

ABSTRACT

We present a brief survey of techniques for modelling polymers, with particular emphasis on the multiscale approach as applied in our laboratory. The measurable properties of polymers depend on a structural hierarchy which ranges from chemical detail, to single chains, to aggregates of chains and up to continuum phenomena. Therefore, complete description of a polymer requires a model encompassing a wide range of length- and time-scales. This would take large amounts of computing resources and also produce redundant detailed information. In practice, coarse-grained models are used in place of fully atomistic representations to extend the time- and length-scales accessible to simulation within reasonable computing times. A process of reverse mapping may then be used to recover fully atomistic detail from the coarse-grained model, bridging the gap between modelling large-scale processes and chemical detail. This survey includes a number of examples of polymer modelling at various levels of detail, and illustrates the application of the reverse mapping process.

1. Introduction

Multiscale modelling is a valuable tool in polymer science for exploring the structure and dynamic behaviour of these materials, allowing a wide range of length and time scales to be probed by mutually interlocking models. Our purpose here is to demonstrate the multiscale approach in action, but by drawing on examples predominantly from the work of the Cambridge group. It has been applied to a wide variety of problems including polymer welding, block copolymer morphologies, and the evolution of liquid crystalline polymer textures. The prediction of an X-ray diffraction pattern from a model structure as part of a process of structure refinement is a widely used aspect of computer simulation. An example from the Cambridge group and collaborators is its application by Welsh and Windle [1] and Welsh, Blundell and Windle [2, 3] to the investigation of structural ordering in random copolyesters: Figure 1 shows an example of experimental and predicted X-ray patterns from their work. The simulation of diffraction patterns and methodology of structure refinement is already a very familiar topic to the fibre diffraction community. Therefore, our aim here is to concentrate on some techniques involved in the modelling of polymers and, in particular, on what a multiscale approach has to offer.

2. Hierarchical Models in Polymer Science

The observable properties of any polymer depend on a hierarchy of structure including: chemical detail at the atomistic level, individual chains, microscopic features involving aggregates of chains such as lamellae and spherulites, up to continuum phenomena at the macroscale. Therefore, the complete description of a polymer typically requires a wide range of length scales from the chemical bond, at around one Angstrom in length, up to chain aggregates extending for many hundreds of Angstroms and beyond. There is also a wide range of timescales, with chemical bond vibrations occurring over tens of femtoseconds and, at the other extreme, collective motions of many chains taking seconds, or much longer. Computer simulation of the macroscopic behaviour of a polymer system in principle could include all chemical detail. However, this would take an inordinate amount of computer resources for anything other than small models over short times. Furthermore, it can also introduce a degree of redundancy, as some of the detailed information is irrelevant to macroscopic phenomena. In practice, models therefore concentrate on a narrow length scale by simplifying the picture to isolate a particular structure or process. Coarse-grained models are used in place of fully atomistic representations to extend the time and length scales

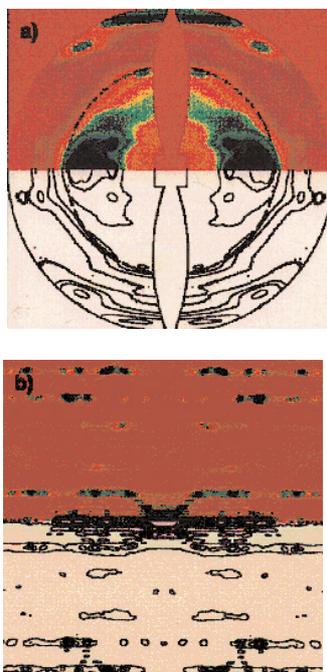


Figure 1: Diffraction patterns from 50% PET/PEN random copolymer: a) experimental pattern mapped into reciprocal space; b) pattern from 3D model. Data extend to 0.5\AA^{-1} in both the vertical and horizontal.

accessible to simulation within reasonable computing times. A process of *reverse mapping* can then be used to recover fully atomistic detail from coarse-grained models generated during a simulation. In this way the gap between modelling large scale processes and chemical detail may be bridged. Figure 2 summarises the relationship between the hierarchy of structures of interest in the study of polymers and the associated modelling hierarchy.

We will begin this survey with an example of modelling at the atomistic level to predict the persistence lengths of polymer chains having specific chemistries, later seeing how the results from this are required as input parameters for microscale models of liquid crystalline polymers.

3. Modelling at the Atomistic Level

Monte Carlo on Chains with Chemical Detail

In the development of synthetic liquid crystalline polymers, the aim is to design molecules that while being sufficiently stiff to form an ordered mesophase, also possess enough chain flexibility for

^a Persistence length (q) is the end-to-end distance of the chain projected onto the first bond vector, averaged over all chain configurations, illustrated in figure 3.

^b Persistence length ratio or persistence ratio is the ratio of persistence length (q) to chain diameter (d), where d is defined as the largest diameter cylinder that can be accommodated inside the unit cell of the polymer in question.

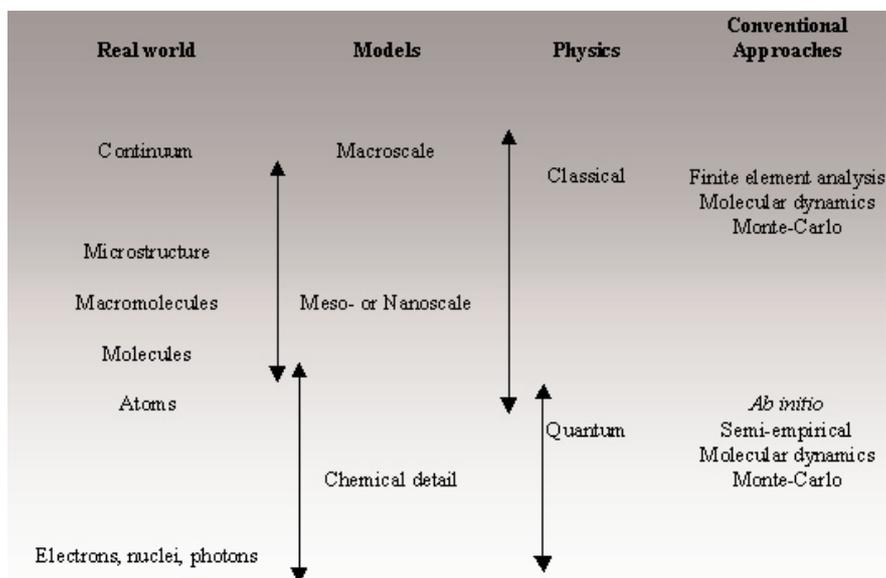


Figure 2: Relationship between modelling and structural hierarchies.

the melting point to lie within the range of practical processing temperatures. Typical means of achieving these properties include the use of flexible alkyl spacers, random copolymerisation to disrupt chain periodicity, or the substitution of bulky side groups onto aromatic rings.

Bedford, Yu and Windle [4] set out to find a simple yet effective parameter for predicting the tendency of a molecule to form a liquid crystalline phase, its *mesogenicity*. A parameter was required that could be derived from a chemically detailed molecular model so that it could potentially be used to target suitable molecules for synthesis of liquid crystalline polymers. Precedents observed in the choice of a candidate parameter were the lattice model of Flory and co-workers [5] which predicts liquid crystallinity for short rigid rods on the basis of their axial ratio, and the use by Kratky and Porod [6] of the persistence length^a (q), illustrated in Figure 3, as a key parameter for describing semi-flexible worm-like chains. Accordingly, the first parameter to be assessed was the persistence length ratio^b (q/d).

Bedford *et al.* [4] restricted the model to a single isolated chain in order that full chemical detail could

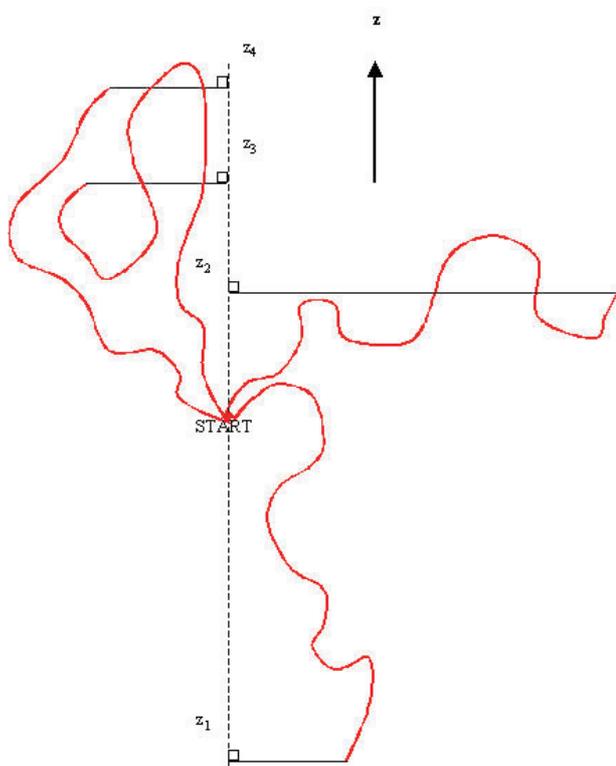


Figure 3: A set of worm-like chains drawn with a common starting direction, showing the persistence length defined as the mean displacement of the chain ends in the direction of the first bond, i.e. $q = \langle z_1 + z_2 + z_3 + z_4 + \dots \rangle$.

be considered, thus ignoring the orientating effects of neighbouring molecules, and thereby underestimating the persistence length in a condensed phase. Isolated chains were simulated in a three-step process: first, the polymer chain was built using mean monomer geometries from the Cambridge Crystallographic Data Bank, or from published *ab initio* calculations on fragments and experimental data; next, the structure was optimised using the CERIOUS molecular mechanics software to assign rotational energy profiles to all non-ring backbone bonds; finally, a Monte Carlo simulation was used to assign rotational angles to the bonds at a given temperature and thus generate many possible examples of the molecular trajectory from which the average persistence length ratio (q/d) could be determined.

The model was applied to a series of thermotropic aromatic polyesters (PES, HBA/HNA, HBA/IA/HQ, and B-ET) of known nematic to isotropic phase transition temperature. Simulations of these polyesters revealed that those in the liquid crystalline phase had a persistence length ratio exceeding five, pointing to this as an approximate critical value for isolated chains. In a further investigation, with a set

of liquid crystalline polymers based on random copolymers of chlorohydroquinone, terephthalic acid and kinked meta-substituted Ph-X-Ph units, where X is $C(CH_3)_2$, SO_2 , S, CH_2 , or O, liquid crystallinity was again found to coincide with a predicted persistence length ratio exceeding five.

Very stiff polymers will have a nematic to isotropic transition temperature exceeding the degradation temperature. However, if a critical persistence length ratio for mesogenicity is known for the type of polymer in question, the atomistic Monte Carlo simulation can be used to predict the nematic to isotropic phase transition temperature. This predictive aspect of the model has applications in the generation of phase diagrams and in forecasting the nematic to isotropic phase transition temperature in candidate molecules for synthesis.

The persistence length ratio was used in the previous example as a measure of straightness in the context of a semi-flexible worm-like chain model. However, when considering a Kuhn chain model, *i.e.* a series of rods separated by flexible spacers, problems are encountered in the use of persistence length ratio as a predictor of mesogenicity. Completely flexible links would allow the rigid units to double back on themselves, giving rise to a very small persistence length ratio despite this arrangement providing an effective contribution to mesogenicity. With this problem in mind, Bedford *et al.* [4] looked at the turn-round length^c as an alternative predictor of mesogenicity for Kuhn-like chains. In the case of a smooth worm-like chain, the turn-round length (L_{tr}) is equal to the persistence length.

Bedford *et al.* [4] modelled a series of main chain liquid crystalline polymers containing flexible sequences of $(CH_2)_n$ in an otherwise rigid backbone. Both q/d and L_{tr}/d were measured for isolated chain models built at the transition temperature. Critical q/d was found to drop below five as the length of the flexible spacers increased, despite liquid crystallinity being observed under these conditions. However, L_{tr}/d was found to be much less dependent on the length of the flexible spacers, remaining at around five as the number of CH_2 groups increased. Therefore, it appears that L_{tr}/d is a better measure of mesogenicity across a range of real molecules that lie between worm-like and freely-jointed extremes.

^c Distance to the first reversal in the direction of an isolated chain with respect to the first link.

In further work, He and Windle [7] applied the Monte Carlo simulation described above to the calculation of persistence lengths in aromatic polyamides. A variety of experimental methods may be used to determine persistence length including light scattering, flow birefringence, viscosity, optical anisotropy and SANS, but the result depends on the method of measurement. Furthermore, interaction between solvent and polymer alters persistence length. Resonance effects in the central C-N bond of the amide group in polyamides, together with partial charges due to protonation by the solvent result in a straightening of the chain, giving higher persistence lengths in solution than in the condensed phase. For this reason lower and upper bound persistence lengths were simulated: the lower bound corresponding to chains in the isotropic melt, and upper bound to those in a strongly interacting solvent.

Atomistic simulation of polymers is limited by the currently available computer resources to small models involving only a few chains over, at most, a nanosecond timescale. However, dense polymer systems exhibit a wide range of structure from the atomistic up to the macroscale, and intermediate levels but full atomistic simulation of dynamic processes involving nanoscale structures and above would require excessive amounts of computing resources. To overcome this problem, a suitable coarse-grained model can be constructed, which disregards atomistic detail and instead, represents the polymer by units corresponding to groups of atoms, monomers or chains, depending on the scale of the model. The structural units are chosen to represent essential collective features of the polymer in question; for example a persistence length or a chain coil diameter in nanoscale modelling, or, at the microscale, groups of chains in for example liquid crystalline polymer domains. The latter case will be discussed in section 5 of this paper, where we will look in detail at the modelling of nematic liquid crystalline polymers. First, we will concentrate on amorphous polymers with a look at a further level of simplification to aid simulating dense polymer systems, in which the coarse-grained modelled units are restricted to lie on a lattice in the *lattice chain model*.

4. Moving up a Level to the Nanoscale

The lattice chain model

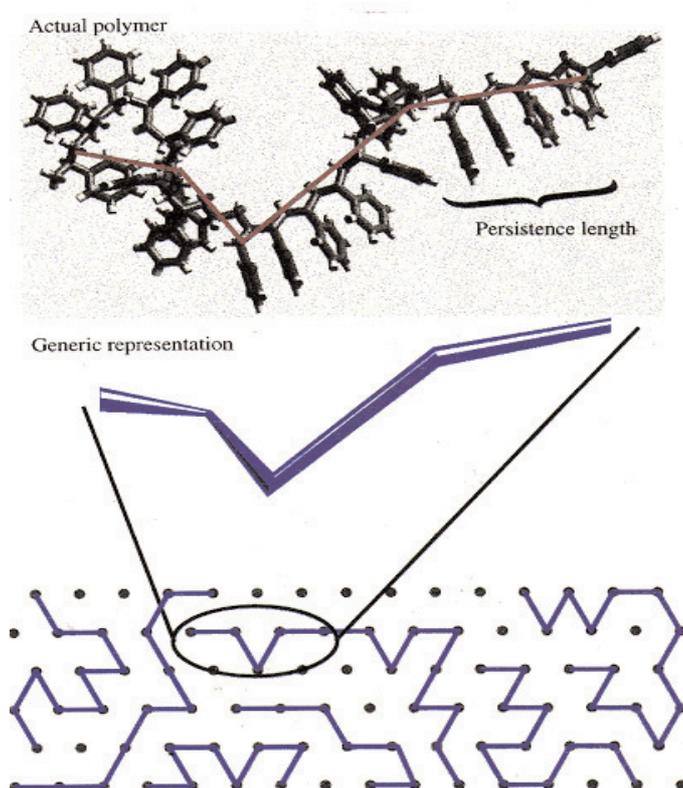


Figure 4: Lattice chain model with the persistence length as the modelled unit.

The scope of a computer simulation may be extended by increasing its efficiency, allowing longer length scales to be probed for greater times. One way of realising this is by restricting the modelled units to lie on a lattice so that self-avoidance is achieved in a straightforward manner. This is the so-called *lattice model* and for polymers, the modelled units can represent atoms, monomers, entire molecules, or assemblies of molecules. The lattice points may be separate, as in for example the modelling of microstructures in nematics, and these will be described in section 5. Alternatively, a polymer chain can be modelled as a set of interaction centres occupying the vertices of the lattice. At the next level of complexity, the polymer chain may be modelled by a set of connected beads, each occupying a lattice site, with the distance between neighbouring beads set, for example, at the persistence length as demonstrated in Figure 4. A bead may represent either a single atom or groups of atoms interacting with bonded and non-bonded neighbours: examples of this applied to polymer welding and microstructures in block copolymers appear in sections 4.2 and 4.3 respectively.

Lattice models can be used to simulate static and dynamic properties. In the static model, the polymer is 'grown' on the lattice according to specified rules, for example by a self-avoiding random walk.

Dynamic behaviour may then be studied by defining rules permitting moves that are physically possible in the real polymer system. The simplicity of the lattice model allows rapid examination of a large number of possible configurations. Alternative chain conformations are created by incorporating vacant lattice sites into the model and allowing these to exchange position with adjacent occupied sites, without breaking chain connectivity. A variety of algorithms has been used in defining sets of rules governing permitted moves to generate new conformations. Simulation is carried out by picking out a lattice site and one of its neighbours at random. If the chosen pair of sites contains a lattice point and a vacancy then a move is attempted, otherwise the attempt is considered to have failed.

In the multiscale approach, lattice model simulations are calibrated so that the timescale of moves on the lattice is proportional to that of a fully atomistic model of the same system. The calibration is done by running an equivalent molecular dynamics simulation on an atomistic model and comparing dynamic properties over the short times accessible to the more detailed model. Additionally, the length scale of the lattice model may be calibrated against the fully atomistic model so that, in principle, a fully atomistic version in continuous space can be recovered from the discrete lattice model. An example of this reverse mapping process is described in the next section where it is applied to the time calibration of a model of chain diffusion in polymer melts.

4.1 Monte Carlo Lattice Model with Reverse Mapping Using Molecular Dynamics

Haire, Carver and Windle [8] showed how a coarse-grained Monte Carlo lattice chain model, applicable to dense polymer systems and previously applied solely to static processes, is valid for studying longer-range dynamic processes such as phase segregation, and welding. Furthermore, they showed that the correct scaling behaviour for the diffusion coefficient, mean square displacement of both the central atom of each chain and of the centres of mass of the chains, and relaxation in orientation can be obtained for both isolated chain and dense polymer melt models. Haire *et al.* [8] calibrated the motions of the *on lattice* chains by interlocking the coarse-grained approach with a fully atomistic molecular dynamics model. This enabled a modelling range from atomistic detail up to the mesoscale to be

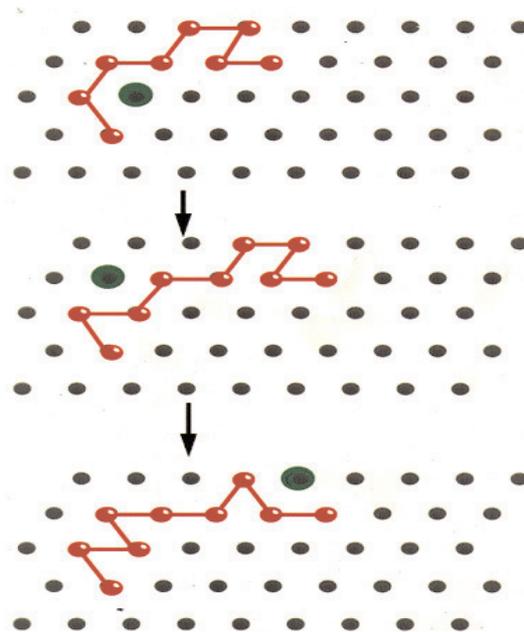


Figure 5: A example of multiple segment movements allowed by a set of chain self-avoidance rules.

covered and corresponds to a range of timescales covering six orders of magnitude from picoseconds up to microseconds.

The system was modelled according to the FCC lattice chain model in which each polymer is represented by a set of connected beads on 3D, cubic F lattice. The cubic F lattice was chosen because it has a coordination number of 12, higher than that of either the primitive or body centred cubic lattice, allowing the greatest number of possible conformations with the least coarse quantization of the bond angles. The unit of time used was the Monte Carlo *step*, defined by the average number of moves required to visit each lattice site once. The Monte Carlo steps can be correlated to real time in systems with physical move sets. The set of self-avoidance rules governing the movements of the beads on the lattice accommodate multiple chain segment movements as illustrated in Figure 5. Haire *et al.* [8] examined the suitability of this model for studying long-range dynamic processes in both isolated chains and dense polymer melts. In the single isolated chain case the centre of mass diffusivity (D) and the relaxation time of the chain end-to-end vector (τ_R) were calculated from simulations for a range of chain lengths (L). The model was found to agree well with predicted dependence of D and τ_R on chain lengths, *i.e.* the power laws applicable to Rouse dynamics under conditions of excluded volume were obeyed, *i.e.* $D \propto 1/L$.

In the case of a dense multiple chain system, equivalent to a polymer melt, the motion of any one chain is restricted by those around it. As the chain lengths are increased, each chain becomes more confined and the dynamic behaviour is expected to move from Rousean to reptative. Haire *et al.* [8] studied the dynamic motion of individual beads as a function of simulation time in terms of the mean square displacement of the central atom of each chain ($g_1(t)$) and the mean square displacement of the centre of mass of a chain ($g_3(t)$). Reptation theory predicts that in dense melts of polymers exceeding the critical entanglement length, $g_1(t)$ should exhibit five different power laws. These correspond to five different dynamic regimes ranging from very short times where individual chain beads move independently of the rest of the chain, to very long times involved in centre of mass diffusion. The simulated motions of individual beads were found to agree with the predictions of reptation theory within the limitation imposed by the model that the beads can only move in discrete steps between lattice sites. Smaller steps are inaccessible to the model and correspond to timescales where each bead is not influenced by its connection to the rest of the chain. Reptation theory predicts three power law regimes for the centre of mass motions. As with the single bead motion, the centre of mass motions were found to deviate from those predicted by reptation theory at short times due to insufficient time resolution. Centre of mass diffusivity was calculated for a range of chain lengths and was found to obey the predictions of reptation theory for chains over 150 repeat units long i.e. $D \propto 1/L^2$.

Having ascertained the suitability of this lattice chain model for studying long range dynamic processes, Haire *et al.* [8] calibrated it using an atomistic molecular dynamics simulation. The lattice model chain dynamics are described in terms of Monte Carlo time steps, which enables trends in dynamic properties to be studied at the mesoscale level, but does not give quantitative results for any particular polymer. Calibration of length and timescales may be done by running equivalent lattice model and atomistic molecular dynamics simulations for the short period of time the latter can simulate. Haire *et al.* [8] gave an example of this calibration for polyethylene (PE). First, a lattice model was generated with realistic PE chain packing density and characteristic ratio while keeping the number of backbone atoms per lattice point to a minimum to achieve the most realistic match between the lattice

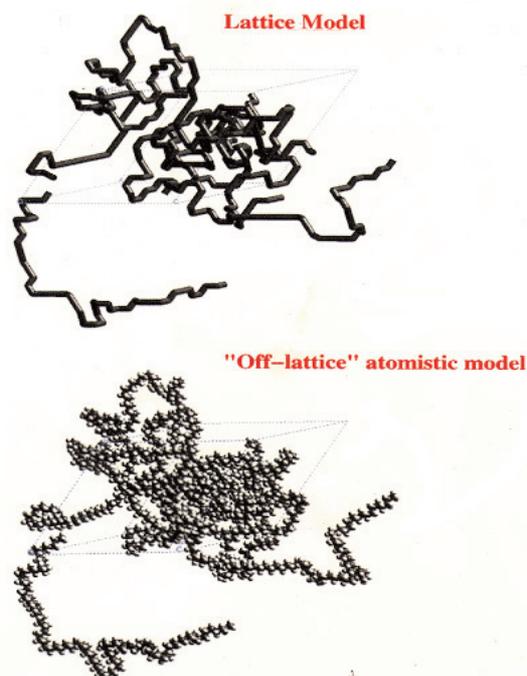


Figure 6: Reverse mapping.

model and the atomistic molecular dynamics. Optimisation of these parameters gave a spatial calibration of one lattice spacing equal to 5\AA . The size and chain dimensions of the lattice model were chosen so that the equivalent simulation run in molecular dynamics would not be prohibitively long. An equivalent off-lattice model was then generated from an equilibrated lattice model configuration as illustrated in Figure 6. The lattice sites were used to map an atomistic fragment, composed of two monomer units of PE, onto the atomistic chain model. The mean square displacement of the chain ends and centre of mass motions were then calculated as a function of time in the molecular dynamics simulation, and as a function of Monte Carlo steps in the lattice model simulation. The chain motion parameters from both simulations were then plotted on the same graph and those from the Monte Carlo lattice chain model were shifted along the time axis to give the best fit to the molecular dynamics data. In this way, a time calibration of one Monte Carlo time step was found to be equivalent to 3.0ps of real time, which compared to a typical molecular dynamics times step of 2fs is an increase by a factor of 1500.

4.2 Application of the Monte Carlo Lattice Model to Polymer Welding

The Monte Carlo lattice chain model, verified by Haire *et al.* [8] for application to long-range dynamic processes, was applied by Haire and Windle [9] to

the simulation of welding of linear polymer chains. The process of polymer welding can be described as the diffusion of chains across the interface formed when two hard planar surfaces are brought together. The welding process is deemed complete when the region of the weld has all the characteristics of the bulk polymer. A model was constructed with a mono disperse polymer system having no interaction energies, which corresponds to the welding of compatible polymers well above the glass transition temperature. Time calibration of the model allowed prediction of the intrinsic weld time. The progress of the simulated weld was monitored by the total number of beads (B_{tot}) to have crossed unit area of the original interface. A weld was considered complete when B_{tot} reached a constant value, and the time taken for this to occur was referred to as the *intrinsic weld time*. An example of the behaviour of B_{tot} is shown in Figure 7 with a plot of B_{tot} versus time for two welds, one formed between two homopolymers composed of chains 50 beads long and the other formed between 200 bead chain homopolymers. In both cases, B_{tot} can be seen to increase until a plateau is reached. In the region between 10^2 and 10^5 Monte Carlo steps, B_{tot} obeys a $t^{1/4}$ power law predicted by reptation theory to be characteristic of the welding process.

Haire *et al.* [9] also used these simulations to study the shapes of the polymer coils and their distortions at the weld interface. This was done by considering the distribution of beads in the chains. Welding is initially driven by the relaxation of chain coil distortions at the interface imposed by the surface before contact. As welding proceeds, the chain coils relax back towards their equilibrium shapes and orientations. The intrinsic weld time was compared to the end-end relaxation time in the bulk polymer, and the two values were found to be very similar. From this it was concluded that the intrinsic weld time is the relaxation time of the end to end vectors in the bulk polymer, agreeing with the suggestion of Wool *et al.* [10] that weld time is that time taken for a chain to completely renew its conformation.

4.3 Application of the Monte Carlo Lattice Model to Modelling Block Copolymers

If the two components of a diblock copolymer are incompatible then phase separation is favoured, but cannot occur due to chain connectivity. Instead, microphase separation takes place producing

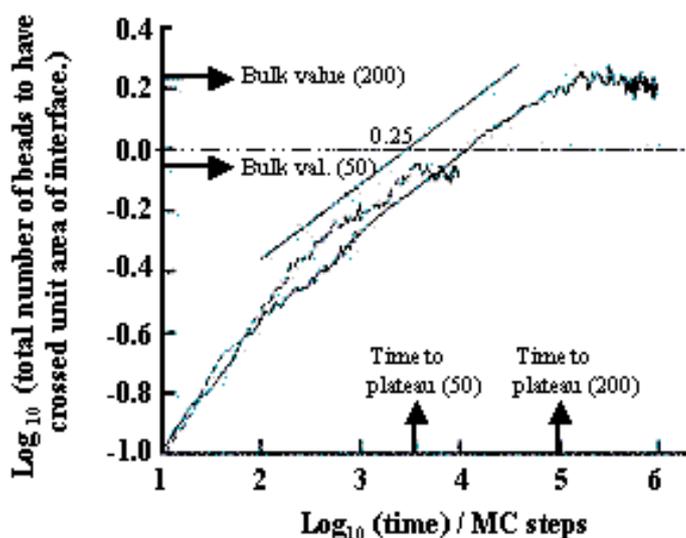


Figure 7: Characteristics of a weld: the total number of beads to have crossed the interface as a function of weld time (redrawn from [9]).

microdomains, which in many cases are highly ordered. This is typical of self-organizing phenomena and can lead to lyotropic liquid crystalline phases when there is a rigid rod polymer chain architecture. The trajectories of chains during the formation of domain structure in diblock copolymers are very difficult to determine experimentally. Computer simulation techniques are an excellent complementary approach, but have been limited in that they are unable to analyse the full size range of interest from chain conformation up to microdomain morphology. Molecular dynamics is useful for studying processes in atomistic detail, but at the much larger microdomain scale the computing time required for atomistic modelling is prohibitively long.

Ding, Carver and Windle [11] addressed this problem using the Monte Carlo lattice model incorporating self-avoiding, diffusive chain motions. An FCC lattice was used with periodic boundary conditions. A generic diblock copolymer with components *A* and *B*. was considered. An occupied lattice site contained a bead representing an *A* or *B* type block and solvent molecules were represented by vacancies to be referred to as *V*. Figure 8 shows the stages in modelling phase separation of a block copolymer composed of hydrophilic and hydrophobic blocks in an aqueous solvent. Hydrophobic *A* blocks and hydrophilic *B* blocks were modelled by setting a negative *AA* interaction energy, and zero *BB*, *VV*, *AV*, *BV*, and *AB* interaction energies. This leads to a

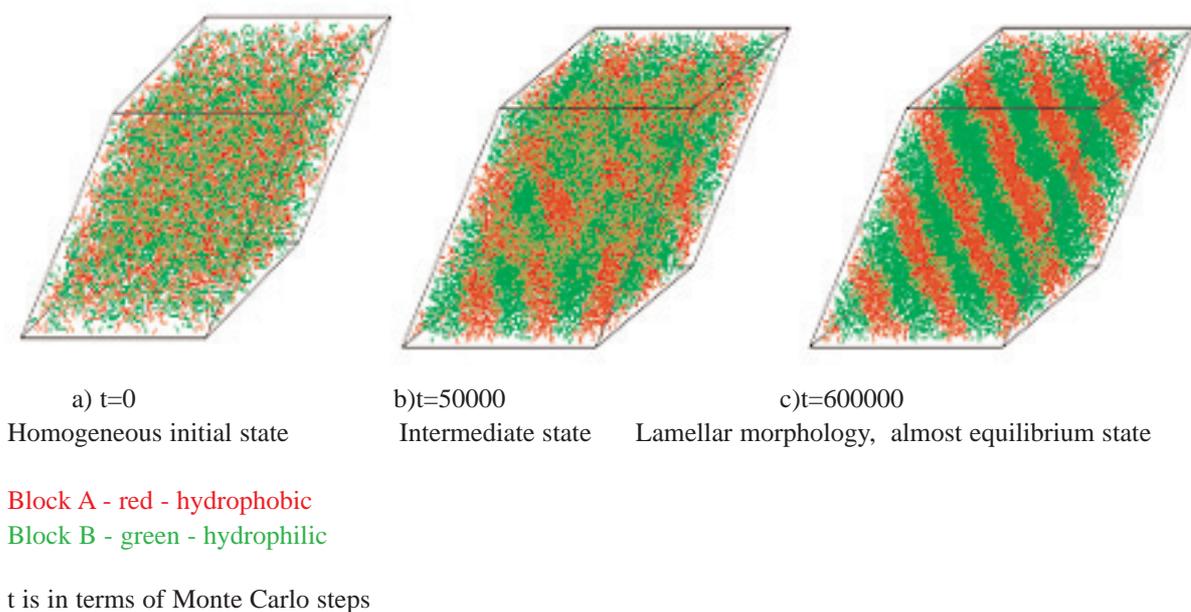


Figure 8: Phase separation in a hydrophilic/hydrophobic block copolymer (redrawn from [11]).

significantly higher vacancy concentration in the B phase after separation as can be seen by the thicker lamellar phase for the B blocks in Figure 8c.

Temperature induced order-disorder transitions were also successfully simulated for this example system. Furthermore, Ding *et al.* [11] showed that the simulation method is capable of predicting different diblock copolymer morphologies. Micelle, hexagonal cylinder, and lamellae were obtained at different diblock compositions. Micellar gel formation was simulated by using long ($A_{16}B_{16}$) blocks as this gave rise to a structure in which B blocks entangle with those of neighbouring micelles.

4.4 Application of the Lattice Chain Model to Polymer Surfaces

In the previous two examples, we have seen how the lattice model can be applied to the prediction of behaviour and morphology in dense polymer systems. The next example shows the use of Monte Carlo lattice model simulation in conjunction with microscopy to provide information at length scales below the resolution of the microscope in addition to aiding the elucidation of structure. Goldbeck-Wood *et al.* [12] investigated the structural organization at

the surface of a typical amorphous polymer, atactic polystyrene (aPS), with a combination of high resolution scanning force microscopy (SFM) and coarse-grained lattice simulation techniques. Theory [13] and diffraction experiments predict relatively short-range interactions, of one or two monomer lengths, operating within the bulk of an amorphous polymer as entanglements screen longer range interactions. The screening at the surface is different due to the asymmetry of the chains near the air interface. Long-range interactions, of the order of the radius of gyration of the chains, are expected corresponding to the dimensions of the macromolecular coils, in addition to the short-range bulk interactions and intermediates associated with several monomers. Grazing incidence X-ray diffraction and electron diffraction, used to study crystalline surfaces, are not very informative when applied to amorphous surfaces. However, SFM is a powerful technique now available for examining the surface morphology and properties of amorphous polymers. Goldbeck-Wood *et al.* [12] operated the SFM in tapping mode to scan over surface areas between $300 \times 300 \text{ nm}^2$ and $5 \times 5 \mu\text{m}^2$. The surface features of interest are nanoscale structures as they are of the order of the radius of gyration of the chains. These are of an impractically large size, in terms of computing resources, to simulate using

classical atomistic methods. Therefore, Goldbeck-Wood *et al.* [12] used the coarse-grained FCC lattice chain simulation method, shown by Haire *et al.* [8] to be a valid for studying dense amorphous polymers. The correct representation of the polymer chemistry was obtained, as described in section 4.1, by setting the parameters of the model to achieve the correct density and end-to-end distance for the polymer in question, aPS in this case. The specific environment, *i.e.* a surface in this case, was set by specifying polymer-air and polymer-substrate interactions. To do this, air was represented by vacancies, and cohesive-energy terms in the form of polymer-vacancy interaction parameters were introduced such that the bulk retained the correct density (occupancy) in a simulation box with a polymer surface. This was achieved by a pair-wise interaction energy between nearest neighbour polymer-vacancy sites of $\varepsilon = +36k_B T$, and an attractive interaction energy of $\varepsilon = -36k_B T$ between the surface polymer and substrate (bulk) to ensure that the polymer/substrate surface remained intact.

A similar mathematical analysis was applied to both the SFM and simulation results, allowing direct comparison of the findings. The polymer surface topology in the SFM images was characterised quantitatively with an autocorrelation function analysis. This indicates the average distance from an arbitrary point in the sample beyond which the correlation in the arrangement of the structural units is lost. A set of aPS samples was chosen to cover a range of molecular weights from 3900 up to 9×10^6 . Likewise, independent simulations were run for different chain lengths selected to overlap with the range of molecular weights used for the SFM. Long relaxation times, associated with long chains, drain computer resources and this limits the simulations to relatively short chain systems, inaccessible to for SFM due to resolution limits. The SFM is able to access the longer chain lengths than simulation, but there is an intermediate region accessible to both, which allows comparison of experimental and simulation results.

Cross section (height profiles) of the SFM images demonstrated a presence of at least two characteristic length scales within the scanned area which, by analogy with more ordered latex particle crystal systems (Bliznyuk *et al.* [14]), was ascribed to two different levels of molecular organization within the system. Autocorrelation function analysis of the SFM images produced curves with an initial

exponential decay followed by a series of peaks of decaying amplitude, as shown in Figure 9, suggesting at least two levels of structural organization. Direct inspection of the modelled structures, shown in Figure 10a, revealed roughness at the level of individual chains and on a larger scale. The effect of the surface on chain orientation can be seen in Figure 10b, where the divergence of the lateral and perpendicular components close to the surface means that the chain envelope is effectively flattened close to the surface, in agreement with previous evidence about chains at weld interfaces in the work by Haire *et al.* [9]. Two characteristic length scales can be extracted from the autocorrelation function curves for the simulated surfaces. Comparison of experimental autocorrelation lengths with simulated results suggests that simulated polymer surfaces have a resolution that is at least five times higher than that seen in SFM experiments. Better comparison of SFM and simulation results requires development of a mathematical procedure for deconvolution of the SFM tip shape from the surface relief. Moreover, the current trend of ever increasing computing sources will allow simulation of longer chain systems, allowing more points for comparison with experiment. Combination of the evidence of simulation and experimental results indicates that a characteristic feature of the surface autocorrelation function has a length scale close to the radius of gyration of the chains (calculated theoretically) over several decades of molecular weight. The calculated values of the radii of gyration are plotted in Figure 11 and show rather good agreement with the larger correlation length of height distribution found in both SFM experiments and independently from simulations.

This work provided new insights into the surface topography of amorphous polymer systems and validated coarse-grained simulation techniques for investigating nanoscale polymer surface features.

Now we move up in scale again from the nanoscale to the microscale with a look at how we can predict the evolution of microstructure in nematic liquid crystalline polymers. Our representation of the structure is coarsened with our modelled unit will now representing groups of chains sharing a common direction.

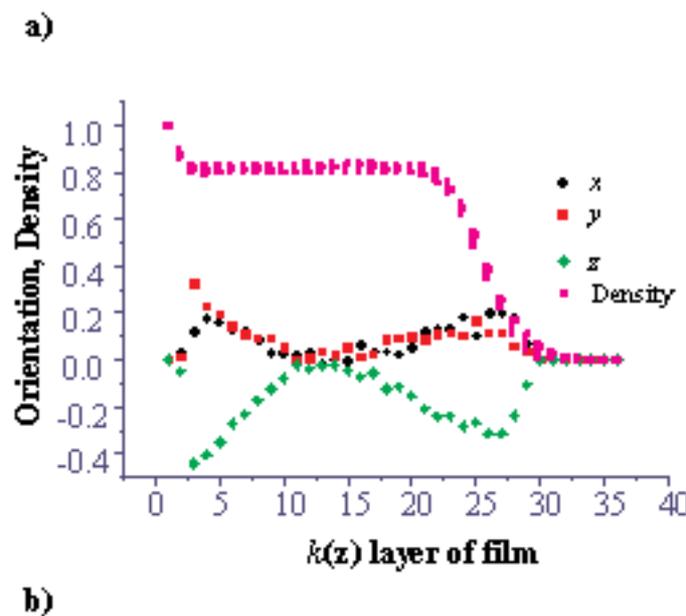
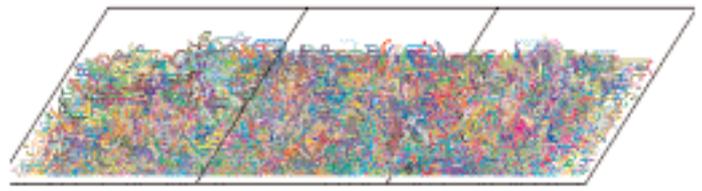
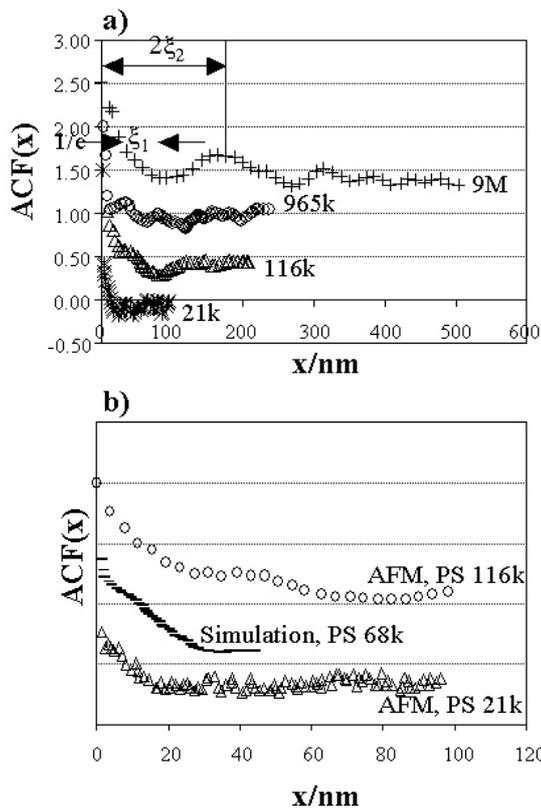


Figure 9: a) Autocorrelation functions calculated from the SFM images for different molecular weight PS samples (the curves have been shifted vertically for clarity.) The principle of the correlation length estimation as $1/e$ level of the exponential decay corresponding to the initial (steep) part of the ACF curve and to the first-order maximum of characteristic oscillations is shown. These two approximations give two different levels of quantitative description of the system: the correlation lengths ξ_1 and long-range correlation parameter ξ_2 . b) The initial parts for some of the experimentally determined ACF curves plotted in a), compared with the ACF calculated for a simulated PS surface of $M_n = 68K$. (Redrawn from [12]).

Figure 10: (a) The side view of a simulated surface. Note the roughness, and the chain ends protruding from the bulk. (b) Components of the orientation distribution along the surface (x,y) and perpendicular to the surface (z), throughout the simulated PS film. Note, the flattening of the chain envelope close to the surface (modified from [12]).

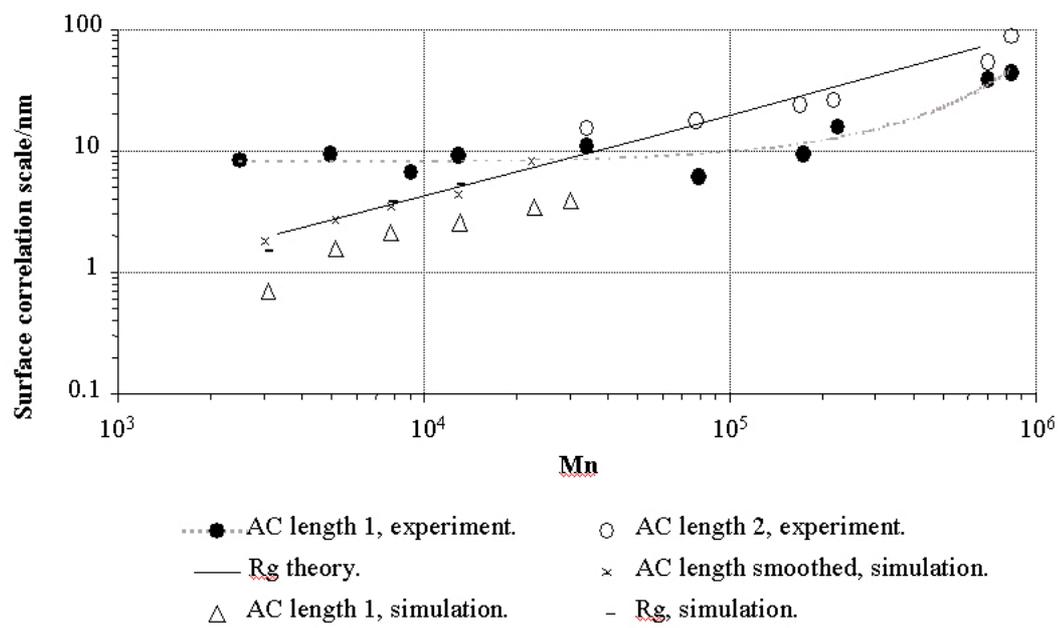


Figure 11: A summary graph of characteristic length scale parameters vs. molecular weight found for amorphous polymer surface. The correlation lengths 1 and 2 are ξ_1 and ξ_2 introduced in figure 9. 'Rg' curves are the theoretically calculated values of radius of gyration for polymer chains in an ideal random coil approximation. (modified from [12]).

5 Modelling Nematic Liquid Crystalline Polymers

The liquid crystalline or *mesogenic* phase is an intermediate between liquid and solid that is possible to achieve with certain molecular architectures. A few concepts associated with liquid crystals, particularly the polymeric variety, will be introduced here but the reader is referred to Donald and Windle [15] for comprehensive coverage of this subject. Liquid crystals flow like liquids but retain some degree of orientational order. Friedel classified liquid crystalline phases as *nematic*, *cholesteric*, and *smectic* and, although this was originally applied to small molecule liquid crystals, these classes are appropriate for liquid crystalline polymers. The modelling work described here is concerned with the nematic *Friedelian* class defined as showing long-range orientational order with only short-range positional order. Two types of liquid crystalline polymer architecture are found: *main chain* in which the mesogenic units arise from a rigid, or more usually, semi-rigid backbone, or side chain which derive their mesogenicity from stiff side-chain units. The microstructure of a liquid crystal is usually described in terms of a unit vectors, known as *directors*, representing the average locally favoured orientations. Liquid crystalline materials exhibit a rich variety of microstructures and liquid crystalline polymers are no exception demonstrating an enormously varied range of textures. This microstructure is a result of spatial variation in the director field arising due to boundaries and defects. Defects in the form of discontinuities in the director field are known as *disclinations*, and may be point or line defects. Optical micrographs of nematic liquid crystalline materials frequently reveal characteristic lines or *threads*, demonstrated in Figure 12a with MBBA in shear flow. These threads are the cores of disclination lines, which scatter light. Another characteristic of the nematic phase is the Schlieren texture, which is seen between crossed polars and showing point singularities as illustrated in Figure 12b.

Continuous distortion of the director field is described in terms of three possible types elastic orientational distortions namely *splay*, *twist*, and *bend*. Three elastic constants, referred to as the Frank constants, K_{11} , K_{22} , and K_{33} respectively, quantify the reluctance of the material to distort in each of these ways. The splay constant varies with the contour length of the macromolecule, while the bend and twist constants vary with persistence length. As

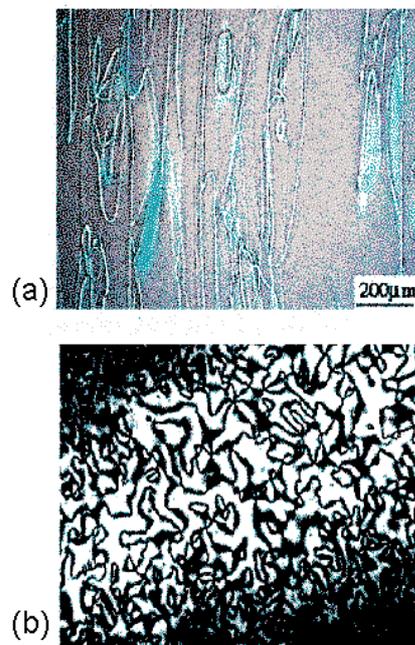


Figure 12: Microstructures in nematics: a) thread texture of MBBA in shear flow under crossed polars and a tint plate; b) Schlieren texture in the polymeric nematic state under crossed polars.

chain length is increased the persistence length reaches a limiting value therefore becoming independent of molecular weight. The contour length, and hence the splay constant, increases with molecular weight, leading to significant anisotropy in the elastic constants in main chain liquid crystalline polymers. The splay constant is usually larger than twist or bend in main chain thermotropic polymers, while bend tends to be the largest in lyotropic main chain and smectic side chain polymers. Splay is entropically unfavourable in main chain thermotropic polymers because it requires chain ends to diffuse to regions of high distortion to maintain constant density and this becomes increasingly unlikely as the chain length increases.

Thermotropic liquid crystalline polymers are widely used in high precision mouldings and can also be drawn to produce very stiff and strong fibres. However, their use is hampered by the presence of defects in the microstructure. Simulation plays a valuable role in understanding how and why these defects arise during processing. An hierarchical modelling approach has been adopted by the Cambridge group for studies designed to predict microstructures observed in main chain thermotropic liquid crystalline polymers as this method can provide considerable insight into the relationships between molecular architecture and microstructure. The simulations typically begin with the system in

the isotropic phase, and then relax structure either by minimising the total free energy of the system (*refs* [17,19-27]), or the overall elastic torque (*refs* [29-32]) thereby aligning directors and reducing the number of defects, coarsening the texture until in some cases a monodomain configuration is reached. We have already introduced atomistic modelling with the prediction of persistence lengths using Monte Carlo simulation by Bedford, Yu, and Windle [4] as described in section 3 of this paper. Moving up one level takes us to the nanoscale where the modelled unit is an entire molecule as adopted by the Lebwohl and Lasher [16] model developed to study the nematic to isotropic phase transition. This is a lattice model containing one molecule per cell, described only by its direction in space. The distribution of molecular orientations is determined by a balance between the randomising influence of the thermal motions and the restoring force defined by the distortion constants. The next level up in scale is the microstructural regime where the modelled unit represents large groups of molecules. At this scale the effect of thermal fluctuations on the interaction energies is reduced, approaching the continuum limit where the thermal fluctuations are considered negligible. Atomistic modelling can provide crucial input parameters for the coarse-grained nano- and microscale models. For example, the elastic constants provide the structural input for coarse-grained simulations of liquid crystalline polymers, but are difficult to obtain from experiment. However, the bend and twist elastic constants vary with persistence length which, as we have shown, can be calculated from atomistic Monte Carlo simulation. This hierarchy of structure involved in the prediction of liquid crystalline polymer microstructure is summarised in Figure 9 and has been discussed in detail by Hobdell, Lavine and Windle [17], and Goldbeck-Wood *et al.* [18].

5.1 Monte Carlo Modelling of Nematic Liquid Crystalline Polymers

The lattice model has been developed in the Cambridge over the last few years to simulate and predict the director fields and textures in nematic liquid crystalline polymers at the microscale. In the first instance, Bedford, Nicholson and Windle [19] used a simple two-dimensional numerical model to simulate the evolution of liquid crystalline texture during isothermal annealing of the isotropic material. The liquid crystal was modelled by a 2D array of directors, represented by unit vectors, each centred

on the lattice point of a primitive square lattice. The orientation of a director was free to vary continuously in two dimensions. Each director represented the average orientation of an assembly of molecules within a domain. This initial model was further simplified by assuming the three elastic constants to be equal and setting them arbitrarily to unity. A sine squared function was chosen to define the interaction energy between adjacent directors so that it is a minimum when they are parallel and a maximum when they are perpendicular. This is shown in equation (1) where θ_i and ϕ_i are the angles of the directors to a reference direction in two adjacent cells.

$$E \propto \sum \text{Sin}^2(\theta_i - \phi_i) \quad (1)$$

Assender and Windle [20] investigated the choice of energy function in the two-dimensional lattice model and found the sine squared function to be the most successful. Bedford *et al.* [19] used a Monte Carlo algorithm to pick a cell at random. Its energy was calculated by summing individual contributions due to disorder in orientation between the director in the picked cell (θ_i) and those in its four nearest neighbours (ϕ_i). The angle ϕ that minimises the energy was found. The process of picking a cell and minimising the energy was repeated many times until there was no further reduction in the energy of the lattice as a whole. This approach successfully simulated the evolution of a director field from multi- to monodomain via the annihilation of opposite signed strength $\frac{1}{2}$ disclinations.

Bedford *et al.* [19] extended this approach to three dimensions by placing the directors on a simple cubic lattice and allowing them to move in three dimensions, minimising the energy of each director with respect to its six nearest neighbours. In three dimensions, this was done by changing the orientation of the central director until an energy minimum was found. As a single elastic constant approximation was used, this model is only valid for small molecule liquid crystals.

In a further study, Bedford and Windle [21] refined the three dimensional model to allow simulation of liquid crystalline polymers by using unequal elastic constants. A sine squared function was still used, but weighted according to the amount of splay, twist and bend distortion between directors. This led to a novel prediction of layering in liquid crystalline polymers resulting from a high splay constant. Windle, Assender, and Lavine [22] made a further adaptation

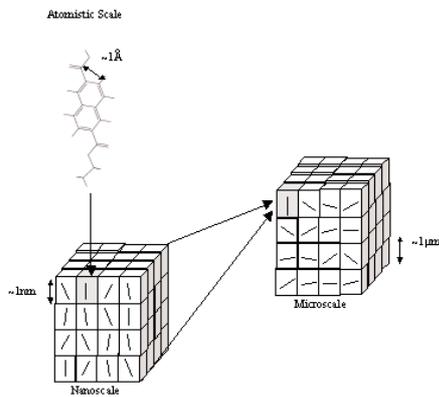


Figure 13: Hierarchy of size-scales used in the prediction of liquid crystalline polymer microstructure.

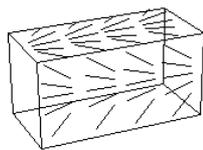


Figure 14: Splay-splay compensation.

in order that the model could be applied to the dynamic simulation of disclination processes in liquid crystalline phases. Cells were picked at random, as before, but the orientation of the director was changed by a small amount down the path of steepest energy gradient.

Processes such as injection moulding and extrusion generate shear fields that alter the microstructure of liquid crystalline materials, often producing large numbers of defects. Lavine and Windle [23] modelled the influence of shear on disclination loops in thermotropic liquid crystals by incorporating flow in the Bedford and Windle [19] lattice model.

A significant limitation of the Bedford and Windle [19,21] model was that it could not completely distinguish between splay and bend distortions, assigning bend to some pure splay situations and vice versa. This problem was tackled Hobdell and Windle [24,25,26,27] who developed a technique for simulating microstructure in liquid crystalline polymers that would distinguish between splay, twist, and bend, identify situations of splay-splay compensation, and also allow non-equilibrium states to be probed. The microstructures observed in polymeric nematics are different from those observed in their small molecule counterparts, a typical example being the swirling patterns observed in thermotropic liquid crystalline polymers. Hobdell *et al.* [24-27] proposed that the origin of these unique microstructures lies in the anisotropy of the Frank elastic constants. In particular, they proposed that the

swirling microstructure arises as it is a texture involving bend and twist distortion which are preferred over those involving splay owing to the high splay energy of thermotropic liquid crystalline polymers.

Hobdell *et al.* [24-27] used the Frank continuum theory [28] to predict the director fields in liquid crystals. Frank's equation gives the total free energy of a liquid crystal with a general distortion of the director field as the sum of the splay, twist and bend components. Using this equation, it is possible to separate the contributions from splay, twist and bend distortions. Minimisation of the Frank free energy is very complicated when the elastic constants are all different; therefore, Hobdell *et al.* [24-27] applied a simple numerical algorithm to find minimum energy director fields. An additional consideration was that the microstructures observed in liquid crystalline polymers are often far from the equilibrium state and so unlikely to be in a minimum energy state. Therefore, a technique was required that follows the evolution of microstructure, and hence includes non-equilibrium director fields.

Hobdell *et al.* [24-27] divided the mesophase into an array of identical cubic cells, each storing a director representing the local orientation. The model was initialised either to simulate a monodomain by aligning all the directors, or giving them random orientations to simulate the isotropic case. Specific boundary conditions were chosen by setting the directors forming the boundaries at particular orientations. The system was then annealed to reduce the total energy of the system by using a Monte Carlo algorithm to pick a cell at random and then assigning the director a random trial orientation. The energy was calculated for the chosen cell by breaking it down into eight corners and at each corner using the three neighbours to calculate the splay, twist and bend distortions. These were calculated for all eight corners, and the average found. If the interaction energy of the trial orientation was lower than that of the original then the trial was accepted. Otherwise, the trial was accepted with a probability that depends on the difference in energy between the original and trial orientations. One complication is that vectors are incapable of representing nematic symmetry of a director field where $\mathbf{d} = -\mathbf{d}$. Hobdell *et al.* [24-27] solved this problem by checking the angle between pairs of vectors and, if it is found to be greater than 90° , flipping one of the neighbours through 180° .

Splay-splay compensation, illustrated in Figure 14, is where the splay distortion in one plane is the equal and opposite of that in a perpendicular plane. These opposing distortions compensate, eliminating the density variation resulting from the two individual splay distortions. Therefore, although splay distortions tend to be unfavourable in large polymer molecule systems, the situation of splay compensation alleviates this. Bedford and Windle [19] model, using the sine squared energy function, does not identify splay compensation, giving the splay-splay compensated region the equivalent energy to a pure splay region. However, in Frank's equation, splay distortion is described by a divergence term, so the method of Hobdell *et al.* [24-27] correctly deals with situations of splay-splay compensation.

The decomposition of + or -1 line defects into a series of point singularities is known as *escape into the third dimension*. Hobdell *et al.* [26] were able to show that strength +1 disclination lines in liquid crystalline polymers will be of the twist escaped strength +1 variety. Experimental observations of fracture surfaces by Windle *et al.* [20] have revealed fractures, which are consistent with twist-escaped strength +1 lines.

One problem associated vectorial form of the Frank elastic free energy used by Hobdell *et al.* [24-27], is that it requires ad hoc director-flipping moves to preserve the nematic symmetry. In the following section, we introduce a different approach using a tensor expression for the elastic torque that automatically conserves nematic symmetry.

5.2 Deterministic Approach to Modelling of Nematic Liquid Crystalline Polymers

The mesoscale lattice models of nematic polymers described in the previous section use a Monte Carlo method for the relaxation algorithm. This has two drawbacks, firstly it is difficult to relate Monte Carlo time evolution to that in a real system, and secondly it does not lend itself readily to the inclusion of external fields, particularly flow fields. In response, Tu, Goldbeck-Wood and Windle [29] took a deterministic approach to the simulation of the evolution of texture in liquid crystalline polymers. They adopted a lattice model as before, but this time they calculated the relaxation in the director field using the Ericksen-Leslie equation which describes the process in terms of a torque due to the curvature

in the elasticity and the rotational viscosity of the system. In this way, minimisation of the overall elastic torque is the driving force behind the relaxation of the director field, rather than the total free energy used in the previous simulations [19-27]. The Ericksen-Leslie relation is an equation of motion for relaxation of the directors, providing the basis for a molecular dynamics approach to the problem.

In the absence of an external field the Ericksen-Leslie equation takes the form shown in (2), where \mathbf{n} is the director field, \mathbf{h} the texture field, and their cross product the torque per unit volume due to the curvature of the elasticity. γ_1 is the torsional viscosity coefficient.

$$\frac{\partial \mathbf{n}}{\partial t} = \frac{1}{\gamma_1} (\mathbf{n} \times \mathbf{h}) \times \mathbf{n} \quad (2)$$

Externally applied torques can be included easily in this equation, making it a more amenable method for modelling the effects of external fields. The texture field is generated by the spatial inhomogeneity of the director field and can be obtained from the Frank elastic free energy. Tu *et al.* [29] treated the Frank elastic constants separately to allow for the elastic anisotropy that is typical of polymeric nematics. The equilibrium state is where the director is parallel to the texture field at each point. Tu *et al.* [29] used the Frank elastic free energy equation in tensorial form as this automatically conserves nematic symmetry, and for this reason their model will be referred to as the *tensor model* when brevity is required. They demonstrated the effectiveness of this model at differentiating splay, twist and bend distortions by successfully reproducing the Fréedericksz transitions, which also have analytic solutions. These occur when an electric or magnetic field is applied to a liquid crystal cell constrained by fixed boundary conditions at two parallel plates.

Tu, Goldbeck-Wood and Windle [30,32] proceeded to apply the tensor model to the simulation of both static and dynamic behaviour of liquid crystalline polymers. In the static case, Tu *et al.* [30] simulated disclination processes in a range of elastically anisotropic two and three dimensional structures. In the two dimensional treatment, used to model thin films, the directors are constrained to lie in a plane so the elastic distortions are restricted to splay and bend. These two dimensional distortions, demonstrated in Figure 15 [31] correspond to the Schlieren textures observed in thin specimens between crossed polars as shown in Figure 12b. The

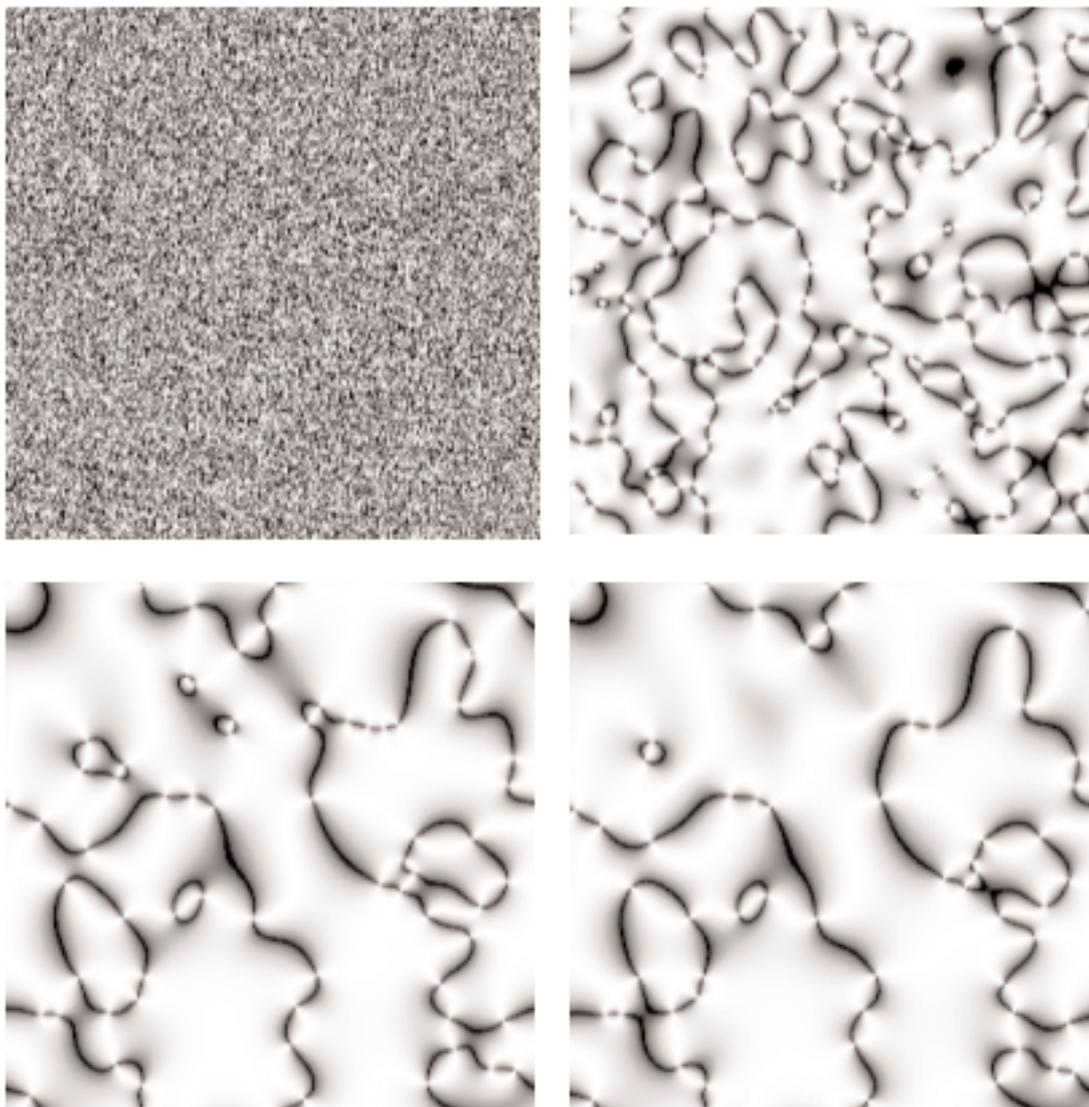


Figure 15: Model structures, presented as their corresponding polarised light intensity profiles, at different time steps: (a) 0s, (b) 600s, (c) 1800s and (d) 2400s .

two dimensional version of the tensor model was used to explore the effect of splay and bend anisotropy on these structures. A three dimensional version of the tensor model was applied to the investigation of disclination lines and loops in bulk samples. This is particularly valuable as it is difficult to obtain this information using currently available experimental techniques. In their application of the tensor model to dynamic behaviour, Tu *et al.* [32] simulated texture evolution of nematics under shear flow. Defects can be generated and multiplied in liquid crystalline polymers under shear flow and understanding the mechanisms behind these processes is useful in applications like extrusion and injection moulding. The Ericksen -Leslie theory predicts director tumbling and flow aligning behaviours in nematics under shear. Tu *et al.* [32] examined the effect of simple shear flow on polymeric nematics. They

compared cases of no elasticity, equal elastic constants, small splay constant, small bend constant and small twist constant respectively. "Log rolling" was predicted to be a consequence of tumbling when the twist constant is smaller than the others as is the case in typical thermotropic liquid crystalline nematics.

6. Concluding Remarks

We began this brief survey with an example of the application of modelling to the prediction of X-ray diffraction patterns in the familiar process of structure refinement. This paper provides a brief insight into how computer modelling can be used proactively as a predictive tool rather than simply as a means to refine diffraction structures. The first example we gave was the prediction of mesogenicity in thermotropic aromatic co-polyesters, showing

how simulation can be used to identify suitable candidate molecules for synthetic liquid crystalline polymers. We then moved up in scale to show how coarse-graining, used in conjunction with the lattice chain model, is a valuable technique for predicting the behaviour of dense amorphous polymer systems particularly where we wish to examine long range dynamic processes, such as polymer welding. Finally, we moved up to the mesoscale where we looked at how the lattice model was used to show that the origin of the textures observed in thermotropic liquid crystalline polymers lies in the anisotropy of the Frank elastic constants in polymeric nematics. This work was developed further with a deterministic modelling approach using a tensorial model well suited to including the effects of external fields on polymeric nematics in order to model the effect of shear flow on these materials.

References

- [1] Welsh, G.E., Windle, A.H. (2001) Levels of Structural Order in Crystals of PET/PEN Random Copolymers. *Polymer*, **42**, 5727-5735.
- [2] Welsh, G.E., Blundell, D.J., Windle, A.H. (2000) A Transient Mesophase on Drawing Polymers Based on Polyethylene Terephthalate (PET) and Polyethylene Naphthoate (PEN). *J Mater Sci.*, **35**, 5225-5240.
- [3] Welsh, G.E., Blundell, D.J., Windle, A.H. (1998) A Transient Liquid Crystalline Phase as a Precursor for Crystallization in Random Co-polyester Fibers. *Macromolecules*, **31**, 7562-7565.
- [4] Bedford, S.E., Yu, K., Windle, A.H. (1992) Influence of Chain Flexibility on Polymer Mesogenicity. *J. Chem. Soc. Fara. Trans.*, **88(13)**, 1765-1773.
- [5] Flory, P.J. (1956), *Proceedings of the Royal Society of London*, **234**, 60.
- [6] Kratky, O., Porod, G.F. (1949) *Recl. Trav. Chim., Pays-Bas*, **68**, 1106.
- [7] He, C., Windle, A.H. (1995) Persistence Lengths of Aromatic Polyamides: a Computer Simulation Approach. *Macromol. Theory Simul.*, **4**, 289-304.
- [8] Haire, K.R., Carver, T.J., Windle, A.H. (2001) A Monte Carlo Lattice Model for Chain Diffusion in Dense Polymer Systems and its Interlocking with Molecular Dynamics Simulation. *Computational and Theoretical Polymer Science*, **11**, 17-28.
- [9] Haire, K.R., and Windle, A.H. (2001) Monte Carlo Simulation of Polymer Welding *Computational and Theoretical Polymer Science*, **11**, 227-240.
- [10] Wool, R.P., Yuan, B.L., McGarel, O.J. (1989) Welding of Polymer Interfaces. *Polymer Engineering and Science*, **29**, 1340.
- [11] Ding, J., Carver, T.J. and Windle, A.H. (2001) Self-assembled Structures of Block Copolymers in Selective Solvents Reproduced by Lattice Monte Carlo Simulation. *Computational and Theoretical Polymer Science*, **11**, 483-490.
- [12] Goldbeck-Wood, G., Bliznyuk, V. N., Burlakov, V., Assender, H. E., Briggs, G. A. D., Tsukahara, Y., Anderson, K. L., and Windle, A. H. (2002) Surface Structure of Amorphous Polystyrene : Comparison of SFM Imaging and Lattice Chain Simulations. *Macromolecules*, **35**, 5283-5289.
- [13] Strobl, G.R., (1997) *The Physics of Polymers : Concepts for Understanding Their Structures and Behavior*. 2nd Edition. Berlin : Springer-Verlag.
- [14] Bliznyuk, V. N., Burlakov, V., Assender, H. E., Briggs, G. A. D., Tsukahara, Y. (2001) Surface Structure of Amorphous PMMA from SPM: Auto-correlation Function and Fractal Analysis. *Macromol. Symp*, **167**, 89-100.
- [15] Donald, A.M., and Windle, A.H. (1992) *Liquid Crystalline Polymers*. Cambridge University Press.
- [16] Lebwohl, P.A., and Lasher, G. (1972) *Phys. Rev. A*, **6**, 426.
- [17] Hobdell, J.R, Lavine, M.S., and Windle, A.H. (1996) Hierarchical Approach to Modelling of Liquid Crystalline Polymers. *Journal of Computer Aided Materials Design*, **3**, 359-368.
- [18] Goldbeck-Wood, G., Coulter, P., Hobdell, J.R., Lavine, M.S., Yonetake, K. and Windle, A.H. (1998) Modelling of Liquid Crystal Polymers at Different Length Scales. *Molecular Simulation*, **21**, 143-160.
- [19] Bedford, S.E., Nicholson, T.M., and Windle A.H. (1991) A Supra Molecular Approach to the Modelling of Textures in Liquid Crystals. *Liquid Crystals*, **10**, 63-71.
- [20] Assender, H.E., and Windle, A.H. (1994) Two-dimensional Lattice Model of Disclinations in Liquid Crystals: Choice of Energy Function. *Macromolecules*, **27**, 3439-3441.
- [21] Bedford, S.E., and Windle, A.H. (1993) Modelling of Microstructures in Mesophases. *Liquid Crystals* **15**, 31-63.
- [22] Windle, A.H., Assender, H.E., Lavine, M.S. (1994) Modelling of Form in Thermotropic Polymers. *Philosophical Transactions of the Royal Society of London*, **348**, 73-94.
- [23] Lavine, M.S., and Windle, A.H. (1997) Computational Modelling of Disclination Loops Under Shear Flow. *Macromolecular Symposia*, **124**, 35-47.
- [24] Hobdell, J.R. (1997) PhD Thesis, Cambridge University.
- [25] Hobdell, J.R., and Windle, A.H. (1996) A Microstructural Model for Liquid Crystalline Polymers. *Mat. Res. Soc. Symp. Proc.*, **425**, 131-136.
- [26] Hobdell, J.R., and Windle, A.H. (1997) A Numerical Technique for Predicting Microstructure in Liquid Crystalline Polymers. *Liquid Crystals*, **23**, 157-173.
- [27] Hobdell, J.R., and Windle, A.H. (1995) Prediction of Microstructure in Liquid-crystalline Polymers. *J. Chem. Soc. Faraday Trans.*, **91**, 2497-2505.
- [28] Frank, F.C. (1958) *Discussions of the Faraday Society*, **25**, 19.
- [29] Tu, H., Goldbeck-Wood, G., Windle, A.H. (2001) Deterministic Numerical Model for Treating the Three Elastic Constants in Nematic Liquid-Crystalline Polymers. *Physical Review E*, **64**, 1704.
- [30] Tu, H., Goldbeck-Wood, G., Windle, A.H. (2002) A Tensor Model of Liquid Crystalline Polymers: Application to Basic Disclination Processes. *Liquid Crystals*, **29**, 325-334.
- [31] Tu, H., Goldbeck-Wood, G., Windle, A.H. (2001) Numerical Simulation of Elastic Anisotropy in Nematic Liquid Crystalline Polymers. *Defects in Liquid Crystals: Computer Simulations, Theory and Experiments*, 201-228, Kluwer Academic Publishers, Netherlands.
- [32] Tu, H., Goldbeck-Wood, G., Windle, A.H. (2002) Simulation of Texture Evolution for Nematic Liquid Crystalline Polymers Under Shear Flow. *Liquid Crystals*, **29**, 335-345.