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Hierarchical Modelling of Polymers

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Polymer modelling and materials design

Polymeric materials are ubiquitous and becoming more important every day in contemporary life, thanks to their processability and to the extremely broad range of properties they exhibit. To control these properties, one can manipulate a very large number of variables, which ultimately determine the molecular composition and morphology of the material. Such variables are the chemical constitution of monomers, the molecular architecture of homopolymer (linear, short-branched, long-branched, tree, star, network) and copolymer (random, alternating, block, graft) chains in the material, the molecular weight distribution, as well as the processing conditions (temperature-pressure history, flow field) and the relative amounts of components in the case of multicomponent materials such as blends and composites.

Materials design problems, as they appear in industrial practice, typically have to do with complex systems whose properties are affected by both synthesis and processing; they are very targeted and have to be solved subject to strong financial and time constraints. For example, one may be seeking the optimal formulation of a pressure-sensitive adhesive, consisting of diblock copolymer, triblock copolymer and tackifier resin, to maximize the work expended when two solid surfaces sticking together across a layer of the adhesive are detached under prescribed conditions of loading and strain rate. Or one may be looking for chemical modifications that would reduce the permeability of a semicrystalline, oriented polymer to carbon dioxide and thus increase the shelf-life of beverage bottles made of this polymer without affecting their mechanical properties. Traditional approaches for solving such problems are based on experimental “screening” of relatively large sets of homologous systems, aided by phenomenological correlations between chemical constitution, morphology and proper-

ties. Such correlations have been systematized in convenient algebraic forms[1] and can be valuable in the hands of experienced and inventive materials researchers.

In the mid-1980s the idea of using rigorous quantum and statistical mechanical theory and simulation in addition to, or in place of, phenomenological correlations towards the design of polymeric materials started gaining ground. Rigorous modelling approaches based firmly on the fundamental molecular sciences offer great advantages over phenomenological correlations: they are based on fundamental understanding, and can therefore be used with confidence to explore “what if” scenarios for which experimental data are scarce; they can explain and predict the effects of subtle changes in tacticity and molecular architecture, which phenomenological correlations are simply too crude to capture; and they offer the possibility of addressing a very wide range of properties using a minimal set of models and parameters. The Achilles’ heel of rigorous modelling is its excessive demand of computer time. The overly optimistic initial expectation that most polymer design problems would be solved by performing atomistic molecular dynamics (MD) simulations soon met with disappointment and considerable loss of interest in modelling on the part of the industrial sector, as the CPU requirements of MD became apparent.

The challenge of multiple time and length scales

Polymers, perhaps more than any other category of materials, are characterized by a very wide spectrum of length scales in their structure and a very wide spectrum of time scales in their molecular motion. Intramolecular correlations and local packing of chains in the bulk exhibit features on the length scale of bond lengths and atomic radii, i.e. a few Å. The Kuhn segment of a typical synthetic randomly coiled polymer is on the order of 10 Å and can be considerably larger for very stiff polymers. The radius of gyration of entire chains in the amorphous bulk scales as $N^{1/2}$ with the chain length N and is on the order of 100 Å for typical molecular weights; the smallest dimension of microphases (lamellae, cylinders, spheres) in microphase-separated block copolymer systems is on this order of magnitude, while crystallite sizes in semicrystalline polymers and domain sizes in immiscible polymer blends may well be on the order of μm .

Even broader is the range of time scales characterizing the dynamical properties of polymers. While localized vibrational modes of chains have periods on the order of 10^{-14}s , conformational transitions of individual bonds over torsional energy barriers in the melt state exhibit waiting times in excess of 10^{-11}s . Longer and longer sequences of segments along the backbone need longer and longer correlation times to rearrange. The longest relaxation time, required for a chain to diffuse by a length commensurate to its size and thus “forget” its previous conformation, is critical to the viscoelastic response of polymer melts in flow. This time scales as N^2 for low-molecular weight melts in the Rouse regime and as $N^{3.4}$ above a critical molecular weight for entanglements, in the reptation regime; for a C_{800} polyethylene melt at 450K this time is on the order of 3 μs , while it easily exceeds the millisecond time scale for the molecular weights encountered in typical processing operations. The time scales for morphology development through nucleation and growth or spinodal decomposition processes typically exceed 1 s, while the characteristic times for volume and enthalpy relaxation in a glassy polymer just 20°C below the glass temperature T_g are on the order of years. Atomistic MD, on the other hand, typically tracks the evolution of model systems of length scale ca. 100 Å for times up to a few decades of ns. While the length scale can

be increased significantly by use of domain decomposition strategies on parallel computers, there is little one can do, even on the fastest machines available today, about the time scale, which falls dramatically short of the times one would wish to address in polymer systems.

There is no reason to despair, however. Recent years have witnessed a growing realization, within the materials modelling community, that theoretical and simulation approaches at different time and length scales can be connected together into hierarchical schemes[2] that are truly reliable and useful as design tools. A modelling hierarchy consists of several levels, each level utilizing a model whose parameters are derived from lower (more fundamental, smaller length- and time scale) levels and providing input to higher (more coarse-grained, larger length- and time scale) levels. Ideally, the hierarchy could span all the way from *ab initio* electronic structure calculations of the geometry and energetics of small structural units of chains to, say, the stress-strain curve, permeability and index of refraction of a finished product consisting of kilograms of polymeric material, the sole input being the monomers, synthesis and processing conditions used for its production. Such complete hierarchical schemes are very rare, and perhaps even unnecessary, as modelling is always accompanied by experimental efforts, which it can use as sources of input as well as guide and interpret. Many partial hierarchies of modelling methods have emerged, however, which provide key connections for understanding structure-property relations and optimizing complex polymeric materials.

Main ingredients of contemporary hierarchical modelling approaches to polymer properties are (a) efficient techniques for sampling polymer configurations and computing free energies; (b) systematic techniques for coarse-graining atomistic polymer models into models involving fewer degrees of freedom; (c) analyses of the paths and rates of infrequent event processes occurring in systems with rugged potential energy terrains, and of sequences of such processes; (d) mesoscopic techniques for the simulation of transport phenomena and morphology development under nonequilibrium conditions. Below we discuss recent developments in each of these fields. The discussion is inevitably brief and tainted by the research interests of the author. The reader is referred to relevant reviews, wherever possible.

Sampling polymer configurations

Although polymeric materials used in practice are most often not in thermodynamic equilibrium, they usually are close to equilibrium at some point in their processing history, and deviations from equilibrium play the role of driving forces for all changes they undergo. Furthermore, equilibrium thermodynamics remains useful as a framework for discussing many properties in configurationally arrested states, such as glasses. Thus, calculation of equilibrium properties (e.g., equation of state and heat capacity, conditions for phase coexistence and phase diagrams, sorption isotherms of small-molecular weight species in polymers, microphase separation morphologies for copolymers, density and conformation profiles for multicomponent polymer systems at interfaces) is a necessary starting point for predicting structure-morphology-performance relations in polymers. Predicting equilibrium properties by simulation requires sampling a sufficiently large number of uncorrelated microscopic configurations, weighted according to the prescription of an equilibrium ensemble. As already pointed out, this “equilibration” challenge cannot be met with MD, at least as regards the long-length scale features of long-chain systems, which decorrelate with characteristic times many orders of magnitude longer than can be tracked by MD. Recent algorithmic develop-

ments, most notably time-reversible multiple time step methods based on Trotter factorization of the Liouville operator[3] have greatly enhanced the stability and efficiency of MD methods, but not to the extent of being able to address these long polymeric time scales. On the other hand, spectacular advances in our ability to equilibrate polymer systems have resulted from the development of novel Monte Carlo moves and methods in recent years. These have been reviewed in connection with the problem of calculating phase transitions in complex fluids[4].

By introducing bold changes in the configuration of dense, multichain systems, Monte Carlo moves can circumvent the bottlenecks limiting dynamical progress in real polymeric systems and in MD simulations, thereby accelerating equilibration by many orders of magnitude. The configurational bias (CB) move[5] cuts a terminal section of a chain and regrows it in a bond-by-bond fashion, while avoiding excluded volume overlaps; the bias associated with the regrowth procedure is taken away in the acceptance criteria. It has been used in Gibbs ensemble simulations for the prediction of vapour-liquid phase coexistence curves for alkanes[6] up to C_{48} and for performing biased Widom insertions to estimate chemical potentials in mixed hydrocarbon phases[7]. It has also been adapted to networks[8] and branched molecules[9]. For long-chain systems the efficiency of CB decreases; Recoil-Growth CB MC[10], a modification using retractable “feelers” to explore available space around the growing chain, is likely to help in this respect.

The concerted rotation (CONROT) move brings about local conformational rearrangements which change the torsion angles of seven or eight consecutive bonds and the positions of four or five atoms along the backbone[11]. It has been used very effectively, in combination with CB, to sample conformations of cyclic peptides[12]. The end-bridging (EB) move[13] was developed with the explicit purpose of equilibrating long-length scale features, such as the end-to-end distance, the radius of gyration and the distribution of chain centres of mass in dense phases of long chains. In EB the end of a chain “attacks” the backbone of a neighbouring chain, cutting it in two parts, one of which is annexed to the attacking chain. Connectivity is thus drastically redistributed in the model system. The simulation is carried out in a semigrand ensemble, wherein the total number of chains and the total number of monomer units are kept fixed and the molecular weight distribution is controlled by imposing chemical potentials for all chain species but two, which are taken as reference species. A variety of chain length distributions can be simulated by imposing appropriate profiles of chemical potentials, the algorithm remaining efficient down to polydispersity indices of 1.02 or so. A remarkable attribute of the EB algorithm[14] is that, for fixed shape and polydispersity of the molecular weight distribution, the CPU time required in order for chain centres of mass to move by a length equal to the root mean square end-to-end distance scales *inversely* with the mean chain length N . Thus, the efficiency of the algorithm is *enhanced* as the mean chain length increases. EB has been successful in equilibrating realistic united-atom models of C_{1000} at all length scales and is currently being tried on C_{6000} . Not only long-length scale properties of chains, but also local density fluctuations are sampled more efficiently by an algorithm based on EB, CONROT and reptation moves than with alternative algorithms[14]. When used with detailed models of the bonded geometry of chains, both CONROT and EB rest on determining all (up to 16) solutions to a geometric problem, that of bridging two dimers by a trimer such that the resulting heptamer has prescribed bond lengths and bond angles. An efficient scheme for solving this problem in Cartesian coordinates has been developed[14], and a more general scheme for bridging through a sequence of rigid bodies connected by rotatable bonds has been implemented[12].

A number of new statistical mechanical ensembles have been used in Monte Carlo simulations of polymeric systems in recent years. The motivation behind much of this work was to alleviate the sampling problems associated with insertions of big molecules in dense phases, required by the Widom test particle method for chemical potentials and by grand canonical MC simulations, or with exchanges of big molecules between dense phases, required by the Gibbs ensemble method for calculating phase equilibria. Semigrand Monte Carlo simulations[15], involving identity interchanges between molecules belonging to different chemical species, have been used effectively in conjunction with coarse-grained models to predict the mixing thermodynamics of symmetric polymer blends[16] and in conjunction with atomistic models to simulate polydisperse melts[13],[14]. Sorption isotherms of a small-molecular weight species in a polymer matrix are readily calculated in a hybrid isothermal-isobaric/grand canonical ($N_1 f_2 PT$) ensemble, wherein the pressure P , the temperature T , the number of (nonvolatile) polymer molecules N_1 , and the fugacity f_2 of the small penetrant are specified[17]; this ensemble is similar to the “osmotic” ensemble proposed for phase equilibria across semipermeable membranes[18]. For the determination of high-pressure phase coexistence properties in binary mixtures of a light solvent and a heavy hydrocarbon, an atomistic simulation scheme involving two boxes simulated in parallel in the $N_1 f_2 PT$ ensemble at common values of P , T , and f_2 has proved useful[7]. The common value of f_2 is revised through a Newton-Raphson iterative scheme leading to equalization of the fugacities of the heavy component in the two boxes. This scheme for simulating phase equilibria of chain systems (SPECS) can be extended to mixtures containing an arbitrary number of light components. Truly polymeric heavy components can be treated by taking advantage of the chain increment Ansatz, which states that the excess chemical potential of a chain inserted in a phase of given temperature, pressure and composition is a linear function of the chain length[19],[7]. SPECS can be considered as a “pseudoensemble” approach, the latter term denoting iterative schemes designed to converge to a desired equilibrium state through successive updates of an intensive parameter, thus circumventing the introduction of moves that would have very low probability of acceptance[4]. For tracing a phase coexistence line, given the properties of coexisting phases at one point of that line, the Gibbs-Duhem integration method has been proposed[20].

Sampling configurations of oriented melts, such as the ones resulting from imposition of a steady-state elongational flow during processing, was made possible by conducting EB MC simulations in the presence of a tensorial thermodynamic field which couples to the end-to-end tensors of chains, inducing orientation[21].

Another way to alleviate problems associated with inserting/deleting large molecules in dense phases for the calculation of phase equilibria is to employ an “expanded ensemble” scheme that inserts or deletes molecules in a gradual manner. In an expanded ensemble simulation configurations are sampled according to the partition function $\sum_{y=1}^M Q_y \exp(w_y)$ where y is a parameter in the Hamiltonian of the system, allowed to range over M discrete values; Q_y is a conventional (e.g. canonical) partition function, evaluated at parameter value y ; and the w_y are weighting factors modulating the probability of appearance of different y values. The scheme allows calculation of free energy differences between thermodynamic states corresponding to different y and can thus be thought of as an application of the free energy perturbation method “on the fly”, within a single simulation[4]. It was originally proposed[22] for the calculation of free energies of solvation at infinite dilution, the parameter y corresponding to the strength of interaction between the solute and solvent molecules. It

has been implemented in the context of extended-ensemble MD simulations to calculate the sorption thermodynamics of gases in glassy polymers[23]. It has also been adapted within a CB MC framework for the calculation of chemical potentials of polymers, with y controlling the length of a “tagged” chain which is allowed to fluctuate in size[4].

The parallel tempering technique[24] has recently proven very promising for sampling systems with rugged potential energy functions that tend to make conventional simulation schemes nonergodic. Parallel tempering considers a large ensemble of n systems, each system equilibrated at a different temperature $T_i (i = 1, \dots, n)$. The system of interest is the system of lowest temperature; the systems of higher temperature usually have the same Hamiltonian as the system of interest and are added in order to aid in overcoming energy barriers and thereby aid in equilibration. The systems of different temperature are considered as independent of each other, so the partition function sampled is actually the product of the individual partition functions at the different temperatures, i.e. of the form $\prod_{i=1}^M Q_i(N, V, T_i)$.

There are two types of moves: Regular “configuration” moves, performed at each temperature, and “swapping moves”, which exchange configurations between two systems i and j . A swapping move is accepted with probability $\min[1, \exp(\Delta\beta_{ij}\Delta\mathcal{V}_{ij})]$, with $\Delta\beta$ and $\Delta\mathcal{V}$ being the differences in reciprocal temperatures and energies between the two systems. A prerequisite for the scheme to work is that the energy histograms of systems adjacent in the temperature ladder should overlap. Parallel tempering has been used with great advantage in sampling configurations of biological molecules[12] and polymers[25]. In the latter case, an escalation in chemical potential, as well as in temperature, has been used to define the different systems and the method has been coupled to an expanded ensemble scheme.

Histogram reweighting methods[26] analyze results from a limited number of simulation runs in order to extract information about the density of states, which is then used to derive properties at thermodynamic state points other than the ones simulated. These methods are particularly useful for the study of phase transitions in the vicinity of critical points and have been applied to explore the critical properties of polymer solutions using lattice models[27].

Coarse-graining the molecular representation

Coarse-graining is an essential element of any hierarchical modelling approach. It entails replacing a detailed molecular model (e.g., an atomistic model with explicit representation of bond angle bending, torsion, intra- and intermolecular excluded volume, dispersive and Coulombic interactions depending on the positions of atoms and partial charges) with a simpler model, cast in terms of fewer variables, without loss of significant information. The simpler (coarse-grained) model is desirable because it is more manageable computationally in simulations and more amenable to theoretical treatment. The parameters of the coarse-grained model must be determinable from those of the detailed model through a rigorous mapping procedure. Inverse mapping (“fine-graining”), whereby well-equilibrated coarse-grained configurations are used to generate (sets of) detailed configurations is also important for the calculation of properties.

A rigorous framework for coarse-graining is offered by the projection operator formalism of statistical mechanics. For coarse-graining to be successful, the coarse-grained variables must evolve slowly relative to the detailed variables being eliminated from the model description. Interactions at the coarse-grained level are described in terms of the potential

of mean force (free energy), derivable by integrating the Boltzmann factor of the detailed model Hamiltonian over all detailed variables being eliminated at each coarse-grained configuration. The efficient sampling techniques discussed above are helpful in extracting such potentials of mean force and in equilibrating the coarse-grained models described thereby. The effects of eliminated detailed variables on the dynamics of the coarse-grained variables are described in terms of stochastic and frictional forces. When there is complete time scale separation between the detailed variables being eliminated and the coarse-grained variables being retained, the in general formidable problem of deriving memory functions for the description of frictional forces is reduced to a calculation of a relatively small number of friction factors. These can be extracted from time correlation functions involving the coarse-grained variables, accumulated in the course of relatively short dynamic simulations of the detailed model.

In practice, rigorous projection operation formalisms are seldom adopted, and coarse-graining of detailed polymer models is performed in a more or less heuristic, nevertheless useful, fashion. A procedure has been developed[28] for mapping polymers, such as polycarbonates, onto the lattice-based bond fluctuation model. This procedure has subsequently been extended to simulating the melt viscosity of polyethylene on the basis of bond fluctuation MC simulations. In an alternative approach, chains represented in terms of a detailed rotational isomeric state model are mapped onto a second-nearest-neighbour diamond lattice[29]. This procedure has been used to look at a number of polymers in the bulk melt and at interfaces. A continuous coarse-grained representation, cast in terms of hard-sphere groups connected by springs, has been employed for polycarbonates[30]. In this work, strategies for both mapping and reverse mapping between the detailed and coarse-grained models are proposed. Coarse-grained bond (spring) stretching and bond angle bending potentials are determined from histograms of the corresponding geometric quantities accumulated in the course of sampling atomistically detailed unperturbed single chains.

An interesting strategy for mapping to an even coarser level, wherein entire polymer chains are represented as soft ellipsoidal particles with dimensions, orientation, and interactions that are governed by their local environment, has been proposed[31]. The ellipsoidal particle shape and density distributions are derived from single-chain bead-spring calculations, and interactions between different ellipsoids are expressed in terms of overlap integrals of their density distributions. The softness of interactions allows for very long effective time steps in dynamic simulations of the coarse-grained model. The soft ellipsoid model has been used to simulate phase separation by spinodal decomposition in a symmetric binary polymer blend.

A coarse-graining approach has been proposed for mapping detailed atomistic polymer melt models onto the dumbbell, Rouse chain and Doi-Edwards tube models invoked in mesoscopic simulations of viscoelastic flow. The free energy of an oriented melt is extracted as a potential of mean force with respect to the conformation tensor (reduced end-to-end tensor) and shown to be of purely entropic origin for long-chain melts subjected to flow fields of low Deborah number[21]. In the case of linear polyethylene, which has been studied so far, the dependence of this elastic free energy on the conformation tensor can be described well in terms of a finitely extensible nonlinear elastic (FENE) model with parameters extracted directly from the unperturbed mean square end-to-end distance and contour length of atomistically detailed chains, while Hookean dumbbell models are less satisfactory. The relation between anisotropy of stress and anisotropy of the refractive index predicted by the simulations obeys the stress optical law with a coefficient very close to that measured exper-

imentally. The EBMC method was of critical importance in enabling these studies of melt orientation and elasticity. The friction factor ζ invoked by the Rouse and reptation models is extracted from atomistic MD simulations initiated at well-equilibrated configurations sampled by EBMC. Friction factor values obtained from the self-diffusivity and from the autocorrelation functions of the two first modes of the chains are consistent; they are chain-length dependent for short chains but assume a constant asymptotic value in the region $C_{80} - C_{150}$. Zero-shear viscosities estimated from these ζ values on the basis of the Rouse model are in excellent agreement with experimental values for unentangled polyethylene melts, as are the self-diffusivities for all chain lengths[32]. The mapping of atomistic to coarse-grained models of linear chain melts is completed by topological analysis of long-chain atomistic configurations equilibrated by EBMC, leading to the identification of entanglement points and the determination of the molecular weight between entanglements[33]. In this way, it becomes possible to generate coarse-grained networks of entangled chains for the simulation of viscoelastic flow and mechanical failure of amorphous polymers out of detailed atomistic configurations.

Analysis of infrequent event processes

Many dynamical processes in polymers occur as successions of infrequent events, wherein the system is led from one energetically favourable region of configuration space (state) into another, across a bottleneck (hyper)surface separating the states. Typically, a relatively small number of system degrees of freedom are involved in such a transition. Whereas a “brute force” MD simulation would expend most of its time tracking the relatively uninteresting fast in-state motion of the system, dynamically corrected transition-state theory[34] (TST) focusses on the (free) energy barriers (saddle points) that have to be overcome for a transition to occur and calculates rate constants for the transition at a small computational cost. The long-time evolution of the system through a succession of uncorrelated transitions can be tracked by kinetic Monte Carlo simulation (KMC), once the state equilibrium probabilities and interstate transition rates are known. A compilation of recent work on the analysis and simulation of infrequent event processes can be found in Reference [35].

An example of TST-based calculations that has found widespread use is the evaluation of diffusivities of small penetrant molecules in low- temperature amorphous polymer matrices. Gas diffusivities in a polymer glass may be on the order of 10^{-8} to 10^{-9} cm^2/s , and therefore not accessible by MD simulation. A useful TST approach was introduced, which relies upon determination of all minima of the polymer+penetrant free energy in the three-dimensional space of penetrant coordinates and all dividing surfaces for transitions between minima[36]. In this approach, all atoms of the polymer matrix are envisioned as executing isotropic harmonic vibrations around their equilibrium positions. A more refined multidimensional TST approach, in which degrees of freedom of the polymer matrix are incorporated explicitly in the transition path and rate constant calculation[37], starts with geometric analysis of accessible volume in atomistic model configurations of the polymer matrix. This geometric analysis yields initial guesses for the penetrant position at the energy saddle points (bottlenecks), which have to be overcome for elementary jumps of the penetrant between clusters of accessible volume to occur. The set of degrees of freedom with respect to which each saddle point is calculated is progressively augmented by including more and more polymer degrees of freedom, until the saddle point energy becomes asymptotic. The entire transition path for

the corresponding jump is mapped out in multidimensional configuration space through a couple of steepest descent constructions initiated at the saddle point. Rate constants for the elementary jumps are used within a KMC scheme to track the long-time diffusive progress of the penetrant.

Infrequent event analysis has also found widespread use in exploring the mechanisms and rates of side-group or main-chain local motions responsible for “Johari-Goldstein”-type local relaxation processes in polymers. TST-based approaches of varying degrees of sophistication have been used to explore skeletal ring flips in glassy bisphenol A polycarbonate[38], side group rotations in methyl acrylate/ethylene copolymers[39], and in PMMA[40], and phenyl group rotations in glassy polystyrene[41]. Predictions are generally in good agreement with solid-state NMR and dielectric spectroscopy measurements.

A challenge in analyzing dynamical processes in systems with rugged potential energy landscapes is the identification of states and transition paths between the states. In some problems, such as diffusion and side-group relaxational motion, this can be guided by geometric arguments; in many other problems, however, it cannot. An elegant method for sampling all relevant transition paths between two given states, termed transition path sampling[42], was proposed recently. For situations where the states are not even known, the recently proposed molecular hyperdynamics method[43] is very promising. This accelerates the progress of molecular dynamics by “filling up” energy wells, using a bias potential that is calculated from local properties of the energy hypersurface. In this way, the system is encouraged to move over barriers, thereby “boosting” the simulation time by a known factor. Efficient numerical techniques for the identification of saddle points which do not require explicit calculation of the Hessian[44] are also likely to help in infrequent event analyses of dynamical processes in polymers.

Mesoscopic simulation

Mesoscopic simulation techniques are designed to fill the gap between molecular simulations and macroscopic analyses based on fluid mechanics and transport phenomena, continuum mechanics and fracture mechanics, electromagnetic theory, and the continuum engineering sciences in general. They focus on length scales of 100 Å to 1 μm and time scales of 0.1 μs to 1s and are particularly needed for dealing with issues of complex morphology development, flow and deformation under highly nonequilibrium conditions.

Mesoscopic simulation approaches must necessarily employ a coarse-grained model representation. The dynamic simulations employing a soft ellipsoid model for entire chains, discussed above[31] are an example of a mesoscopic approach. A mesoscopic approach that has been used considerably to analyze viscoelastic flows in complex geometries is CONNFFESSIT[49] (Computation of Non-Newtonian Flows by Finite Elements and Stochastic Simulation Techniques). This employs stochastic simulations of coarse-grained molecular models, such as dumbbells, to track the stress and velocity fields within the finite element regions used to analyze a macroscopic flow, and thus obviates the need for closed-form analytic constitutive equations.

Dissipative Particle Dynamics[45] (DPD) is a stochastic dynamic simulation technique which tracks the evolution of large particles, each particle representing a “packet” of many atomistic degrees of freedom (e.g. fluid molecules or polymer segments). As a result of this coarse-graining, interactions between the particles are very soft and numerical integration

can be performed using a long effective time step. An advantage of the method is that it has built-in hydrodynamic interactions. DPD has been used to simulate phase separation and domain growth processes in systems containing low-molecular weight solvents, randomly coiled polymers, rigid rod polymers and copolymers. Predicted phase transitions and morphologies are in qualitative agreement with experiment. Dealing with entangled polymer systems is a challenge, due to the softness of interactions, but recently algorithms have been developed which incorporate uncrossability of interparticle bonds[46]. A more basic challenge is how to extract the soft interparticle interactions of DPD from atomistic interaction potentials. Some promising steps in this direction have been taken for simple fluids[47].

Many mesoscopic techniques constitute numerical solutions of sets of integrodifferential equations, which are derived from a general nonequilibrium thermodynamic formulation and cast in the coarse-grained variables. Although the problem of writing down a general nonequilibrium thermodynamic formulation that can be used to track the spatiotemporal evolution of mesoscopic variables such as mass, momentum, energy density and conformation fields is a very challenging one, recently there have been promising developments in this direction in the area of analyzing polymer flows. One such development is the Poisson bracket formulation[48], another is its generalization, the GENERIC formulation (General Equation for Nonequilibrium Reversible-Irreversible Coupling)[50]. These formulations have been used primarily to test rheological models proposed in the literature for thermodynamic consistency, to modify such models and to explore flow phenomena at interfaces.

In recent years, considerable effort has been devoted to developing a dynamic mean-field density functional method, derived from generalized time-dependent Ginzburg-Landau theory[51]. The time derivative of the local concentration of each species is expressed in terms of gradients in the chemical potentials of all species multiplied by nonlocal Onsager kinetic coefficients, and of a random noise term obeying the requirements of the fluctuation-dissipation theorem. The chemical potential is typically expressed as an ideal part (corresponding to Gaussian single-chain statistics) and a nonideal part (mean field potential resulting from interchain interactions, involving Flory χ factors). The formulation is solved numerically by discretizing space into an array of cubic elements. Applications have been presented for surfactant aggregation in solution and phase separation of quenched block copolymer melts under quiescent conditions and under shear. Predicted morphologies are in qualitative agreement with experimental observations. An independently developed density functional theory approach has been used to track the effects of solid particles in a phase-separating polymer mixture[52].

A promising mesoscopic approach for the simulation of large-scale deformation and fracture in condensed polymer phases is entanglement network modelling. The polymer is represented as a network of chains entangled pairwise at specific points in three-dimensional space. Positions of chain ends and entanglement points are the coarse-grained degrees of freedom with respect to which the simulation is performed. Deformation at a certain strain rate is introduced as a series of stepwise changes in the model “specimen” dimensions. Each such change is followed by (free) energy minimization and KMC simulation of elementary events leading to topological changes in the network, such as slippage of a chain across an entanglement point or breakage of a strand between entanglements. This KMC simulation is carried out according to specific rate expressions involving the local stress state around the nodal points for the time interval that elapses until the next deformation step. Application of such a scheme to polyethylene has allowed the observation of brittle fracture, necking, and homogeneous deformation with strain hardening phenomena as the molecular weight

of chains is increased, in good agreement with experimental observations[53]. A simple network of random-walk chains was used for this purpose, although the actual polymer is semicrystalline. Efforts to incorporate crystallinity explicitly have also been undertaken[54]. More recently, methods have been proposed for setting up entanglement networks to represent polymer interfaces in a manner consistent with the composition and conformation profiles yielded by a self-consistent field theory, and for expressing the free energy function and rate coefficients involved in the KMC simulation in terms of interatomic potential parameters and segmental friction factors[55]. These developments, along with techniques for identifying entanglement points through topological analysis of well- equilibrated atomistic long-chain configurations[33], create the possibility of linking this type of entanglement network modelling all the way down to the atomistic level.

Putting the pieces together

Having all the above methodological advances at our disposal, we can start thinking of hierarchical modelling schemes to address design problems such as the ones we mentioned in the introduction. For example, in the case of the pressure-sensitive adhesive consisting of diblock and triblock copolymers and low-molecular weight resin, the material design variables are the chemical constitutions and molecular weight distributions of the copolymer blocks and resin and the composition of the mixture (relative amounts of the three components). The work expended in destroying an adhesive bond across the material under prescribed temperature and strain rate must be maximized as a function of these variables. One can envision a hierarchical scheme which starts with efficient atomistic MC simulations at representative compositions[14], with possible use of coarse-graining and fine-graining[30] to facilitate equilibration, in order to determine equilibrium binary phase diagrams and enthalpies of mixing, from which effective χ interaction parameters could be extracted. Analogous MC simulations at free surfaces and next to the solid substrate of interest could yield equilibrium surface tensions and contact angles, while topological analyses of the well- equilibrated configurations could be used to extract spatial distributions of entanglements and entanglement spacings in the bulk and at interfaces. Atomistic MD simulations initiated at well-equilibrated short-chain configurations generated by MC could be used to extract the friction constant required in Rouse and reptation theory descriptions of the dynamics as a function of temperature and composition. From then on, one could envision two stages of mesoscopic modelling. The first would track morphology development under the conditions of formation and deposition of the adhesive, using an approach such as dynamic density functional theory[51] with coarse-grained chain elasticity parameters, χ factors, and Onsager coefficients based on the atomistic investigations. The second would take representative morphologies from bulk and interfacial regions of the adhesive film, coarse-grain them into networks of entanglement points[55] with the help of atomistic entanglement analyses, and simulate their deformation under a variety of strain states and rates to derive forms and parameters for a constitutive equation describing their rheological behaviour. The thermodynamic and rheological information extracted in this way could be used in a macroscopic analysis of the debonding process, treating the adhesive film as a continuum with position- and deformation history-dependent properties, to simulate all stages of the debonding process (e.g. nucleation of cavities in the adhesive, elongation of cavities and formation of fibrils, extension of fibrils and ultimate breakage or detachment of the fibrils from the solid

as the two solid surfaces are pulled apart with the adhesive in-between). In this way, the work required to destroy an adhesive bond would be determined. Validation against experiment could be sought at the level of structure, mixing thermodynamics and equilibrium phase diagrams, chain conformation and linear viscoelastic properties, surface tensions and contact angles estimated from atomistic simulations; at the level of morphology predicted from dynamic density functional theory; at the level of rheological behaviour predicted by the entanglement network modelling; and at the level of mechanism of debonding and stress-strain behavior in actual and simulated adhesion tests.

For our second example problem, that of optimizing the barrier properties of a polymer consisting of oriented glassy and crystalline domains, the chemical constitution of the chains and the morphology are the main design variables. To assess the effect of chain chemical constitution under given morphology, one could envision a hierarchical scheme which first coarse-grains the atomistic representation into one wherein, e.g., rigid aromatic moieties are represented as soft ellipsoidal particles[30]. Simulations at this coarse-grained level in the absence or presence of orienting fields, using an efficient MC algorithm[14],[21], would then yield well-equilibrated melt configurations corresponding to different degrees of orientation, which could be mapped back to the atomistic level. Collections of isotropic and oriented glassy configurations could be generated from the corresponding melt configurations through energy minimization and molecular dynamics. Henry's law constants describing the sorption equilibrium of the gaseous penetrant in each of these configurations could be obtained via Widom insertions, while entire sorption isotherms could be predicted using $N_1 f_2 PT$ MC simulations or expanded-ensemble molecular dynamics[23] atomistic simulations. On the other hand, diffusivity tensors for the penetrant in each (isotropic or oriented) glassy configuration could be obtained through multidimensional TST analysis and KMC simulation[37]. Thus, given the spatial distribution, connectivity and orientation of amorphous regions in the material (crystallites being impermeable) one would be in a position to know the local solubility and the local diffusivity tensor at every point in the material. A macroscopic simulation of the permeation process through a specimen of given morphology by finite difference, finite element or kinetic Monte Carlo methods, using this information as input, would yield the permeability. Validation against experiment could be attempted at the level of structure (experimentally accessible through diffraction), volumetric properties and free volume distribution (experimentally accessible through positron annihilation lifetime spectroscopy) of the atomistically simulated configurations, at the level of predicted sorption isotherms and diffusivities in the amorphous material for various degrees of orientation, and at the level of the permeability of entire specimens of given morphology.

Challenges for the future

Realizing grand hierarchical modelling schemes, such as the ones outlined in the last section, entirely computationally sounds extremely complex and perhaps even unrealistic today; nevertheless, many of the techniques required are already in place. The biggest challenge is in interfacing the different levels of modelling into a coherent hierarchy so as to minimize the loss of information in going from one level to the other, maximize predictive ability and versatility, and minimize computational cost. Global familiarity with efforts and advances at all levels and willingness to work collaboratively towards the development of problem-oriented multilevel approaches would certainly help the scientific community make computer-aided

polymeric materials design a reality.

At each level of modelling, comparative studies of the performance of alternative methods on representative benchmark problems would be useful. For example, how do continuum and lattice-based strategies for deriving coarse-grained atomistic models, equilibrating at the coarse-grained level, and fine-graining back to the atomistic level, compare in terms of their computational requirements and in terms of the structural and thermodynamic properties they ultimately predict? Which, among the several MC strategies that have been proposed in recent years, can equilibrate melt models most efficiently, and how could different strategies (e.g. EB and parallel tempering) be combined to achieve even better results? At the mesoscopic level, how do DPD and dynamic density functional theory compare in terms of the morphology predictions they give, e.g. for phase-separation of a binary blend under shear flow conditions, and in terms of their computational requirements?

There are problems for which it is still unclear how one could best proceed to formulate a hierarchical modelling approach, and significant methodological advances are necessary. One such problem is crystallization of polymers, especially under flow conditions. Technologically this is an extremely important problem, as the semicrystalline morphologies one encounters in real-life polymers vary widely with thermal and processing history and have profound effects on properties. Crystallization is a problem in which different length- and time scales seem to be inextricably interwoven, as evidenced by the complex hierarchical structure of a spherulite. Although significant advances have been made, for example in predicting melting temperatures for long-chain alkanes[56], in calculating the dependence of melting temperature on structural defects due to incorporation of comonomers along the chains[57], and in simulating lamellar growth through coarse-grained KMC simulations[58], we are still far from being able to predict semicrystalline morphology from chemical constitution and processing flow history.

Another outstanding problem is how to best model polymer glasses. It is frustrating that generating a computer glass with a history that is both well-defined and realistic (comparable to what is used in applications) is impossible. One can certainly glassify liquid configurations at a well-defined cooling rate of 10^{10} K/s or so with MD; this rate, however, is very far removed from those of typical experiments (ca. 1 K/min). Many simulation studies focus on the region above the calorimetric T_g and present comparisons against the predictions of mode-coupling theory[59]. These simulations, although instructive and leading to very satisfactory agreement with theory, are still of limited utility for predicting T_g or simulating a real-life glass. Atomistic MD simulations of segmental motion above T_g [60] yield strongly temperature-dependent correlation times in good agreement with experimental relaxation (e.g. NMR, QENS) measurements. At low temperatures, the time correlation functions from MD do not decay to zero over the simulation time, but their extrapolation using, e.g., a stretched exponential (KWW) form which seems to be obeyed in the region accessible by MD yields reasonable results. This makes one hope that atomistic MD simulations of low-temperature melts and accumulation of segmental correlation times as a function of T , with appropriate extrapolation, may be a reliable way for estimating T_g through simulation; it does not solve the problem of generating realistic glassy configurations, however. Techniques based on energy minimization and MD, using some form of chain growth procedure based on the rotational isomeric state model to generate initial guess configurations, have been devised to build model polymer glass configurations. An early technique of this kind is the “amorphous cell”[61] method, a more recent one that gives better predictions for chain conformation is “Polypack”[62]. These techniques have the disadvantage that they do not

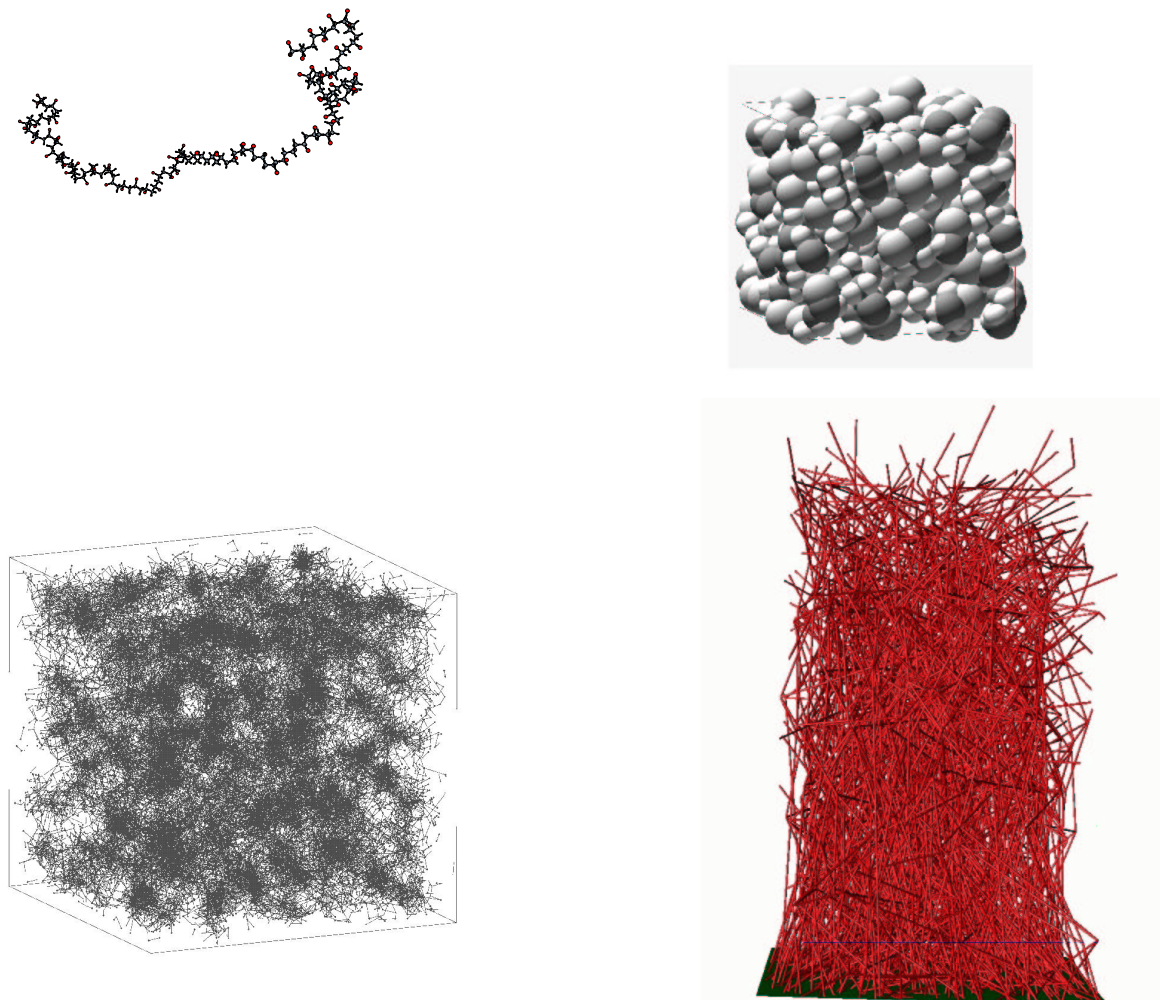
correspond to a well-defined glass formation history. Nevertheless, for some properties, such as elastic constants, they have been shown to yield very satisfactory predictions, provided the glass density is correctly reproduced.

Predicting physical ageing and stress-induced relaxation phenomena in glasses introduces an additional level of difficulty. Although transition-state theory approaches have been used to study local “Johari-Goldstein”-type motions, such as methyl group rotations and aromatic ring flips in polymer glasses, no clear methodology is available yet for connecting these calculations with the main α -relaxation associated with the glass transition, with the volume and enthalpy changes observed over long times in the presence or absence of mechanical load, and with the frequency-dependent dynamic mechanical moduli of polymeric glasses.

Polymer dynamics in confinement and how it affects glass transition and relaxation phenomena is another subject, of great importance to the properties of composite materials, where advances in simulation methodology are needed.

Research on these challenging problems is very active today. New, useful ideas are generated every day and the realm of what is computationally possible is constantly expanding. Time is certainly on our side, as large-scale computing becomes ever more powerful and affordable, and bright young people are educated in multiscale modelling of materials. There is every reason to believe that, besides being intellectually fascinating, hierarchical modelling of polymers will be increasingly important for future technological developments.

Four model representations for amorphous polypropylene



Top left: unperturbed single chain, used in Monte Carlo calculations of intramolecular correlations and chain dimensions in the melt. Top right: atomistic multichain configuration used in extracting PVT properties and segmental dynamics[60] and as a starting point for gas permeability calculations[37]. Bottom left: network of sorption sites, generated on the basis of accessible volume and multidimensional TST analysis of configurations of type (a) and used for KMC simulations of diffusion of methane in glassy atactic polypropylene[37]. Each node represents a site in which a methane penetrant molecule can reside and each line represents a transition path between two sites, to which a forward and a reverse rate constant are assigned. Bottom right: entanglement network model used in simulating interfacial fracture of polypropylene-polyamide interfaces[55]. Nodes are chain ends or entanglement points and lines represent chain strands of known contour length between the nodal points.

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