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REVIEW

Scale-Hopping in Computer Simulations of Polymers[#]

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ABSTRACT

Polymer simulations can be performed at many different length scales by using techniques ranging from quantum chemistry to finite element via a hierarchy of coarser and coarser particle or field-based methods. Recent years have seen many efforts to connect simulations at different levels to 1) indirectly predict large-scale properties starting from fundamental models and 2) to accelerate the equilibration at more fundamental levels via the detour of coarse-grained levels. It is the purpose of the present synopsis to review some of the recent methodological advances concerning the systematic and, where available, automatic bridging between different levels of polymer simulation.

Key Words: Polymers; Course-graining; Scale-bridging; Molecular simulation.

[#]The author of this review has agreed to write a short follow-up to this article that will incorporate information provided by the readers. If you have comments, additions, clarifications, or remarks concerning this article, please send them to the author within 3 months after this article has appeared. The author will review them and collect them into a feedback article, which will appear in one of the coming issues of *Soft Materials*.

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THE PURPOSE OF MULTISCALE SIMULATIONS

Polymers, as many other systems, can be described at different levels of detail, or synonymously: different length scale, resolution, or granularity, retaining relevant degrees of freedom. When we describe quantitatively chemical systems, it is useful to use the appropriate level of detail. For example, to study the reaction of oxygen and hydrogen to give water, it is necessary to consider the change in the electronic wavefunction. To describe the solvation of a compound by water molecules, one can use an empirical potential energy surface (vulgo force field), in which the electrons are included only implicitly, and the molecular positions and orientations now become the pertinent degrees of freedom. For the flow of bulk water, even the molecules are disregarded. Water is treated as a continuum, characterized by certain thermodynamic, mechanical, and dynamic properties. The basic building block is now a volume element. Depending on the problem investigated, simulations of water can take place anywhere in the hierarchy electrons-molecules-volume elements, the techniques being quantum chemistry, molecular simulation, and computational fluid dynamics. Using the appropriate level guarantees efficiency, accuracy, and ease of understanding.

This example of water illustrates the concept of systematic coarse graining (or mapping or scale bridging or multiscale simulation). It is one of the more fortunate cases in which we know—at least in principle—the connections between the levels. Quantum chemistry can be used not only to form a water molecule but also to generate the potential energy surface for molecular dynamics simulations. The quantum-chemical potential energy surface may then be fitted by the more efficient mathematical form of a force field (although there might be better ways to obtain a force field). Therefore, a rigorous path exists from the costly, more fundamental model to the cheaper coarse-grained model. The transfer is done by taking the output results of the calculation of the more detailed model and converting them into the input parameters of the Hamiltonian of the less detailed model. This is a general concept in many scale-bridging approaches.

Two general points can be noted in the water example. First, scale bridging can also take us from the molecule level to the next level, namely, liquid water as a continuum. A molecular dynamics simulation produces the properties of liquid water—equation of state, mechanical, dielectric, and dynamic properties—that are the necessary input for the continuum description of water. The machinery that provides the connection is statistical mechanics. Hence, through the use of a hierarchy of simulation methods with rigorous links between them, it is indeed possible to predict *indirectly* from first principles the macroscopic flow behavior of water, which would have been impossible to predict *directly* in a first-principles simulation. The indirect prediction of large-scale, long-time quantities from short-ranged, slow methods is the first objective of multiscale simulation.

Second, a good coarse-graining method also allows the reverse process, denoted as fine-graining or reverse mapping. It is obvious how to go from an atomistic description of an assembly of water molecules to a quantum-chemical description: keep the atom positions and reinsert basis functions and electrons. This is necessary to calculate electronic properties such as the polarizability of a water aggregate after structural relaxation. Remapping leads to a second use of multiscale

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simulation. The coarse-grained model is used as a computational route to faster generate samples for fine-grained analysis. This sometimes demanding detour would not be worth taking if it did not lead over the high-speed motorway of the coarse-grained description.

WHY ARE MULTISCALE SIMULATIONS SO DIFFICULT TO DO FOR POLYMERS?

Fig. 1 illustrates a few scales and methods that are being used to simulate polymers. The scales range from Ångströms and subpicoseconds for the vibrations of atomic bonds to millimetres and seconds for crack propagation in polymer composites. There are many computational tools. They include quantum chemistry, atomistic force field simulations, continuous or lattice-based simplified models, soft fluid models, or continuum, such as finite-elements methods. All these methods and many others have been applied independently of each other to polymers, for many years and with some success. Until recently, however, solid bridges between the different scales have been few and far between.

The reason is the connectivity of polymer molecules that enforces an interdependence between features on different scales. As a consequence, the choice of where one building block ends and the next one begins is not unique, and it is not obvious how to abstract from a fundamental degree of freedom and use it in an implicit way in a coarser-grained model. Yet, it would be highly desirable to have multiscale methods available, despite the conceptual and technical difficulties associated with them. Many polymer properties cannot be viewed on one length scale alone. An illustrative example is the temperature dependence of the viscosity of bisphenol-A

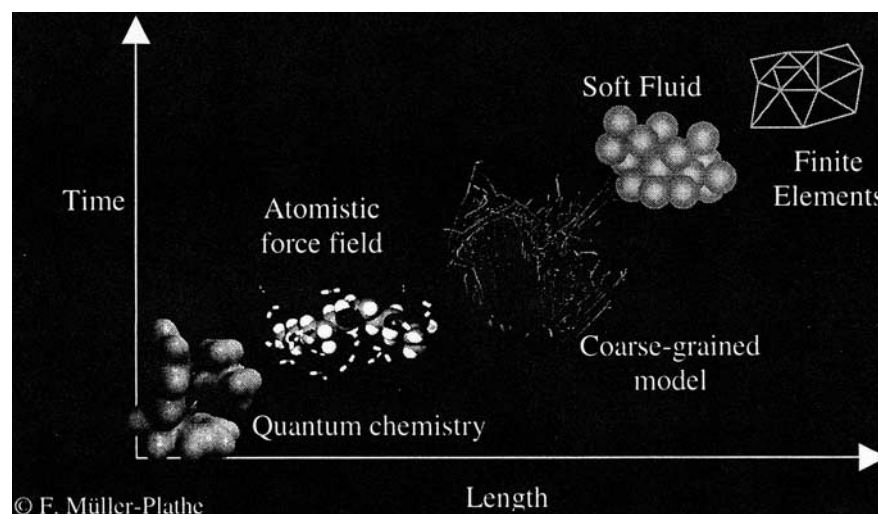


Figure 1. Length scales, associated time scales, and computational methods in polymer simulation (reproduced with permission).



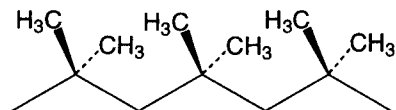
polycarbonate melts:^[1] Reducing the processing temperature from 500 to 470 K increases the viscosity by a factor of 10. This increase could also be brought about by a suitable modification of the monomer with a resulting increase in the activation energy equivalent to a temperature decrease of 30 K. This would correspond to a local change of the chemical nature of the polymer. The same viscosity increase can also be achieved by changing the global structure of the polymer leaving its chemical nature intact. In the present case, doubling the length of the linear polymer also increases the viscosity by a factor of 10, because the viscosity is proportional to $MW^{3.4}$, with MW the molecular weight of a polymer chain. This example shows that both detailed material-specific information of the chemical composition and generic chain length and connectivity information are necessary for a complete view on the melt viscosity. The first needs to be described by an accurate atomistic model to capture the subtleties of the interactions. The latter must be treated by a more mesoscopic model to cover the length scales and time scales inherent in the shearing process. An ideal multiscale ansatz would combine the advantages of both approaches. There are many more polymer properties, for which a combined approach is necessary. A few examples of how architectural features on different length scales influence polymer properties are collected in Fig. 2.

Considerable progress has been made in recent years in systematically linking simulation methods belonging to different length scales. It is the purpose of this review to highlight some of this work. The older literature has already been adequately covered (e.g., Refs. [2–4]). Here we focus on methods that use models of different scales sequentially (i.e., that perform a fine-grained simulation, use its results to systematically define a coarse-grained model, simulate the coarse-grained model, and, if need be, remap to the fine-grained model for local analysis^[5,6]). We exclude methods that treat a part of the system by a fine-grained model and simultaneously embed this part into an environment treated by a coarse-grained model (e.g., the quantum-mechanical/molecular-mechanical hybrid methods^[7,8] or solutes embedded into some effective or coarse-grained solvent^[9–11]). We also exclude the multitude of coarse-grained protein models termed statistical or low-resolution force fields,^[12] inasmuch as they are usually developed for different goals by using a different methodology. Finally, we exclude what is the oldest and best-documented example of systematic coarse graining, namely, the derivation of atomistic potentials with the help of quantum-chemical calculations.^[4,13]

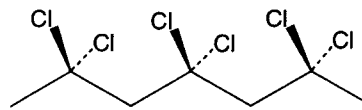
A HIERARCHY OF POLYMER MODELS

To avoid ambiguities, it is necessary to classify the hierarchy of polymer models by the nature of the basic building block or degree of freedom, as shown for example in Fig. 3. Presently, terms, such as “coarse-grained” or “mesoscopic,” are used indiscriminately and can mean different things, depending on the point of reference. For example, “mesoscopic” falls between “microscopic” and “macroscopic.” If microscopic signifies atomic resolution and macroscopic signifies the micron range, then mesoscopic might be equivalent to a typical polymer coil diameter of, say, 100 Å. If microscopic signifies “visible in a microscope,” viz. micrometers, and macroscopic

Chemical detail

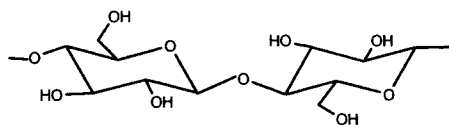


Polyisobutylene:
amorphous rubber
($T_g=200$ K, $T_m=320$ K)

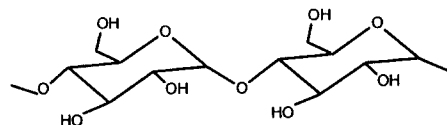


Poly(vinylidene chloride):
semicrystalline, brittle
($T_g=255$ K, $T_m=470$ K)

Tacticity (Stereochemistry)



Cellulose:
crystalline, insoluble



Starch (amylose):
soluble in water

Sequence

-B-B-S-B-S-S-S-B-B-S-S-

Random-poly(butadiene-co-styrene):
synthetic rubber

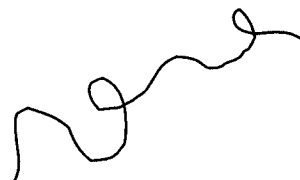
-B-B-B-B-B-S-S-S-S-S-

Block-poly(butadiene-co-styrene):
high-impact polystyrene (HIPS)

Topology



Low-density polyethylene:
branched, shopping bags



High-density polyethylene:
linear, bullet-proof vests

Figure 2. Structure on different scales can influence the macroscopically observed behavior of polymers.

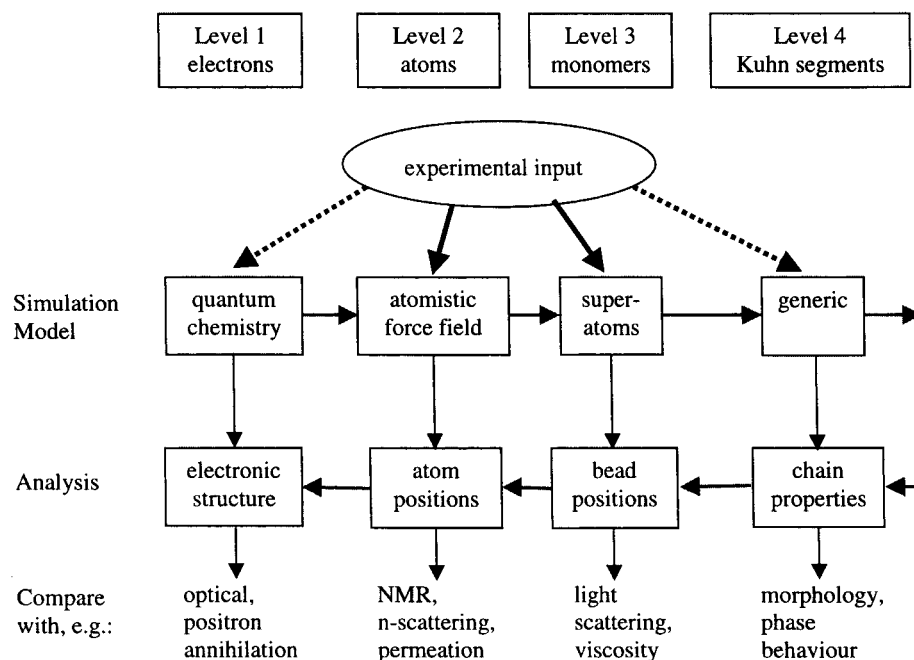


Figure 3. Scale-bridging concept in polymer simulation. Traditionally, simulations have been performed at different levels independently (vertical black arrows); The models have taken different amounts of experimental information in their parameterisation. The simulations (say atomistic force field) have been run, they have been analyzed at the same level (say for inter-atomic distances) and have been compared with experiments at the same level (say NMR results). In contrast, scale bridging involves hopping between levels (horizontal red arrows): output from simulations at the lower level (say level 2) is used to parameterize the model at a higher level (say level 3); level 3 is then simulated; the simulations are used 1) for direct analysis of properties on the inherent length scale of level 3 (say viscosity) and 2) the equilibrated coarse-grained structures may also be used, after reintroduction of the atoms and maybe postequilibration, to calculate atom-based properties and to compare to experiments that probe the atomistic scale.

refers to the dimensions of a product, then mesoscopic might be the millimeter scale. Therefore, we try to avoid the terms mesoscopic and mesoscale altogether. The terms “coarse-graining” and “fine-graining” are used, without reference to specific dimensions, to denote generically the passage from a higher-resolution to a lower-resolution model and vice versa. The scales are denoted as follows:

Level 1: Electrons

The basic degree of freedom is the electron or the molecular electronic wave function. Electronic structure methods are used: quantum chemistry, molecular density-functional methods, solid-state electronic structure methods.



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Level 2: Atoms

The fundamental degree of freedom is the atom. Every atom present in nature is modeled as a separate interaction center. The interactions between atoms are modeled as accurately as possible. Techniques are labeled atomistic and can be as diverse as molecular mechanics, molecular dynamics, Monte Carlo, etc.

Level 2.1: United Atoms

A variant of atomistic models where a small number of real atoms are collected into one interaction center. Typical united atoms are CH, CH₂ and CH₃ groups.

Level 3: Superatoms, Monomers, or Residues

One interaction center (sometimes referred to as “bead”) contains of the order of 10 real non-hydrogen atoms or approximately one chemical repeat unit. Examples are as follows: a styrene unit in polystyrene, an amino acid in a protein, four methylene groups in polyethylene, half a monomer of bisphenol-A polycarbonate. A polymer described at level 3 still retains some of its chemical identity. In contrast to the lower levels, lattice models may be used as well as continuous models. Equations of motion can be stochastic dynamics or Monte Carlo.

Level 3.5: Near Generic

The model (continuous or lattice) is simple in its nonbonded interaction (e.g., excluded-volume only). However, the distance between basic interaction centers is smaller than the Kuhn length, so that the chain has a finite stiffness.

Level 4: Generic

One interaction center (referred to as “bead” or “blob”) comprises a stochastic segment of a polymer chain (i.e., at least one Kuhn segment). The resulting polymer chain is fully flexible and behaves as a Gaussian coil. At the intramolecular level, there is no chemical identity (i.e., all polymers are modeled alike). The interaction between polymers of different type may be described by simple intermolecular potentials. Models can be continuous, lattice, or analytical.

Level 5: Soft Fluid

One interaction center incorporates an entire polymer chain or at least a substantial fraction of a chain. The objects can interpenetrate (“soft”) and/or deform. The interaction between polymers of different type may be described by simple intermolecular potentials. Models are mainly continuous.



Level 6: Density Fields

In contrast to all previous models, this level is not particle based. The basic degrees of freedom are concentrations of components in volume elements. These elements have a typical size of 100 Å (i.e., roughly the same as the objects of level 5). The interaction between polymers of different type may be described by simple potentials. The pertinent equations of motion (Fick, Fourier, etc.) are solved numerically on a lattice.

Level 7: Micromechanical

Micron-sized volume elements form the basic degree of freedom. Their size and shape may vary in a simulation, but not their composition.

Level 8: Macroscopic

Anything visible with the naked eye. Typically solved by using finite-element methods.

ATOMS TO MONOMERS (LEVEL 2 TO LEVEL 3)

Reproducing Structure and Thermodynamics

So far, the “essential” features chosen to be reproduced by level 3 models have been structural, thermodynamic, or both. We do not know of any coarse-graining scheme that has tried to tune a level 3 model to reproduce explicitly dynamic or elastic properties of a polymer: In some applications, such properties may later have been calculated with a level 3 model, but they were not included among the original target properties against which the model was optimised.

The structure of an ensemble of polymer chains in an environment is described by distributions of certain geometric quantities, which can be intramolecular (distances between two adjacent superatoms, angles between three subsequent superatoms, dihedral angles between four subsequent superatoms, principal values of the radius of gyration tensor, etc.) or intermolecular (distances between superatoms belonging to different chains or being topologically distant on the same chain, distances between the centers of mass of different chains or chain fragments, etc.). All these can be used as targets to be reproduced by the coarse-grained model. Which ones are actually being used depends on the intended purpose of the coarse-grained model. Here, choices have to be made, because all simplifications necessarily lead to models that reproduce fewer features of the polymer. For automatic approaches, it is essential to define some penalty function that measures the deviation from the target distribution and that can be minimized by a suitable numerical procedure. For example, in the case of a radial distribution function (RDF), the penalty function $f(\mathbf{p})$ is often an error integral of the form

$$f(\mathbf{p}) = \int_0^{\text{cutoff}} w(r) [\text{RDF}(r, \mathbf{p}) - \text{RDF}_{\text{target}}(r)]^2 dr \quad (1)$$



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Here, both the penalty function and the actual radial distribution function $RDF(r, \mathbf{p})$ depend on the current values of the adjustable parameters \mathbf{p} ; $w(r)$ is an optional weight function. The target $RDF_{\text{target}}(r)$ is obtained from the simulation of the atomistic (level 2) model but defined in terms of the superatoms of the level 3 model. Therefore, the RDF and other structural distributions provide the systematic link between the two levels, and the penalty function defines a way of obtaining a superatom model from an atomistic model. It is minimized in the space of the adjustable parameters by standard numerical methods such as the amoeba simplex.^[14,15]

To use Eq. 1, more choices have to be made by the developer of the coarse-grained model. First, there is the functional form of the interaction potentials with their adjustable parameters \mathbf{p} . Second, the degree of coarse graining needs to be chosen, or how many real atoms are collected into one superatom. The ability of the model to reproduce some properties depends on this choice. An example is bisphenol-A polycarbonate, for which schemes with two and four superatoms per chemical repeat unit are available.^[5,6,16,17] A third choice concerns the placement of the superatoms among the real atoms. Their positions can coincide with the positions of real atoms, or they can occupy other positions defined with respect to the real atoms such as the center of mass or the geometrical center of a subunit. The effect of location of the superatoms on the level 3 potential has been investigated for aqueous sodium polyacrylate solutions.^[18]

Thermodynamic properties have been used as targets as well. If available, they are taken from experiment, rather than, from atomistic simulations. Examples are the choice of the nonbonded interactions in the second nearest neighbor diamond model^[19–21] to yield zero pressure (Second Nearest Neighbor Diamond Lattice) and the use of pressure information together with structure in the refinement of numerical potentials.^[18,22,23]

Continuous Model—Intermolecular

Many different potential forms have been tried for the intermolecular part of level 3 potentials. These are interactions between superatoms of different chains but also between topologically distant (typical 1–5 and higher) superatoms on the same chain. They range from excluded volume purely repulsive potentials such as the truncated Lennard-Jones or Weeks-Chandler-Andersen potential^[5,6,24,25]

$$V(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + \varepsilon, & r \leq \sigma\sqrt[6]{2} = r_{\text{cutoff}} \\ 0, & r > r_{\text{cutoff}} \end{cases} \quad (2)$$

including their nonspherical extensions,^[16] to simple attractive potentials like the (full) Lennard-Jones potential^[26]

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (3)$$

or generalized $1/r^n$ expansions like^[26]

$$V(r) = \frac{C_{12}}{r^{12}} + \frac{C_{10}}{r^{10}} + \frac{C_8}{r^8} + \frac{C_6}{r^6} \quad (4)$$

In several cases even these potentials were not flexible enough to capture the intricacies of the target RDFs. More complicated potentials, such as the following piecewise analytical function, were tried^[26,27]

$$V(r) = \begin{cases} \varepsilon_1 \left[\left(\frac{\sigma_1}{r} \right)^8 - \left(\frac{\sigma_1}{r} \right)^6 \right] & r \leq \sigma_1 \\ \varepsilon_2 \left[\sin \frac{(\sigma_1 - r)\pi}{(\sigma_2 - \sigma_1)2} \right] & \sigma_1 \leq r \leq \sigma_2 \\ \varepsilon_3 \left[\cos \frac{(r - \sigma_2)\pi}{(\sigma_3 - \sigma_2)} - 1 \right] - \varepsilon_2 & \sigma_2 \leq r \leq \sigma_3 \\ \varepsilon_4 \left[-\cos \frac{(r - \sigma_3)\pi}{(\sigma_4 - \sigma_3)} + 1 \right] - \varepsilon_2 - 2\varepsilon_3 & \sigma_3 \leq r \leq \sigma_4 \equiv r_{\text{cutoff}} \end{cases} \quad (5)$$

which has four different functional forms in four regions, and after optimizing all the ε and σ , reproduces complicated RDFs very well. Polymers treated with these types of analytical model include sodium poly(acrylic acid) in dilute aqueous solution,^[18,22] poly(vinyl alcohol) in the melt,^[22,28,29] polyisoprene melts,^[22,23] and various polycarbonate melts.^[5,6,17,25,30,31]

The necessity of ugly and complicated potential functions with uninterpretable parameters such as Eq. 5 has led to the most recent development, namely, tabulated fully numerical potentials. They contain no parameters at all but offer the ultimate flexibility and are usually able to reproduce structural distributions to within line thickness (i.e., 0.1% relative deviation) in a few iterations of the optimization algorithm. One method was originally used by Soper^[32,33] to construct a numerical atomistic force field for liquid water that reproduced OO, OH, and HH radial distribution functions from neutron scattering (there is an early precursor to this work by Rahman^[34]). The procedure is readily adapted to the problem of coarse-graining polymer models and is known as iterative Boltzmann inversion.^[22,23,35] If a target radial distribution function $\text{RDF}_{\text{target}}(r)$ is available (in the original from experiment, in coarse-graining applications from the more fundamental simulations), one starts the zeroth simulation with a guessed tabulated pair potential $V_0(r)$. Its simulation yields a radial distribution function $\text{RDF}_0(r)$, which is different from $\text{RDF}_{\text{target}}(r)$. However, it can be used to obtain a first correction to the potential

$$V_1(r) = V_0(r) + kT \ln \frac{\text{RDF}_0(r)}{\text{RDF}_{\text{target}}(r)} \quad (6)$$

k being Boltzmann's constant and T temperature. This process can be iterated until the potential $V_n(r)$ and the $\text{RDF}_n(r)$ generated from it are self-consistent

$$V_{n+1}(r) = V_n(r) + kT \ln \frac{\text{RDF}_n(r)}{\text{RDF}_{\text{target}}(r)} \quad (7)$$

It usually takes less than 10 iterations before the coarse-grained RDF can no longer be distinguished from the target RDF. A good choice of the starting potential



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$V_0(r)$ is the potential of mean force that is obtained by Boltzmann inversion of $\text{RDF}_{\text{target}}(r)$

$$V_0(r) = -kT \ln \text{RDF}_{\text{target}}(r) \quad (8)$$

Iterative Boltzmann inversion is a local update scheme: The potential correction at the distance r is obtained only from the deviation of $\text{RDF}(r)$ at this distance. In the second approach, due to Lyubartsev and Laaksonen,^[36] the correction to the potential of the n -th iteration $\Delta V_n(r_i)$ at a distance r_i

$$V_{n+1}(r_i) = V_n(r_i) + \Delta V_n(r_i) \quad (9)$$

is a function of the deviations of the RDF at *all* distances $\{r_j\}$

$$\Delta V_n(r_i) = f(\{\text{RDF}_n(r_j) - \text{RDF}_{\text{target}}(r_j)\}) \quad (10)$$

Because of this nonlocality, one would expect faster convergence for Lyubartsev-Laaksonen, since in the Soper method, any deviation takes several iterations to filter through to the point of correction. In practice, the number of iterations necessary seems to be very similar for both methods. The Lyubartsev-Laaksonen method has not yet been used in the context of connecting polymer models of different scales. It has been applied to aqueous solutions of NaCl. The reference RDFs came from fully atomistic simulations including water and were used to parameterize effective ion-ion potentials, which would give the same ion distribution in the absence of an explicit solvent.^[36] Other uses include the development of effective ion-DNA interactions for water-free simulations^[37] and an atomistic Li^+ -water force field from Car-Parrinello calculations.^[38] Recently, the method was combined with the equation of motion of dissipative-particle dynamics.^[39]

Both numerical methods share the same fundamental advantages and disadvantages compared with analytical potentials. The numerical potentials achieve a match of the corresponding RDFs or other structural distribution functions, which to all intents and purposes is perfect. However, they lack adjustable parameters with physical interpretation. In addition, there is the problem of nonuniqueness. In principle, there is a one-to-one correspondence between a pair potential and the RDF generated by it, at least for simple fluids. Notwithstanding, we have encountered examples where visibly different potentials gave rise to RDFs which were identical to within line thickness.^[22] This means that these RDFs have residual deviations ($<0.1\%$) from the target RDF much smaller than the accuracy of the target RDF itself. This applies in particular when the simulations are being run at constant volume, because the volume constraint helps to keep RDF peaks at their proper positions.

Continuous Model with Analytical Potential—Intramolecular

In addition to intermolecular nonbonded interactions, chain molecules need local intramolecular interactions: bond stretch (two-body), angle bend (three-body), torsion



(four-body). There have been different routes to parameterizing these interactions given atomistic distributions. The first choice is whether to (mis)use a potential of mean force as a potential energy or not. A distribution $P(x)$ of a degree of freedom x (say a bond length or an angle) obtained from an atomistic simulation can always be Boltzmann-inverted to yield a potential of mean force $A(x)$ along x

$$A(x) - A(0) = -kT \ln \frac{P(x)}{P(0)} \quad (11)$$

Using $A(x)$ as the coarse-grained potential is a very easy route. However, $A(x)$ really is a free energy, not a potential energy. It incorporates not only the effects from a finite temperature but also from the neglected degrees of freedom. Strictly speaking, it cannot be used as a potential energy function for the corresponding interaction. Nonetheless, there have been attempts to do just that.^[5,18] This approximation can be good enough if, first, the free energy of the interaction is dominated by the energy, so entropy can be neglected, and second, this distribution is not influenced much by other interactions within the system. For example, a good candidate is the bond stretching between two neighboring superatoms. This is usually a stiff interaction mediated by real chemical bonds, which is rather unaffected by the environment of the polymer (e.g., melt or solution).

With bond-angle and torsion interactions, the choice is less clear, because they are softer and often do respond to changes in the environment. But there have been approaches that use Eq. (11) also for angles and/or torsions (continuous model,^[5,6] lattice model^[40,41]). In these cases, the systems were melts of apolar polymers. Thus, θ conditions were assumed, and the conformational statistics in the melt was taken to be that of a phantom chain (chain in vacuum with only topologically close interactions included) following the Flory argument.^[42] It appears, though, that this approach is limited to special situations. In general, an automatic optimization strategy similar to that for the intermolecular potentials is necessary: Parameters of an analytical potential energy function are adjusted until the relevant structural distribution $P(x)$ is reproduced. This philosophy has proven useful for melt as well as solvent conditions.^[18,22,23]

Lattice Models

Bond Fluctuation Model

Atomistic models have been mapped to a variety of level 3 lattice models, one of the earliest mappings being the bond-fluctuation model.^[43] The underlying lattice is cubic primitive. An excluded-volume superatom occupies eight lattice sites (four in two dimensions). Bond distances and angles are allowed to vary between different discrete possibilities. These possibilities are restricted in a way that different polymer chains cannot pass through each other. Although the nonbonded interactions are typically limited to excluded-volume interactions, the bonded terms can be parameterized by fitting to the moments of the respective structural distributions to reflect the chemistry of the polymer under study.^[40] The bond-fluctuation model has been tried as a coarse-



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grained model for polyethylene and bisphenol-A polycarbonate already in 1991^[44,45] with considerable improvements later. Coarse graining using the bond-fluctuation model has been exhaustively reviewed elsewhere.^[4,46]

Second Nearest Neighbor Diamond Lattice

Mattice et al. developed a mapping from a rotational isomeric state (RIS) description^[47] of a polymer onto a lattice model suitable for polymer melts, solutions, and surfaces. The underlying lattice is the second nearest neighbor diamond lattice that is identical to a cubic-closed-packed or face-centered cubic (fcc) lattice.^[48] The “atomistic” RIS model serves as reference for the intramolecular interactions. It involves rotational conformers around a single C—C bond in the polyolefine backbone. The RIS weights are derived from experimental static chain properties or are calculated (e.g., by quantum chemistry) conformational equilibria of oligomers.^[47] In a first step, the atomistic RIS model is mapped to a slightly coarsened one involving rotational conformers around hypothetical bonds between second nearest neighbor backbone carbons. The resulting RIS transfer matrix is more complicated than the atomistic one (9×9 instead of 3×3), but it can be obtained by enumerating the underlying atomistic rotational states.^[19]

The intermolecular potential of the original model for polyethylene contains finite repulsive interactions between nonbonded superatoms occupying neighboring lattice sites and attractive interactions for superatoms occupying second nearest neighbor lattice sites. These interactions are balanced to give a second virial coefficient of zero (θ conditions). The nonbonded interactions are fine-tuned until the radius of gyration of the chain with nonbonded interactions equals that of the unperturbed (“phantom”) chain without nonbonded interactions.^[19,20] This concept was later refined further to link the interactions of the lattice model to atomistic information.^[21] Because a superatom on the lattice corresponds to two methylene units, the known effective Lennard-Jones parameters $\epsilon/k = 185$ K and $\sigma = 0.44$ nm of C_2H_4 are used as a basis. Lattice neighbors are grouped into five shells according to their average distance. All members of one shell have the same interaction energy, which is mapped from the atomistic Lennard-Jones potential. The interaction energies for the five shells of the polyethylene model are +12.3654, +0.1660, -0.5443, -0.1219, and -0.0316 kJ/mol, respectively. The first shell is strongly repulsive, the second is mildly repulsive, and the outer ones show a decreasing attraction, as in the parent Lennard-Jones potential.

By modification of the intramolecular potential to allow for asymmetric torsions and a longer-ranged nonbonded interaction (up to nine shells), the model accommodated polypropylene also.^[49,50] It was able to discriminate correctly between melts of isotactic and syndiotactic polypropylene, both in the static (characteristic ratio) and dynamic behavior (decorrelation of the end-to-end vector). In addition, the known phase separation of isotactic and syndiotactic, but not of isotactic and atactic, polypropylene could be qualitatively reproduced.^[51] Local Monte Carlo moves of crankshaft type are used with this lattice model. The introduction of multiple-bead crankshaft Monte Carlo moves led to a significant speed-up for nonsymmetric potentials.^[52]



Meanwhile, the method was extended to different topologies (diffusion of linear vs. cyclic polyethylene^[53]), geometries (polyethylene films rather than bulk^[54]) and processes (structure formation upon cooling^[55]).

fcc Lattice

Another coarse-grained model using an fcc lattice has been proposed by Haire et al.^[56] for polyethylene. It differs from the Mattice et al. approach (see Second Nearest Neighbor Diamond Lattice) in several ways: 1) The mapping is coarser: there are four, rather than two, CH₂ groups per lattice point, which leads to a lower concentration of vacant lattice sites (10–30%, rather than 75%). 2) The nonbonded interactions are limited to a hard core without attractions. An additional repulsion of $E/k=500$ K between neighboring lattice sites is introduced ad hoc for technical reasons. 3) The intramolecular interaction is limited to an angle-bending interaction, which is adjusted to reproduce the known characteristic ratio $C_n = \langle R_{ee}^2 \rangle / Nl^2$ of C₁₀₂ chains in the melt, with N the number of monomers and l the bond distance between monomers. Although not an atomistic quantity per se, in the present case, the value happens to originate from atomistic literature data.^[57] 4) In contrast to the implementation of the second nearest neighbor diamond lattice, the Monte Carlo scheme allows multiple-bead moves in addition to the standard end rotations and crankshaft moves, which are best depicted as internal reptation of a segment of a few monomers. Such moves are local, yet efficient.

This model was compared with united-atom MD simulations of a melt of C₁₀₁H₂₀₄. The diffusion of the lattice polyethylene and that of the atomistic model show the same characteristics. Superposing the subdiffusive anomalous regimes of the mean-squared displacements, the time scale of the lattice model could be gauged, and a diffusion coefficient could be obtained. It agreed well with experimental values as well as with other, much longer, atomistic simulations.^[58] The model was subsequently used to simulate the interdiffusion of chains across a polymer-polymer interface (polymer welding^[59]).

Although the fcc lattice model was not derived systematically from an atomistic model but from experimental information, we list it here. The a posteriori comparison to the atomistic model showed that both have the same diffusion regimes, and it served to map the time scale.

Back to Level 2: Reinserting the Atoms

An important purpose of level 3 models is the generation of well-equilibrated atomistic amorphous polymer structures. The apparently cumbersome procedure (atomistic simulation \Rightarrow derive coarse-grained model \Rightarrow coarse-grained simulation \Rightarrow reverse mapping to atomistic model \Rightarrow local relaxation of the atomistic model) is, in fact, an efficient route to relaxed structures. This approach has been followed in the multi-scale treatment of various polycarbonates.^[5,6] Not only the behavior of chains as a whole could be reproduced correctly: For example, the Vogel-Fulcher temperature of short-chain bisphenol-A polycarbonate was calculated as 361 K (experiment 387 K) and the temperature dependence of the viscosity matched that of experiment. After threading an atomistic model through the coarse-grained chains followed by local



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relaxation during 200 ps of molecular dynamics, also “atomistic” properties, which depend on the behavior of individual atoms, could be calculated. Examples are the structure factors of differently deuterated bisphenol-A melts,^[25] the diffusion of phenol molecules through them,^[60] and, after carrying the reverse mapping one step further to the electron level, the lifetimes of ortho-positronium in cavities.^[61,62] The bisphenol-A polycarbonate reverse mapping is the most thoroughly examined example to date. It shows that coarse graining/fine graining is a reliable method to generate atomistic structures, at least as probed by neutrons, positronium, and small penetrants.

BEYOND LEVEL 3: SUPERATOM AND GENERIC CHAIN MODELS TO SOFT FLUIDS AND DENSITY FIELD DESCRIPTIONS

Fig. 1 shows that for a full understanding of a polymeric material it may not be enough to control the atomistic (level 2) and the superatom scale (level 3). There are features that depend on longer scales (e.g., the morphology of blends and block-copolymers). These length scales are too large even for the superatom models. Consequently, there have been attempts to systematically develop models that reach even coarser-grained scales. At present, there are particle-based as well as field-based models.

Soft-Particle Models (Level 5): Dissipative Particle Dynamics and Related

When an entire polymer or a large fraction of it is mapped onto a single particle, this particle has to be “soft”: Two particles can occupy the same position and penetrate each other. This is a consequence of the fact that the centers of mass of two polymer chains can be at the same point, whereas two atoms or monomers cannot. This limits the application range of these methods, because a soft-core potential does not provide for the noncrossability of polymer chains, an essential ingredient of polymer dynamics. Hence, the soft-core potentials are restricted to the description of static properties, unless the noncrossability is accounted for by other means.^[63]

A popular model is dissipative particle dynamics (DPD),^[64] originally developed for liquids and later adapted to polymers. It consists of a momentum-conserving thermostat, which has been reviewed recently^[65] and is not of interest in the present context, and a short-ranged repulsive soft-core potential, which models a collection of liquid molecules or of monomers of a polymer as a single blob.

$$V(r) = \begin{cases} a(r_{\text{DPD-cutoff}} - r)^2 & r \leq r_{\text{DPD-cutoff}} \\ 0 & r > r_{\text{DPD-cutoff}} \end{cases} \quad (12)$$

Of the two adjustable parameters, the cutoff $r_{\text{DPD-cutoff}}$ is fixed by the degree of coarse graining (i.e., by how many monomers make up one blob). Thus, only the force constant a is left for tuning the interactions between, say, a polymer and a solvent or two different polymers. For liquids, it may simply be adjusted to the compressibility. For polymers, the situation is less clear, because a rigorous derivation of a from more fundamental interactions is still amiss. Hence, it is no surprise that DPD has been used mainly for describing the properties of generic polymers. To our knowledge, there have



not yet been calculations on polymers with a specific chemical identity. Notwithstanding, useful results have been obtained: the structure of a chain in solution,^[66] interfacial tension between two different polymers,^[64] morphology of diblock copolymers,^[67] structure and dynamics of a single polymer as a function of solvent quality,^[68] the aggregation of polymers and surfactants in solution,^[69] and the upper and lower critical behavior of polymer solutions.^[70]

In these calculations, the repulsion parameter a for the interactions between various species are either assumed ad hoc or they are obtained via an empirical mapping^[64] from Flory-Huggins χ interaction parameters.^[71] Therefore, the DPD calculations inherit the known problems caused by the mean-field nature of the Flory-Huggins model.^[72,73] This finding has led to fixes analogous to those in the Flory-Huggins community such as temperature and pressure-dependent a values.^[70] The DPD potential [Eq. 12] has also been used in Gibbs-ensemble Monte Carlo simulations (i.e., without the DPD equation of motion), aimed at the phase behavior of polymer solutions.^[74] These calculations are very efficient, making use of continuum configurational bias techniques as well as novel identity swaps between polymer and solvent.

A second family, the so-called soft ellipsoid models, reflects in the interaction potential the fact that the underlying objects are polymer chains, rather than liquid droplets.^[75] Three assumptions are made: 1) The potential energy can be separated into an intrachain and an interchain part. 2) The particles are “soft” not only in the sense that they are interpenetrable but also because they are deformable (i.e., have internal degrees of freedom). This follows from the energetic degeneracy of a polymer coil, which allows it to be deformed at practically no energy cost, with the restoring force being entropic. If one abstracts the monomer density $\rho_i(\mathbf{r})$ of chain i into its inertia tensor \mathbf{S}_i , then the internal part of the free-energy can be written

$$A(\mathbf{S}_i) = -kT \ln P(\mathbf{S}_i) \quad (13)$$

where $P(\mathbf{S}_i)$ is the probability of finding a given \mathbf{S}_i . This probability can be assumed from analytical models, or it may be calculated in a simulation of a detailed polymer chain. $A(\mathbf{S}_i)$ is then directly used as the internal potential energy for the deformation. 3) The interaction between two chains is assumed to be repulsive and proportional to their overlap density

$$V_{ij} = \varepsilon_{ij}(N) \int \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (14)$$

where $\varepsilon_{ij}(N)$ is an interaction parameter that depends on the chain length N . For efficient evaluation of the integral in Eq. 14, the monomer densities may again be approximated by their second moments, after which V_{ij} can be tabulated. With this model, the phase behavior of polymer blends has been successfully studied.^[75] The model has been improved to the so-called Gaussian-ellipsoid model by first introducing self-interactions and second by approximating the monomer densities by suitable Gaussian expansions.^[76]

The soft-ellipsoid and Gaussian-ellipsoid models have advantages over the simpler DPD potential. For example, the deformability allows the prediction of chain shape fluctuations in response to changes in the composition.^[76] However, they share the limitation of the current DPD versions to some extent, because they are also a variation

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of an off-lattice implementation of the Flory-Huggins model. In the absence of other sources of interactions, both can only produce results as good as given by a corresponding Flory-Huggins parameterization.

Attempts to derive soft-particle (level 5) potentials directly from chain-chain radial distribution functions obtained by simulation of the underlying chains could potentially overcome these problems. A first step in this direction is the numerical procedure by Briels et al. They have coarse-grained a melt of level 4 excluded-volume Gaussian polymer chains of 10 beads into either one or two ‘‘blobs’’ at the centers of mass of 10 or 5 beads each.^[77] As an ansatz for the potential, they used Gaussians whose prefactor (\leftrightarrow interaction energy) and width (\leftrightarrow particle size) are the adjustable parameters. They were optimized to reproduce radial distribution functions of the generic bead-and-spring type (level 4) polymer chains. The optimization did not involve the minimization of a penalty function like Eq. 1, but it was done by either extended-system molecular dynamics with the potential parameters being dynamic variables, or by Metropolis Monte Carlo in parameter space. They have also systematically investigated ways to derive a Langevin-type equation of motion for the coarse-grained model from level 4 molecular dynamics^[78] and the implications of the coarse-graining strategy for the calculated pressure.^[77,79] In addition, Padding and Briels tried to combat the known effect that the coarser the model is, the softer the bead-bead interactions become, and the more likely it is that two polymer chains cross each other.^[63]

Finally, a recent method obtains soft (level 5) potentials by an analytical inversion of level 4 radial distribution function using the hypernetted chain closure of the Ornstein-Zernicke equation.^[80]

Field-Based Models (Level 6): Mesodyne

A method often used to study microphase separation and morphology of specific polymers and their mixtures is a mesoscopic free-energy density functional ansatz whose implementation on a lattice goes by the name of mesodyne. Its various aspects have been described in detail in the literature (see, e.g., Refs. [81–89]); alternative field-theoretical approaches were recently reviewed.^[90] Here, we only discuss its connections to other simulations scales. The free-energy density functional $A[\rho]$ consists of various components. The place where system-specific information enters is the the so-called nonideal part which, for a system of two components A and B with densities $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$, is modeled as

$$A^{\text{non-ideal}}[\rho] = \frac{1}{2} \int \int \{ \varepsilon_{AA}(|\mathbf{r} - \mathbf{r}'|) \rho_A(\mathbf{r}) \rho_A(\mathbf{r}') + \varepsilon_{AB}(|\mathbf{r} - \mathbf{r}'|) \rho_A(\mathbf{r}) \rho_B(\mathbf{r}') + \varepsilon_{BA}(|\mathbf{r} - \mathbf{r}'|) \rho_B(\mathbf{r}) \rho_A(\mathbf{r}') + \varepsilon_{BB}(|\mathbf{r} - \mathbf{r}'|) \rho_B(\mathbf{r}) \rho_B(\mathbf{r}') \} d\mathbf{r} d\mathbf{r}' \quad (15)$$

where $\varepsilon_{AB}(|\mathbf{r} - \mathbf{r}'|)$, etc. are nonlocal interaction kernels for interactions between polymer chains, which are taken to be Gaussian

$$\varepsilon_{AB}(|\mathbf{r} - \mathbf{r}'|) = \varepsilon_{AB}^0 \left(\frac{3}{2\pi a^2} \right)^{3/2} \exp \left[-\frac{2}{2a^2} (\mathbf{r} - \mathbf{r}')^2 \right] \quad (16)$$



The spatial extent of a chain (nonlocality) is related to a , the interactions between pairs of species to the parameters ε_{AB}^0 . The latter combine into a Flory-Huggins parameter

$$\chi_{AB} = \frac{1}{\nu kT} (\varepsilon_{AB}^0 + \varepsilon_{BA}^0 - \varepsilon_{AA}^0 - \varepsilon_{BB}^0) \quad (17)$$

with ν being the volume of a statistical segment. One notes that also in the mesodyne approach polymers show their chemical identity via a Flory-Huggins type interaction parameter, like in the particle-based level 5 model (Soft-Particle Models (Level 5): Dissipative Particle Dynamics and Related). In addition, there are other material-specific parameters. For example, the dynamic variant of the theory contains the monomer diffusion coefficient, which needs to be mapped to define a time scale.

If the density-functional method is to be used for realistic polymer-solvent or polymer-polymer mixtures, the ε_{AB}^0 have to be mapped either from experiment or theory. In the best-studied real system, (ethylene oxide)-(propylene oxide)-(ethylene oxide) triblock copolymers with water,^[89] the coefficients for the polymer-water interactions were obtained from vapor pressure measurements and for the (ethylene oxide)-(propylene oxide) interactions from group contribution methods.^[91]

In principle, there is no reason why Flory-Huggins parameters could not be calculated by atomistic simulations, because they are essentially enthalpies of mixing $\Delta H_m/kT$, which can be obtained rather straightforwardly from molar enthalpies of vaporization

$$\Delta H_m(x_A) = \Delta H_{AB}^{\text{vap}}(x_A) - x_A \Delta H_A^{\text{vap}} - (1 - x_A) \Delta H_B^{\text{vap}} \quad (18)$$

with x_A being the mole fraction of A in a binary system. The molar enthalpies of vaporization are calculated as the negative of the corresponding intermolecular nonbonded energy. Alternatively, one may use the detour via the Clausius-Clapeyron equation

$$\frac{d \ln p_A}{dT} \approx \frac{\Delta H_A^{\text{vap}}}{RT^2} \quad (19)$$

and the temperature dependence of the corresponding partial pressures p_A , which are accessible through numerous free-energy techniques.^[92] The reason for atomistic approaches not being used routinely is probably the fact that ΔH_m results from the subtraction of large numbers. This requires very accurate calculations and places high demands on the force fields used; for an example, see Ref. [93].

MISCELLANEOUS COARSE-GRAINING APPROACHES

Coarse Graining to the Primitive Path (Level 2 or 3 to Level 4)

The primitive path is a well-established concept in the theoretical description of polymer melts.^[94] It removes some of the loops and wiggles of a polymer chain to yield the essential conformation. Kröger et al. proposed a projection technique to map a chain conformation onto its primitive path.^[95] Although their initial polymer is not



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truly atomistic but based on repeat unit positions, it provides a way of further reducing the complexity of a polymer chain.

Atomistic to Near Generic (Level 2 to Level 3.5)

A study of polyisoprene melts that used atomistic molecular dynamics and Monte Carlo simulations as well as stochastic dynamics simulations of a simplified model (excluded-volume bead-spring chains with added stiffness) has been reported.^[96,97] The stiffness was adjusted so that the persistence length of the near-generic model matched that of the atomistic model. The center-of-mass diffusion coefficient of decamers in the melt simulated in both models served to determine the time unit of the near-generic model. It is interesting to note that, with the same time scaling, the reorientation behavior of local segments obtained by both models could be superposed as well, whereas Rouse times differed by no more than a factor of 2. The segment dynamics compared qualitatively to that obtained by solid-state NMR spectroscopy.^[98] This example also offers the possibility of comparing a level 3 and a level 3.5 model for polyisoprene. The static chain properties are perceptibly different. The authors blamed this on torsional potentials present in the level 3 model but absent in the level 3.5 model.^[99]

Atomistic to Macroscopic Continuum (Level 2, 3, or 4 to Level 7): Multiphase Systems

Multiphase materials (semicrystalline and filled polymers, polymer composites) can be described by suitable continuum simulation techniques, such as finite differences or finite elements, if the one-phase regions can be regarded as homogeneous and interface effects can be neglected. If the phase morphology is known and the relevant material constants can be obtained from atomistic, monomeric, or generic particle-based models, they can be fed into the continuum description to yield the behavior of the multiphase system. The finite-element machinery has been developed by Gusev.^[100,101] It has been used for predicting the elastic behavior of composites,^[100] of fiberglass,^[102] of fiber-reinforced rubber,^[103,104] and of semicrystalline poly(trimethylene terephthalate).^[105] In addition, the method has been applied to the thermal expansion coefficient of talcum-reinforced, rubber-thoughened polypropylene, a three-phase composite.^[106] In addition, the effect of the geometry and packing of platelet-shaped fillers on the barrier properties has been studied in this way,^[107] as has been the effect of voids on the dielectric properties.^[101] Solving the respective Laplace equations using finite elements is computationally faster than the use of random walkers^[108,109] and it is much more versatile than analytical approaches.

An alternative approach to the elasticity of filled elastomers is due to Sharaf et al.^[110,111] The nominal stress f^* following a deformation α of the material is given by

$$f^* = -T \left(\frac{\partial \Delta A}{\partial \alpha} \right)_T \quad (20)$$

where the ΔA is obtained from the free energy associated with an affine deformation of a single chain of the elastomer. The free energy of a chain at a certain end-to-end distance R_{ee} is related to the probability of finding the chain at this extension

$$\Delta A(R_{ee}) = A(R_{ee}) - A(R_0) = -kT \ln \frac{P(R_{ee})}{P(R_0)}. \quad (21)$$

Curves of $P(R_{ee})$ vs. R_{ee} are obtained from large numbers of RIS chains,^[47] which are generated as Monte Carlo realizations in the presence of filler particles of given size, shape, and concentration. This is the atomistic part of the calculation. Chains that overlap with any of the filler particles are rejected. Thus, the presence of fillers changes the chain end-to-end distribution. This affects the elastic behavior of the two-phase composite on the mesoscale.

The strength of filled polymers has been approached in a similar spirit.^[112] The level 7 model for stress-strain relations and failure requires as input the forces necessary to stretch a polymer chain from an equilibrium coil conformation and to detach a polymer chain from the surface of a filler particle. Both are obtained by atomistic molecular dynamics simulations. With the model, the stress-strain behavior of poly(dimethyl siloxane) filled with surface hydroxylated silica was calculated in qualitative agreement with experiment.

Atomistic to Analytical

In some applications, it is possible to map from the atomistic simulation to a coarse-grained analytical theory, rather than a coarse-grained simulation model. An example is the calculation of shear viscosities and other rheological properties of short-chain (molecular weight $MW \leq 2200$ g/mol) polyethylene melts.^[58] Such chains are below the entanglement length, so their dynamics follows the Rouse model. The shear viscosity of a melt of Rouse chains is given as

$$\eta = \frac{\rho RT \langle R_{ee}^2 \rangle}{36D \cdot MW}, \quad (22)$$

where ρ is the mass density, and R is the gas constant. The center-of-mass diffusion coefficient D of individual chains as well as their mean-squared end-to-end length $\langle R_{ee}^2 \rangle$ can be obtained from atomistic molecular dynamics simulations (note that Eq. 22 is only unique for true Rouse chains^[113]). The same holds for other rheological properties such as the stress relaxation rate.^[114]

Another example concerns the diffusion coefficient of polymer chains in the melt studied in the framework of the analytical lateral-motion model. This model describes the chain-length dependence of the diffusion coefficient and needs as input, among other geometrical parameters, the effective monomer diameter σ and the bare-monomer (short-time) diffusion coefficient D_0 . For polyethylene, poly(ethylene oxide), poly(dimethyl siloxane), and polystyrene it was shown that σ can be obtained to good enough accuracy from simple atomistic molecular mechanics calculations. The results for D_0



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were not yet as reliable, so that it still must be treated as an adjustable parameter.^[115] It is not clear if the uncertainty is due to too short simulation times (~ 50 ps) or to ambiguous assumptions in the extraction of D_0 from the simulations.

Small-Scale Continuum to Large-Scale Continuum (Levels 6 and 7 to Level 8)

Multigrid schemes have a long tradition in structural mechanics. The concept has also found its way into polymer-engineering simulation. An example is the simulation of the crystallization of a macroscopic ($2\text{ cm} \times 1\text{ cm}$) sample of polyethylene.^[116] A coarse grid (21×11) is used to solve the thermal transport by finite differences. The evaluation of the crystallization fronts is tracked on a fine grid (1000×500). A stochastic model handles the spherulite nucleation. The simulations produce the spherulite structure of the crystallized polyethylene sample as a function of the applied temperature gradient.

Special Case: Permeation

Coarse graining of various types has been used for both the permeation of small molecules through polymer matrices and the permeation of oligomers (usually long-chain alkanes) through zeolites. Coarse-grained approaches of small-molecule permeation are variants of the transition-state theory introduced by Gusev et al.^[117] who mapped the cavities in a fully atomistic amorphous polymer onto a network of possible penetrant residence sites. Transition probabilities between the sites are calculated from atomistic simulations combined with transition-state theory. Finally, random-walk Monte Carlo simulations are performed on the network. The restrictions of the original approach to transitions that are facilitated by the positional fluctuations of relatively few atoms have been removed by multi-dimensional variants.^[118–120] Recently, it was shown how to generate more complex sorption-site networks from the statistical information about the sites.^[121]

By describing sorption and diffusion of long n -alkanes in zeolites, one can make use of the regular sorption-site network provided by the periodic host.^[122,123] For small rigid molecules, one can calculate transition rates between neighboring cavities directly from atomistic simulation. In flexible molecules, however, the conformational freedom of the penetrants must be allowed for. It can be sampled atomistically by configurational-bias Monte Carlo.

AUXILIARY COMPUTATIONAL TECHNIQUES

This section describes a collection of recently developed computational methods that either have some bearing on the problem of coarse graining or may be potentially useful in the context of coarse graining. Usually, they have not (yet) been applied to the coarse-graining problem.



Generation of Equilibrated Amorphous Polymer Structures

Methods of generating amorphous structures other than the route via coarser-grained models followed by remapping (Back to Level 2: Reinserting the Atoms) are, on one hand, competitive, but on the other hand, could further speed up the equilibration process, if used together with the coarse-graining concept. Some go back several years. For example, the early Theodorou-Suter method,^[124] continues to be popular because of its commercial availability, despite known limitations. A new simulation approach that combines rotational isomeric state information of the polymer with an increasing window for atom-atom interactions and clever Monte Carlo moves in polymer torsional space is able to generate dense amorphous packings of polyethylene and polystyrene without the old problem of conformational statistics changing along the chain.^[125,126] Although this algorithm so far was only applied to atomistic models, there is all reason to assume that it would speed up the coarse-grained relaxation as well.

A different line of approach could be described as “fine graining without preceding coarse graining.” These approaches start from a generic (level 4), rather than specific, coarse-grained model, equilibrate it, and subsequently thread the atomistic polymer onto the trace of the coarse-grained chains. One example is the use of Gaussian chains on a lattice to prepare the structure of amorphous polystyrene.^[127] Another one uses the nonintersecting streamlines of a continuous vector field as a coarse-grained scaffold, onto which atomistically detailed models of polyethylene are mapped.^[4,128]

Clever Sampling Techniques

Atomistic simulations often use Newton’s equation of motion or some variant (Brownian dynamics, Langevin dynamics, dissipative particle dynamics, etc.). These motions mimic physical atomic motions. Complicated collective moves are often hard to implement because of the complex topological and geometrical constraints of detailed models. The much simpler topology of coarser models (level 3 and above) makes it much more viable to devise and implement efficient Monte Carlo moves.

Therefore, it is no surprise that, in addition to Langevin dynamics (e.g., Ref. [5]), pivot Monte Carlo has been used for lattice and continuous models of polymers in solution.^[22,129,130] Effective local moves, such as parallel rotation^[126] or concerted rotation,^[131] are in principle possible but are waiting to be tried. Nonlocal schemes are also possible, such as continuum configurational bias Monte Carlo^[132] or the connectivity-altering, end-bridging Monte Carlo.^[131] The latter has mastered a number of moderately complex atomistic polymers beyond polyethylene^[133] such as *trans* and *cis* polyisoprene.^[96,134,135] A recent reformulation of end-bridging moves into configurational-bias-type moves, so-called direct bridging moves, looks very promising for further gain of efficiency.^[136]

SUMMARY AND OUTLOOK

From this synopsis, it is evident that scale-bridging efforts are presently underway at all levels of polymer simulation. It is conceivable that before long integrated si-



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mulation approaches that encompass several simulation methods for different scales and rigorous connections between them will be available. This would change the mode of operation for polymer simulators compared to today. Presently, many simulators operate as method driven (i.e., they know a small number of computational techniques and select those scientific questions that can be solved with them). With robust coarse-graining and fine-graining techniques at hand, simulators will operate as problem driven (i.e., pick a scientifically challenging or technologically important problem and use a hierarchy of polymer models to solve it). This will make simulations even more useful. The desire to operate in this way is evident from the fact that scale bridging is best developed for certain special applications, such as permeation, or for certain polymers, such as polycarbonates. With the validity of the scale bridging quantitatively proven for many polymer systems and properties, simulators will eventually be able to avoid the dilemma of either having to study systems too small to be considered polymeric (level < 3) or of having to use models too inaccurate to be problem-specific (level 3 and above). With systematic scale bridging, one can have the best of both worlds.

To establish scale bridging as a robust technology in polymer simulations, many scientific challenges still have to be met. The existing methods have to be tried on many more systems to establish their powers and limitations. Approaches have to be made generally applicable (rather than limited to one polymer), tunable to specific properties (not only polymer structure and thermodynamics but, e.g., rheology), systematic (proven coarse-graining algorithms with demonstrated capabilities), and automatic (to have a coarse-grained model available in a short span of time). Obviously, this entails much effort. Scale hopping will continue to be a research topic. However, we are already witnessing the first examples of scale bridging being used as a research tool. Problems of polymer science are being solved by simulation, and much of the menial task of deriving the appropriately detailed model is transferred to the computer.

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