Characteristics of parameter reduction in multiscale simulations of polymer chains

Ahmed E. Ismail, George Stephanopoulos, and Gregory C. Rutledge
Department of Chemical Engineering, Massachusetts Institute of Technology
Cambridge, MA 02139

One of the challenges underlying successful multiscale models is the creation of appropriate intra- and intermolecular potentials describing the behavior of molecules at the coarse-grained scale. While the implicit goal of coarse-graining is the creation of a model that is as simple as possible, the process of constructing coarse-grained degrees of freedom generally leads to coupling between these degrees of freedom that cannot in general be predicted a priori. However, being able to determine and, to a lesser extent, predict this behavior is essential to developing multiscale algorithms capable of simulating polymers.

We have developed the wavelet-accelerated Monte Carlo (WAMC) framework [1, 2] for the study of molecular systems with self-similar behaviors, such as lattice models and polymers. The basic principle underlying the WAMC framework is that behavior of small fragments of a much larger simulation can be used to construct the coarse-grained degrees of freedom necessary to simulate the whole system. To construct the coarse-grained model, we perform a detailed simulation on a small portion of the overall system, including all atomistic interactions on the relevant length scales. From this detailed simulation, we can gather the statistics necessary to compute the probability distributions for the coarse-grained variables.

Thus, in the case of polymers, we study “short” chain segments, on the order of tens or hundreds of repeat units, to develop the intra- and intermolecular potentials to describe chains with hundreds or thousands of repeat units. The representation of these chains at the coarse-grained scale is as a chain of beads, each of which represents some number of repeat units of the original chain. The exact resolution of the coarse-graining—that is, the number of repeat units that are mapped to a single coarse-grained bead—is an adjustable parameter, allowing for greater flexibility.

In the development of our coarse-grained models, we have discovered that the coarse-grained degrees of freedom—bond lengths, bond angles, and torsion angles—have distributions which are much more complicated than are typically employed in coarse-grained simulation techniques. This coupling of behavior is observed even when the model studied is as simple as a freely-jointed chain. Moreover, there is interdependence between the different coarse-grained internal coordinates. To achieve sufficiently accurate agreement between our coarse-grained and atomistic polymer chains, it was necessary to parametrize the bond-angle distribution according to the larger of the bond lengths on either side of the given bond angle.

In addition, Monte Carlo simulations have allowed us to establish the existence of numerical scaling laws for the overlap probabilities which we invert to determine the

intra- and intermolecular potentials as a function of the number of repeat units as well as the ratio of repeat unit (or bead) size to the bond length. These results are compared to the results obtained from analytical derivations based on the freely-jointed chain which show qualitative agreement between the two approaches. For example, it can be shown that the length scale of potentials which describe overlap between freely-jointed chains scale as $N^{0.5}$, while the length scale of potentials for self-avoiding chains scale as $N^{0.4}$. The coarse-grained bead size is also an important parameter in determining the overlap potential. As the bead size a decreases, the coarse-grained potential shows an a^3 dependence.

Consequently, we can use take the potentials determined by a simulation performed at one resolution of coarse-graining and derive from the scaling laws new potentials which describe the behavior at another resolution. This allows us to “tune” the WAMC algorithm to obtain results more efficiently than would be possible with algorithms that operate at fixed levels of coarse-grained resolution.

References

[1] A. E. Ismail, G. C. Rutledge, and G. Stephanopoulos. *J. Chem. Phys.* **118** 4414 (2003)
[2] A. E. Ismail, G. Stephanopoulos, and G. C. Rutledge, *J. Chem. Phys.* **118** 4424 (2003)