some of the recent developments in the three key areas of single-site-coarse-grained models, atomistic models and multi-site coarse-grained models.

4. Developments in single site coarse-grained models

The early simulations of single site off-lattice models provided the first "molecular level" pictures of how liquid crystal molecules were arranged in a bulk phase. In the early days it was sufficiently difficult to simply obtain liquid crystal phases within a simulation, but recent work has made it possible to be able to map out an entire phase diagram as a function of pressure and temperature; and to follow phase boundaries with a good measure of accuracy.[17] It is also possible to move to far larger systems sizes than possible in the early days. For continuous potentials, which can be integrated with molecular dynamics methods, parallelisation can be readily achieved making it possible to run simulations using many processors. This has opened up the possibility of simulated systems which would make no sense to study unless large numbers of molecules were present. Classic examples of this are the TGB-A (twist-grained boundary A phase), where simulation has shown the presence of grain boundaries and screw dislocation lines within the boundaries;[18] and simulation of defects around colloidal particles, where the presence of defects leads to interaction between the colloidal particles through the distortion of the liquid crystal director.[19]

The relative simplicity of single site potentials has made them the ideal testing ground for the development of methods for the prediction of material properties. Here, it is necessary to use statistical mechanics to make a link between microscopic coordinates and bulk material properties. A good example is provided by the elastic constant work of Allen and co-workers.[20] For bulk nematics three elastic constants exist: splay (K_{11}), twist (K_{22}) and bend (K_{33}). These govern the ease of distorting the director in three different modes of deformation, and so are important in all electro-optic devices that depend on changes of the director alignment (including all displays). There has also been success in producing techniques to calculate viscosity coefficients for nematics, including the important rotational viscosity, γ_1. Here, a wide range of methods are available using equilibrium molecular dynamics, based on the mean squared displacement of the liquid crystal director or fluctuations in the director angular correlation function; and some non-equilibrium methods.[21] An interesting discussion of the various expressions and methods, which can be employed to calculate material properties has been provided by Allen and Masters.[22]

With the developments described above it might seem reasonable to look at ways of tuning single site potentials to better reflect the interactions of real thermotropic mesogens. This would allow for the study of how material properties are influenced by changes in molecular interactions. Some attempts have been made to do the first part of this for Gay–Berne particles by fitting to *ab initio* or atomistic potentials.[23] However, it should be stressed that work in this area has been rather limited and there are distinct problems to be overcome. One major problem is the fact that the density change at a isotropic–liquid crystal phase transition for single site potentials is typically large ($\sim$10% or more) whereas in real low molecular weight liquid crystals this is small ($\sim$1% or less). This factor become even more problematic as molecular length increases. It may yet be possible to overcome this problem and to this end it is useful to mention two recent approaches. In the work of Paramonov and Yaliraki[24] a new pair-potential is written, which can more effectively be tuned to model the interactions between two mesogens than a Gay–Berne. In the work of Muccioli and Zannoni, a Gay–Berne can be adapted to allow it to change shape.[25] Shape changes mimic real mesogenic molecules, which are often able to adopt a different weighting of molecular conformations in a liquid crystal bulk phase compared to a liquid. So it seems appropriate that a potential for thermotropic mesogens should also allow molecules to change shape slightly in going from one phase to another. The same phenomena has been noticed from results of atomistic simulation (see below) and may be one of the reasons responsible for the smaller density change seen in real thermotropic mesogens.

5. Developments in atomistic simulation models

Most of the early atomistic simulations of liquid crystals shared the problem of being hampered by a lack of computer time. This was manifested in the ability to run only a few state points corresponding to a few different temperatures, and the inability to show thermodynamic stability by running for long enough to transform a nematic phase to an isotropic phase, or *vice versa*. None-the-less even in the early atomistic simulations, setting up simulations in a pseudo-nematic configuration and attempting to equilibrate from there, produced some useful insights into the behaviour of molecules in nematic fluids. Here, it was discovered that there is a strong coupling between molecular structure and phase behaviour.[14,15] For example, the dihedral angles for an alkyl chain attached to a phenyl ring exhibit an odd–even effect, such that *gauche* conformations of even dihedral angles normally allow the chain to lie along the molecular axis (favoured in a nematic), while *gauche* conformations of odd dihedrals lead to the chain lying at an angle to the molecular axis (disfavoured in a nematic). Such an effect was predicted by molecular field theory and often manifests itself in a similar odd–even effect in transition temperatures seen experimentally.[14]

Recent atomistic work has benefited by the huge increases in computer power seen over the last decade. It is now possible to grow a nematic phase from an isotropic liquid, thereby demonstrating thermodynamic stability.[26] For united atom models without the complication of partial charges, this appears to occur relatively easily within around 10–15 ns, as shown in the work of the work of McBride *et al.*[15] and Hanna *et al.*[27] However, for fully atomistic models, with long range partial-charge interactions, the time scales required appear to be longer. Zannoni has specifically looked to predict transition temperatures for systems of a series of molecules which exhibit an odd–even effect.[14] Here, starting from a nematic and looking for the transition to an isotropic liquid required runs of approximately 50 ns close to the transition. Peláez and Wilson have considered quenching an isotropic phase for two systems. Here in one case, runs of 100 ns were required to see the full growth of the nematic phase for a system of 256 molecules in a liquid crystal mixture (Fig. 4).[28]

Of crucial importance to accurate simulation is the pair potentials used. The current generation of force fields available today are now considerably improved in their predictive capacity. Good quality *ab initio* quantum mechanical calculations using the MP2 method or density functional theory (DFT) now provide quite good quality intramolecular potentials for a wide range of molecular structural features. In particular, dihedral angle potentials, where small energy changes in energy corresponding to rotation about a bond can lead to radically different molecular shapes (and hence different packing of molecules in a liquid crystal phase) are predicted well.

As mentioned above, a few hundred molecules is sufficient to provide a reasonable representation of a nematic and for this reason most atomistic simulation has concentrated on this phase. However, it could be argued that in terms of what

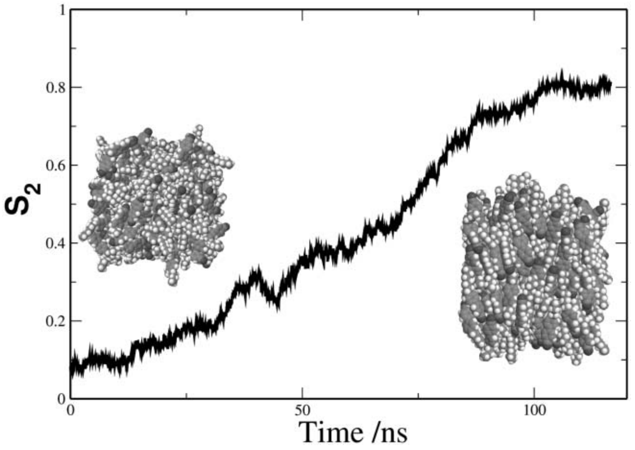

Fig. 4 Growth of a nematic phase from an isotropic liquid phase for a liquid crystal mixture, E7, simulated with an all-atom model. The graph shows the growth of the orientational order parameter, $S_2 = \langle P_2(\cos(\mathbf{n}.\mathbf{u}))\rangle$ for the molecular long axis vector u and the snapshots illustrate the molecular order in each phase. Figure taken from ref. 28, reproduced by permission of the PCCP Owner Societies.

molecules themselves are doing, atomistic simulations may well play a more important role in providing better understanding of more complex phases in the future. There are a few recent examples of this. Early simulations of smectic phases have been published;[29] and the first simulation of the recently discovered biaxial nematic phase in a low molecular weight material, showed very unusual ordering of molecules into ferroelectric domains.[26] As yet, what can be achieved is severely limited by system sizes but it would be extremely interesting in the future to get a "molecular picture" of the ordering of molecules in banana phases; or spontaneous layer polarization in ferroelectric and antiferrorelectric smectic-C phases; or even to get a better picture of molecular packing, the degree of flexibility and the relative ordering of the molecular core and alkyl chains in tilted smectic phases. It is immensely difficult to get experimental probes of this type of molecular behaviour, and so simulation is likely to provide the major breakthroughs here.

A crucial element of modelling fluids is the ability to predict the density of the phase as accurately as possible. For liquid crystals it is not reasonable to obtain suitable intermolecular potentials from quantum mechanics. Firstly, even the best quantum mechanical calculations for molecular pairs will miss part of the correlation energy and this is reflected in a lack of dispersion interactions. Secondly, for today's level of available computer power, liquid crystal simulations at the nanosecond time scale are restricted to pair potentials, *i.e.* polarizability and many body interactions are ignored. So in order to obtain a good prediction of the density it is necessary to "lump" these missing interactions into effective pair potentials. (Indeed, many potentials such as the OPLSA-AA force field of Jorgensen are specifically fitted to reproduce the density of simple molecular liquids.)

For soft single site molecular potentials (above) it was noticed that phase changes invariably were more sensitive to the density than to the temperature. The same is true for atomistic modelling. Consequently, if the density predicted in a nematic phase is too high by a few percent, the order parameters predicted from the simulation will be larger than the experimental ones, the nematic range will be extended, the clearing point will be too high and the temperature dependence of the order parameter will not be correct. While there have been attempts to produce force fields specifically designed for liquid crystal molecules,[30] it seems clear than much more is required to advance to the next level of predictive capacity.

A potential valuable feature of atomistic studies is the ability to make predictions for materials properties. For atomistic models of liquid crystals accurate prediction is still in its infancy. None-the-less, some recent progress has been made by borrowing techniques, which were originally developed for single site models (discussed above). Some success has been achieved for key material properties of bulk nematics, such as rotational viscosity[31] and flexoelectric coefficients. Based on work from single site potentials, it is unlikely that atomistic models can yet be used to obtain elastic constants, until system sizes can be readily extended to a few thousand molecules. The best techniques for elastic constants rely on wavevector dependent director fluctuations, and best results are achieved if the director can be constrained (not easy in atomistic modelling) and/or simulations sizes are large enough to allow successful extrapolation to the low $|\mathbf{k}|$ limit.

An interesting area of material property prediction has been helical twisting powers for chiral dopants. If a normal nematic is doped by a small quantity of chiral material, the whole phase becomes chiral with a pitch P. The helical twisting power of an individual molecular species is measured by

$$\beta_M = (P c_w r)^{-1}, \tag{5}$$

where c_w is the weight concentration of the chiral molecule in a liquid crystal. A number of methods have been developed with predictive capacity for β_M, but in the most successful it is not even necessary to simulate the bulk liquid crystal. Instead it is possible to calculate a measure of the chirality for a single molecule (the two used commonly are termed the *chirality order parameter* or the *scaled chirality index*), which can be successfully used to calculate β_M.[32] These methods are sufficient quick and accurate that simulation can here be used to screen chiral molecules to look for high helical twisting powers prior to (a possibly) lengthy synthesis.

6. Developments for multi-site coarse-grained models

Coarse-graining can be carried out at a variety of levels. Here the most important choice is in terms of "throwing away" more or less chemical detail. This is reflected in some of the recent progress made in this field. At the more "chemical" end of the spectrum, there is the coarse-grained models of Wilson and co-workers[1,33] for liquid crystal dimers, polymers and dendrimers, which keep a high level of chemical detail by coarse-graining chains in terms of united atoms and rigid parts of the molecule in terms of Gay–Berne particles. At a less chemical level, there is the possibility to coarse-grain beyond united atoms to the level of rods and spheres following the approaches of Glotzer and co-workers for tethered nanorods,[34] or Wilson for dendrimers[1] or Al Sunaidi *et al.* for polymers.[35] Here some chemical details are lost but the key structural features of the molecule (*i.e.* the rigid and flexible constituent parts and their molecular connectivity) are kept.

In most types of coarse grained model, formation of liquid crystal phases can be a time consuming process, relying on slow self-organisation. The preferred simulation methods have tended to be molecular dynamics and Langevin dynamics. The latter introduces a stochastic element, which may be useful in improving sampling of phase space. The work of Al Sunaidi *et al.*[35] uses a dissipative particle dynamics (DPD) approach. Here, the underlying potential is ultra-soft in nature, meaning that particles can, in principle, pass through each other. (This is realistic if one considers that coarse-grained particles represent group of atoms.) In practice the softness of the underlying potential means that DPD models allow for a longer time step than can be used in conventional molecular dynamics models, in addition to a stochastic element in the dynamics. This is designed to allow for much faster equilibration of mesophases. Indeed this has been shown rather nicely in an early simulation of an A–B block co-polymer, which formed a lamellar phase, a perforated lamellar structure, hexagonal rods and micelles, depending on the amount of A and B present in the chain.[36] One problem for DPD-type models of thermotropic phases, is that in the absence of anisotropic attractive forces, mesophase formation often relies on excluded volume effects, *i.e.* mesophase formation is driven by the competition between translational entropy (maximised when molecules are aligned) and rotational entropy (maximised when molecules are free to rotate). Softening potentials greatly reduces excluded volume effects and so much of the driving force for mesophase formation is removed.

One of the successes of the more chemical coarse-grained models is the ability to obtain information about the molecular structure within a macromolecular liquid crystal. This is illustrated in Fig. 5, which shows the arrangement of constituent parts of a liquid crystal side-chain polymer. As a smectic-A liquid crystal phase starts to form, the polymer backbone is excluded from the liquid crystal layers with a resulting change in the radius of gyration of the backbone. The flexible spacer, which links main chain and liquid crystal forms a sheath around the polymer backbone.

Coarse-grained models of the types discussed here have their counterpart in several related fields of study. Of major interest are coarse-grained models of lyotropic systems and membranes. Usually in such systems, anisotropic potentials are eschewed in favour of different types of spherical sites used to model hydrophobic and hydrophilic interactions. A classic example of such a model is provided by the work of Marrink and co-workers.[37] Here, it is possible to use a coarse-grained lipid model with a single site solvent model (a solvent molecule here corresponds to 4 real water molecules) to predict the formation of lamellar and non-lamellar phases. Model membranes formed from such models are of particular interest and present work is providing valuable insights into membrane phenomena such as the formation of pores and lipid rafts.

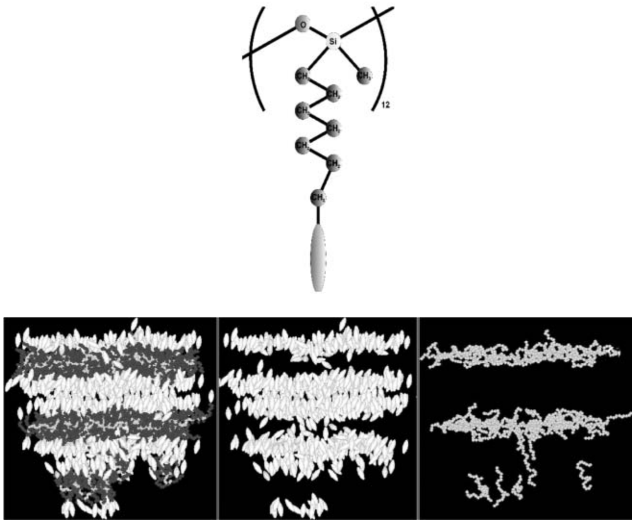

Fig. 5 Top: schematic diagram of a coarse-grained multi-site simulation model for a side-chain liquid crystal polymer. Bottom: snapshots from a simulation of a side-chain liquid crystal polymer showing the formation of smectic liquid crystal layers.[33] The centre and right hand diagrams show a decomposition into mesogenic units and the polymer backbone respectively.

Finally, it is worth considering methods for carrying out coarse-graining. In the main, coarse-grained models for liquid crystals have tended to be empirical and only a few systematic attempts have been made to coarse-grain from atomistic level detail. However, considerable progress has been made in the related field of polymer simulation[38] and it is likely that many of these ideas can be used for liquid crystal work.

7. Conclusions

This tutorial review describes some of the progress made in computer simulations of liquid crystals from the early development of lattice models, to off-lattice coarse-grained models and atomistic modelling. These studies have provided reference models for studying structure and dynamics, and have provided valuable insights into molecular order within nematic and smectic phases.

The role of ever-increasing computer power over the next few years should not be overestimated. It would certainly be wrong to suggest that the major discoveries have already been made. Some of the newest developments outlined above, point to interesting possibilities for the future. These are likely to include better prediction of material properties; a better understanding of banana phases and complex smectics; a better understanding of the role played by molecular chirality; a more sophisticated understanding of molecular structure in complex liquid crystals formed by macromolecular systems and polyphilic molecules; and an improved picture of both structure and dynamical processes in model membranes.

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