Multiscale Problems in Polymer Science: Simulation Approaches

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Polymer materials range from industrial commodities, such as plastic bags, to high-tech polymers used for optical applications, and all the way to biological systems, where the most prominent example is DNA. They can be crystalline, amorphous (glasses, melts, gels, rubber), or in solution. Polymers in the glassy state are standard materials for many applications (yogurt cups, compact discs, housings for technical equipment, etc.). They often combine relatively low specific weight with ductility, and they can be processed at moderate temperatures. In the melt state, polymers are viscoelastic liquids. Added to a solvent, polymers can be used as either shear-thickening or shear-thinning viscosity modifiers. Polymer networks form gels or rubber. Applications range from gels in (e.g., low-fat) foods, to hydrogels used in modern body care (e.g., diapers), to biological systems (cytoskeletons), and all the way to classical elastomers (e.g., car tires).

This range of applications is due to the variability of physical properties, which is based on the many different molecular building blocks, molecular architectures, and molecular weights of polymers. It is the combination and the rather subtle interplay of local chemical and more global architectural and size properties that makes macromolecules so versatile. This means that many different length and time scales are relevant; understanding the properties on one scale is not sufficient.

Chemical Repeat Units: Material-Specific Aspects

The simplest polymers are chain molecules with identical segments, repeat units, or monomers. Examples are listed in Table I.

These simple examples range from polyethylene (PE) (e.g., plastic bags) to bisphenol-A polycarbonate (BPA-PC) (e.g., compact discs). There are also many complex cases (e.g., DNA, proteins, copolymers), where several different building blocks are present in one molecule. While most polymers are not water-soluble, poly(ethylene oxide) (PEO) has the exceptional property of being both water- and oil-soluble. Other water-soluble polymers include polyelectrolytes, which dissociate ions into water and stay in solution even if their backbone is hydrophobic. Although polyelectrolytes are beyond the scope of this article, the typical simulation approaches for polyelectrolytes are conceptually very similar to the ones discussed here.[1–4]

Architecture/Morphology: Universal Structural Aspects

The simplest polymers are long linear objects of identical repeat units. Due to their intrinsic flexibility, they can assume distinct spatial conformations of the order of $O(q^N)$, where q represents the number of torsional states of the subsequent bonds, and N is the number of repeat units in a melt or solution. PE, for example, has stiff bond angles between subsequent carbon–carbon bonds. Each added bond is in principle allowed to take one of the three torsional states (*trans*, *gauche*$^+$, or *gauche*$^-$). Due to excluded volume effects, q is typically slightly smaller than 3 and depends also on temperature. Thus, already the individual polymer chain with its almost $O(3^N)$ degrees of freedom needs a statistical mechanical description. Depending on solvent properties, the chain in solution can be expanded ($\langle R^2 \rangle \propto N^\nu$, $\nu \approx 3/5$, where $\langle R^2 \rangle$ is the mean-squared extension of the chain), if in a good solvent. In marginal or Θ-solvent, where the monomer–monomer attraction just compensates the mutual chain–chain excluded volume, one finds that $\nu = 1/2$, while chains in poor solvent collapse into a dense globule and precipitate out of solution. In a melt, the other chains essentially act as a marginal solvent, resulting in $\nu = 1/2$. Some polymers crystallize, displaying very rich kinetics. Mixtures of polymers pose special problems, as tiny differences in the interaction energy are sufficient to initiate phase separation, since the interaction is to be compared with the translational and not the conformational entropy of the overall chain. A striking example is the phase-separation of hydrogenated and deuterated polystyrene (PS) for long enough chains.

Current research deals with more complicated architectures, such as star polymers, dendritic structures, cross-linked systems, and so on. Another special class are block copolymers. These range from long chains consisting of blocks of A and B repeat units to random copolymers or objects containing flexible and rigid pieces. Though of utmost scientific and technical interest, they will not be discussed here.[5]

Length and Time Scales for Polymer Simulations

Let us start with the shear viscosity η of a polymer melt, which illustrates the whole complexity of the problem. If one changes the process temperature of a BPA-PC melt from 500 K to 470 K, the viscosity rises by a factor of 10. This effect is a direct result of interactions on the atomistic level, as it could also have been achieved by an equivalent change in the chemical structure of the monomer. On the other hand, increasing the chain length by a factor of 2 also shifts the viscosity by a factor of 10 because, for long chain melts, $\eta \propto N^{3.4}$. This power law is a universal polymer

Table I: Examples of Simple Polymers.

Polyethyelene (PE)	$(CH_2)_n$
Polystyrene (PS)	$(CH_2(CH(C_6H_5)))_n$
Poly(ethylene oxide) (PEO)	$((CH_2)_2O)_n$
Bisphenol-A polycarbonate (BPA-PC)	$((C_6H_4)C(CH_3)_2(C_6H_4)CO_3)_n$

property and holds for all known linear polymers, independent of the chemical structure of their backbone. Thus, both material-specific as well as universal properties produce a comparable variation of the dynamic macroscopic properties and therefore of relevant time scales. This variation can easily extend over several orders of magnitude.

At first sight, it might be tempting to perform an all-atom computer simulation of a polymer melt. However, there are several complications. The first stems from the choice of interaction potentials, while the second is related to the many scales involved. Such an all-atom simulation uses a classical force field based on a classical energy function between all atoms. All quantum simulations (Car–Parinello density functional simulations, path integral quantum Monte Carlo simulations, or combinations thereof) are still confined to very small systems.[1]

Although the force-field approach sounds conceptually straightforward, it contains a number of unsolved complications. First, although usually not considered, are quantum effects. One might think that typical temperatures for macromolecular systems (room temperature and higher) are well above the Debye temperature of the relevant atoms. This is true for the carbon atoms, but not necessarily for the many hydrogen atoms present. Their thermal de Broglie wavelength at room temperature is about 1 Å. A recent paper by Martonak et al.[6] revealed that even at room temperature, quantum effects are crucial to understanding the anisotropic thermal expansion of PE crystals. Though a rather special finding, it should be kept in mind. For the classical force-field approach, the intramolecular interaction along the backbone is derived from a parameterization of quantum calculations of chain fragments. To parameterize the nonbonded interactions, experimental quantities are usually used, such as the heat of vaporization of low-molecular-weight liquids. It is often impossible to optimize all properties to the same degree of accuracy and confidence. Thus, one has to be very careful, and there is no universal force field for a system that, without further verification, can be used at significantly different temperatures or for different mixtures. Keeping this in mind, force-field simulations can be very useful and have provided many important insights into microscopic properties over the last few years.[2,4]

It is actually questionable whether such a fully atomistic simulation, if possible, would be useful at all. Almost all the information generated would be irrelevant for the questions under consideration (e.g., the previously mentioned viscosity η). In order to make suggestions for material improvements, or to qualitatively and quantitatively understand properties, it is crucial to structure and understand the results rather than just collect measured quantities. This is often easier with simplified models.

Polymers are characterized by a hierarchy of different length and time scales. Figure 1 illustrates this and shows the typical range involved. On the microscopic level, the properties are dominated by the local vibrations of bond angles. The typical time constant is about 10^{-13} s, resulting in a simulation time step of about 10^{-15} s. This angstrom regime is well characterized by the bond angles and bond lengths. The properties on this level are solely determined by all the details of the atoms or molecules involved.

On a more coarse-grained level, one cannot resolve all atomistic details of the chains anymore. The chain looks like a more or less flexible thread. This is the universal entropy-dominated coil regime. The many possible conformations of the chains and the many ways to pack chains in a melt determine the morphology. On the mesoscopic level, many properties can be understood on the basis of simple coarse-grained ("bead spring") models, which represent chains as spherical beads connected by anharmonic springs. Characteristic time and length scales are indicated in the figure. On the even coarser, semimacroscopic level, the behavior is dominated by the overall relaxation of the chain conformations. Typical times depend on chain length and vary between N^2 and $N^{3.4}$. As explained before, prefactors originating from the microscopic interaction of the monomers cause an equally large variation of scales. The resulting characteristic times can reach seconds or more if one approaches the glass-transition temperature. Thus, a satisfactory numerical description of material properties needs a combination of microscopic and coarse-grained models.

Mapping from Atomistic to Mesoscopic Models—and Back

The successful mapping from an atomistic model to a mesoscale model has the advantage that time and length scales are accessible that are far beyond atomistic simulations. Thus, qualitatively different physical problems can be treated. A useful mesoscale model preserves enough of the original chemical identity of the atomistic model to reproduce certain aspects of, say, PS or polypropylene chains under the corresponding conditions. It is no surprise that in recent years, a number of atomistic-to-mesoscopic mappings have been published (see, e.g., References 7–14; a review encompassing scales bridging from electronic to macroscopic degrees of freedom is presented in Reference 2).

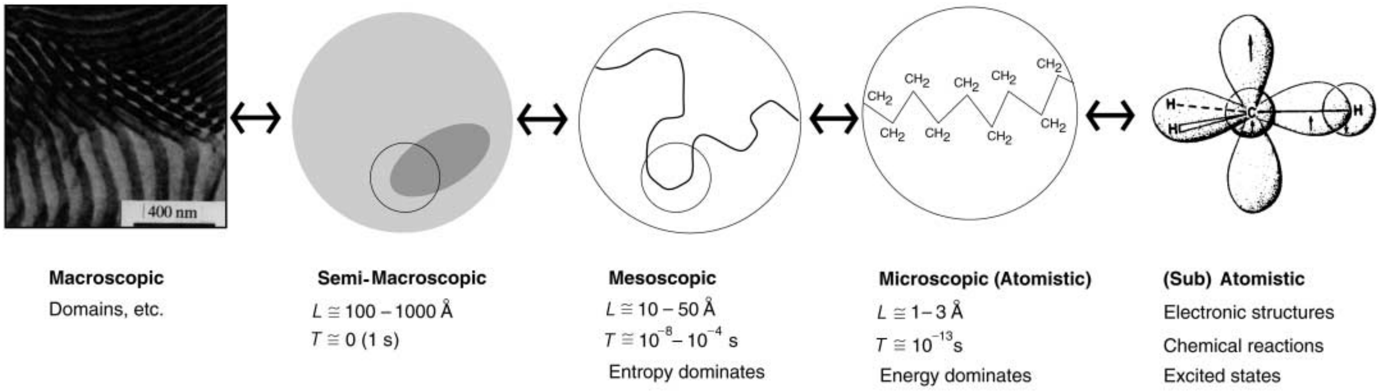

Figure 1. Polymers exhibit phenomena on many length scales (from entire devices down to electrons) and associated time scales (from years to femtoseconds). For details, see text.

It turns out that coarse-grained models are useful not only for studying large-scale phenomena; they are also a powerful tool for the generation of well-equilibrated atomistic structures, provided that one can perform a reverse mapping from the mesoscopic model back to a fully atomistic model. This is often needed because experimental information involves atoms, as in nuclear magnetic resonance spectroscopy,[15] neutron scattering,[8] or positron annihilation spectroscopy.[16]

The approaches to coarse-graining vary substantially; to date, no "standard" procedure has emerged. The mesoscopic models include both continuous models[6,8–10] and lattice models.[11–14] For a given complexity of the model (e.g., the range of the nonbonded interactions), continuous and lattice models seem to be roughly comparable, as far as static polymer properties are concerned. The continuous models have advantages when it comes to dynamic problems such as shear behavior or to questions requiring changes in the simulation volume (swelling properties, etc.). To study dynamical quantities, continuous models allow equations of motion (often molecular or Brownian dynamics), which are well-controlled approximations. Monte Carlo calculations show physical dynamics, but only if well-known standard criteria for the motion of the beads are obeyed.[1,3,17] Then the dynamics can be viewed as Brownian. The most important condition is that the motion is local, involving only a small number of beads at a time.

A successful example of mapping atomistic to coarse-grained models is the study of different polycarbonate melts.[7] In the case of BPA-PC, the atomistic monomer is mapped onto two coarse-grained beads (Figure 2), one centered at the isopropylidene group (S_1), the other at the carbonate moiety (S_2). A reduction of the number of interaction sites per monomer from 33 to 2 is thereby achieved. What remains of the chemical identity of the polymer is contained in four intrachain interactions: one bond stretch (S_1–S_2), two bond angles (S_1–S_2–S_1 and S_2–S_1–S_2) and one torsion (S_1–S_2–S_1–S_2). These interactions are parameterized in three steps: First, the atomistic potential-energy surface of a fragment is calculated by *ab initio* quantum chemistry. Second, with this potential surface, a Monte Carlo calculation of a single random-walk chain in free space is performed, from which distributions of the four intrachain degrees of freedom are extracted. These distributions contain the complete intrachain information of the coarse-grained model chain. This information is used in the third step, as the distributions are transformed into an effective coarse-grained potential-energy function (potential of mean force) by simply taking the logarithm of the distribution functions. This determines the interaction potentials without any adjustable parameter or fitting. Taking the melt density from experiments, with this approach one is able to reproduce the shift of the Vogel–Fulcher temperature T_0 for three different polycarbonate modifications almost quantitatively and the shift in the generalized activation energy qualitatively, with energies in the right order of magnitude. Taking this, one can estimate viscosities; Figure 3 shows this for BPA-PC. The interchain interactions are modeled as purely repulsive in order to keep the interactions short-ranged and the simulations fast. The melt, however, has no intrinsic cohesion, but is kept together by the constant-volume condition or an applied (high) pressure. This is acceptable, as long as one is interested in bulk polymers of known homogeneous density. When the simulated system is expected to develop density heterogeneities (e.g., in the presence of several phases), or if one is concerned about properties of free surfaces, one has to adapt the model. Work is currently under way to develop attractive coarse-grained potentials.[11]

Automatic Coarse-Graining

The systematic development of mesoscopic polymer models based on first principles is a cumbersome process. A number of steps have to be made:

1. The degree of coarse-graining and the positions of the coarse-grained beads in relation to the atoms have to be determined.
2. The form of the intra- and interchain potentials need to be chosen, as they can-

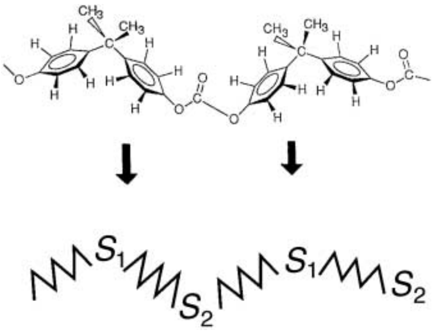

Figure 2. Atomistic bisphenol-A polycarbonate (BPA-PC) is mapped onto a coarse-grained model consisting of two beads per monomer, which are centered at the isopropylidene and the carbonate groups (from Reference 7).

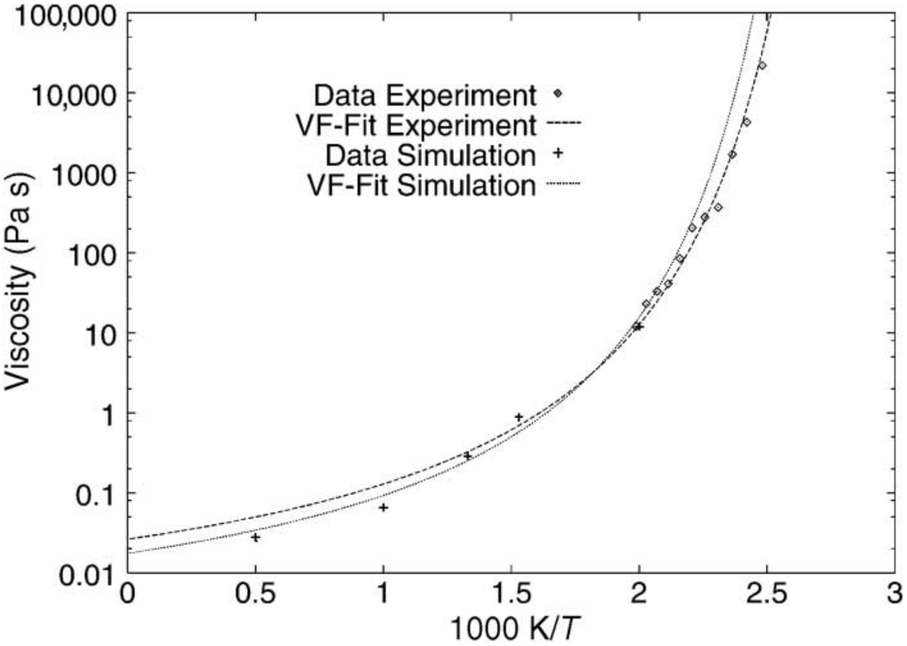

Figure 3. Plot of the viscosity for BPA-PC determined from simulation of the coarse-grained model and data taken from experiment. The simulation and experimental data are used to extrapolate into the other regime within the Vogel–Fulcher (VF) scheme. The highest temperature for experiment and the lowest for simulation is $T = 500$ K, allowing an absolute time scaling (from Reference 7).

not always be directly derived from the distributions.

3. Free parameters, especially for the nonbonded interactions, have to be optimized.

While (1) and (2) are intellectual challenges, (3) is often a menial task.

This section describes a recent approach to systematically and automatically parameterizing the interaction parameters of mesoscale models. The purpose is to carry out the parameterization (3) for a given choice of degree of coarse-graining (1) and form the potential (2) quickly and reproducibly.

We started by obtaining reference data. These were structural properties of the polymer of interest, the sodium salt of poly(acrylic acid) (PAA) as an aqueous solution of about 2 wt%. The data were obtained by performing an atomistic simulation of an oligomer (23 monomers) solvated by about 3200 water molecules. The coarse-grained model contained 1 bead per monomer, centered at the center of mass of the atomistic monomer, reducing the number of polymer atoms by eight. More importantly, the coarse-grained model disposed of the explicit solvent, so that the total number of sites was reduced from approximately 3350 to 23 (Figure 4). The coarse-grained intrachain interactions consisted of a harmonic bond potential, the multiple-minima bond-angle potential, and a short cosine expansion of the dihedral-angle potential. The nonbonded potential between monomers is pieced together from different factors. Such a potential has proven useful,[11] as it contains enough flexibility to encompass an effective description of the solvent. The reference data include distributions of bond lengths and bond angles as well as radial distribution functions $\mathrm{RDF}_{\mathrm{target}}(r)$ obtained from the atomistic simulation but calculated for the coarse-grained beads. Since here the bonded and nonbonded parts of the effective interaction potentials cannot be separated anymore, a direct Boltzmann inversion to get the potential of mean force would not properly count the interactions in solution.

In order to avoid these problems, the same 23-mer of PAA was simulated with the coarse-grained model. The coarse-grained parameters were adjusted until the target RDFs and other distributions were reproduced satisfactorily. We defined a least-squares merit function $f\,(p_1, p_2, \ldots)$ which was minimized, where $p_1, p_2, \ldots$ are the parameters in the optimization set. For the minimization, we use a standard simplex scheme.[19] Note that every evaluation of f involves an entire molecular-dynamics (or Brownian-dynamics) simulation of the coarse-grained system. Here, the apparently straightforward scheme can become technically tricky and computationally expensive.

With the coarse-grained model parameterized, the simulation was extended to much longer chains of PAA in aqueous solution. The results for the calculated hydrodynamic radius of such chains closely match the results from dynamic light scattering (Figure 5). This shows that the coarse-grained model retains enough of the true identity of PAA to reproduce its structure on a scale much larger than that of the atomistic model from which it was developed. In the meantime, this approach has been extended not only to other polymers in solution but also to bulk polymer melts.[20]

Atomistic Results after Reverse Mapping

After equilibration of coarse-grained models, they can be mapped back to an atomistic model. If the position of a coarse-grained site is defined in terms of the atom positions of the atomistic model, the reverse mapping is relatively straightforward. The atomistic monomers are placed at or near the corresponding positions in space and oriented such that as many as possible of their intrachain degrees of freedom are in low-energy conformations. Local stresses, close contacts between different chains, and so on are left to relax out by standard atomistic MD simulations.[21]

Large equilibrated samples of BPA-PC have been used to compare structure factors to neutron-scattering data.[8] Simulation and experiment compare very well (Figure 6), which indicates that the atomistic structures generated by means of a coarse-grained equilibration are faithful representations of the microscopic structure of BPA-PC. This was further supported by an analysis of the polycarbonate structures with a new method for the calculation of positron lifetimes.[16] Such large equilibrated computer samples are now used for other "applications," where the atomistic details are essential. One example of immediate industrial relevance is the study of the diffusion of the polycondensation byproduct phenol in BPA-PC melts.[22] These studies have not only led to a hitherto-unknown mechanism of penetrant diffusion in polymers, but also to more accurate values of diffusion coefficients that have already found their way into polycarbonate production. None of these studies would have been possible without the help of systematic coarse-graining and the subsequent fine-graining of polymer models.

Beyond Particle-Based Chain Models

So far, the coarsening in terms of the length scale was on a level such that a given coarse-grained bead represented

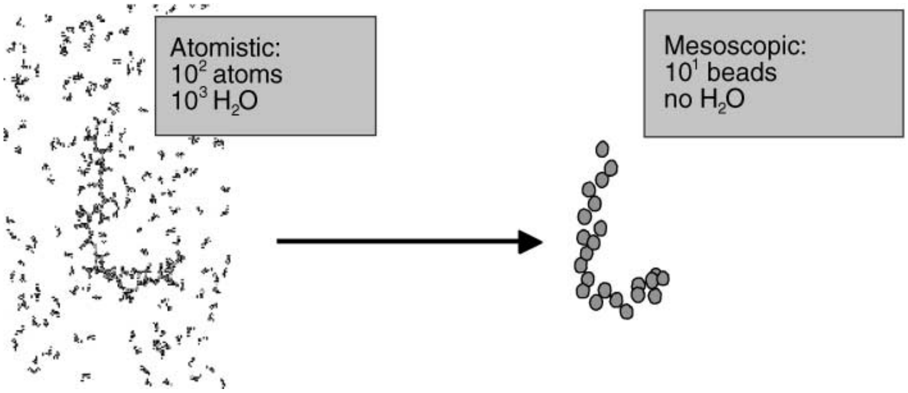

Figure 4. An example of mapping between atomistic and mesoscopic models: the sodium salt of poly(acrylic acid) (PAA) (2 wt%) in aqueous solution (from Reference 18).

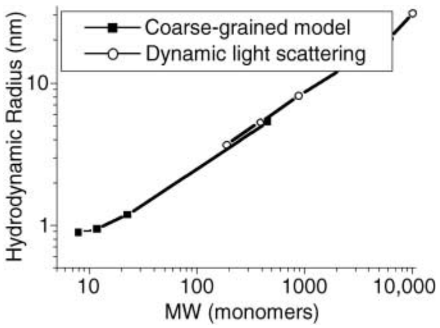

Figure 5. The hydrodynamic radius of PAA in aqueous solution as a function of molecular weight (MW). Experimental data courtesy of Beate Müller and Simone Wiegand, Max-Planck-Institut für Polymerforschung (unpublished).

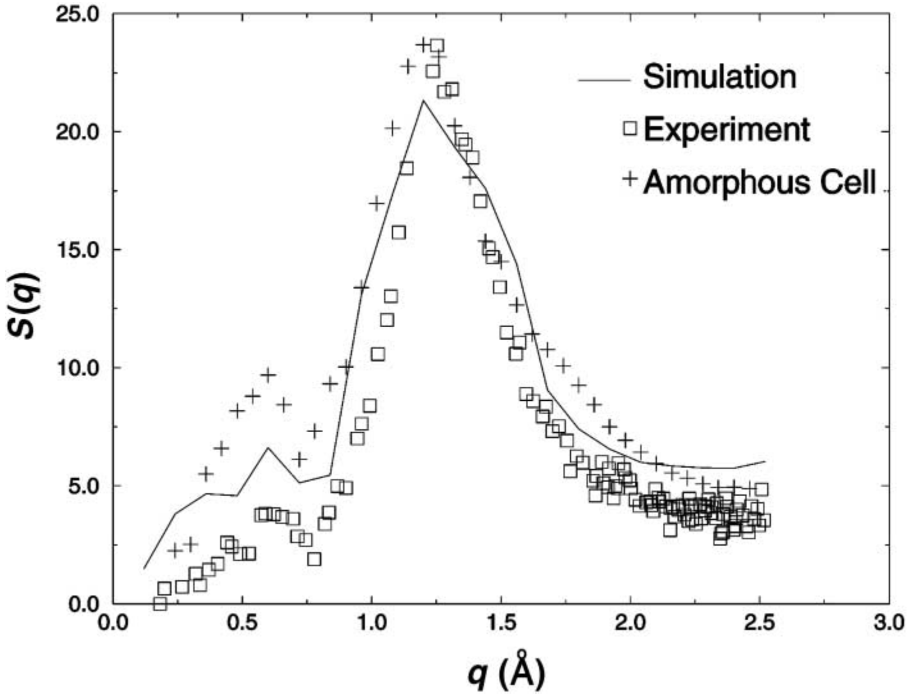

Figure 6. Structure factor S_q *at wave vector* ***q*** *of fully protonated BPA-PC from simulation (solid line) and neutron scattering (open squares).*[8] *For comparison, results obtained with a commercial ad hoc method for generating polymer structures ("Amorphous cell," +) are also shown.*

roughly one repeat unit of the underlying polymer. Thus, the objects under consideration still contained many particles. On this level, a number of other approaches have been followed where mean-field theories and random-walk statistics were combined.[23] The wide applications, especially for the understanding of morphologies of block-copolymer systems, can be found in a series of papers by Fredrickson and Bates.[5] A commercially available simulation program employing those and related methods can be obtained through the MesoDyn project headed by Fraaije.[24]

We want to mention here another approach to coarse-graining the models further.[25–27] So far, the number of degrees of freedom to be considered is proportional to the number of monomers of a given chain; in large systems with many chains, this leads to a high number of degrees of freedom to be monitored. To arrive at a situation where one can simulate many chains, we go back to Figure 1. The previous section discussed mapping between the microscopic and the mesoscopic regime. Now we consider the next step, namely, to map the chains from the mesoscopic level up to the semimacroscopic regime. The chain is replaced by soft ellipsoidal particles, which will overlap in the melt. The whole chain, or at least large parts of it, is represented by one particle with three internal degrees of freedom given by the axes of the mass tensor $\underline{\underline{R}}$ of the chain. To do this, one can follow a philosophy very similar to that of the coarse-graining procedures discussed before and separate the free energy of a system into an intra- and an interchain part.[25] The intrachain contribution to the free energy from chain i is given by $F^{i}_{\text{intra}} = -k_B T \ln P(\underline{\underline{R}}^{i})$, where $P(\underline{\underline{R}}^{i})$ is the probability of a mass tensor $\underline{\underline{R}}^{i}$ of chain i. This defines, as before, an intrachain potential of mean force. With the assumption that the inter- and the intrachain parts are additive, the interchain interaction is proportional to the pairwise density overlap ρ_i and ρ_j of the ellipsoids representing the different chains i and j.

In a melt of chains of length N, approximately $\sqrt{N}$ chains overlap, thus the computational cost per step can, at best, be reduced by a factor of $\sqrt{N}$. The most significant time savings, however, comes from the fact that, to a first-order approximation, the computational cost to run one relaxation of the ellipsoids becomes independent of N. This formula has been tested on simple bead-spring polymer models. An extension to a more refined coarse-grained model (e.g., polycarbonate) is an objective of current work. Within this scheme, it was possible to simulate, on one DEC-Alpha processor, polymeric melts of the order of several thousands of ellipsoids to represent chains. Typical runs consist of 10,000 ellipsoids. The procedure is a standard Metropolis Monte Carlo simulation for translation, rotation, and shape-change of the ellipsoids. By doing this, one is able to investigate phase separation and morphology development of micrometer-sized polymer samples. Hydrodynamic properties on a coarse-grained level beyond the bead-spring chain picture without topological constraints can be studied by dissipative particle dynamics.[28,29] There, the chains also can move freely through each other. So far, this has not been used for chain models, where the properties of the "bead" are derived from micro- or mesoscopic information.

Beyond such particle-based methods, continuum approaches are used to study the properties of macroscopic samples, such as the finite element method.[30] Recently, this approach was combined with Monte Carlo techniques in order to study composite materials by Gusev et al.[31] While globally homogeneous, composites are locally heterogenous. These authors used Monte Carlo simulations to generate "samples" of small composites and studied the size and number of systems needed to reproduce, for example, elastic constants of fiber-reinforced materials.

Conclusions and Outlook

Despite all of the progress made over the last few years, a number of key challenges remain. On each level of description, new and improved methods have been developed. Yet, significant progress is still needed. Of most importance is the controlled and systematic improvement of links between the different simulation schemes; for example, systematic coarse-graining procedures, including the inverse mapping step, need to be improved and developed further. Steps must cover the micro (many atoms) ↔ meso (many monomers) ↔ macro (many chains) regimes and link to quantum simulations at the low end and to self-consistent field calculations and/or finite-element-like approaches at the upper end. This is crucial in order to achieve the longstanding goal of predicting material properties. The efforts certainly are not intended to replace experiments; however, they should in the long run help to reduce experimental tests or allow much more focused testing. One condition for this progress is improvement on each level of description, such as

- Quantum simulations of reasonably sized systems (Car–Parinello techniques, path integral quantum Monte Carlo calculations, and combinations of both), coupling electronic and conformational degrees of freedom.

- Improved methods to parameterize and validate force fields for microscopic classical molecular simulations; suitably parameterized intermolecular interactions (for polar molecules) are especially needed.
- New methods for static and dynamic studies on the semimacroscopic to macroscopic levels, such as dissipative particle dynamics for composite materials.

These advances require a significant coordinated effort of researchers coming from different fields of expertise. Such projects are under way at a number of places around the world and range from more software-development-oriented activities, such as the NEDO project in Nagoya, Japan, and European efforts within the Training and Mobility of Researchers program of the European Commission, to more basic method-development-oriented activities, such as the "Center for Excellence in Materials Simulation" funded by the German ministry of science and technology, which is coordinated by our group.

Acknowledgments

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