Coarse-grain models of polymer melts: Tools and methods for preserving structure and dynamics

Lead Investigator: Frederick R. Phelan Jr., Materials Science & Engineering Division, National Institute of Standards & Technology (NIST), frederick.phelan@nist.gov.
Investigator: Lilian C. Johnson, Materials Science & Engineering Division, National Institute of Standards & Technology, lilian.johnson@nist.gov.
Keywords: Molecular Dynamics (MD); Coarse-grained force-fields (CGFF); Iterative Boltzmann Inversion (IBI); Dissipative Potentials; Friction Parametrization; Polymer Dynamics.

Project Scope

We are developing software and data tools which parametrize coarse-grained force-fields in a systematic way while preserving the chemistry, thermodynamics, and dynamics of the underlying atomistic system. Our approach is based on statistical thermodynamics where we utilize conservative potentials to model the molecular forces and dissipative potentials to account for the smoother potential energy landscape arising from the loss of configurational entropy. For conservative potentials, we have developed a software code based on the Iterative Boltzmann Inversion (IBI) method. For dissipative potentials, we are developing tools and approaches to parametrize friction based the Langevin thermostat as a first and the most basic approach to approximate the lost degrees of freedom.

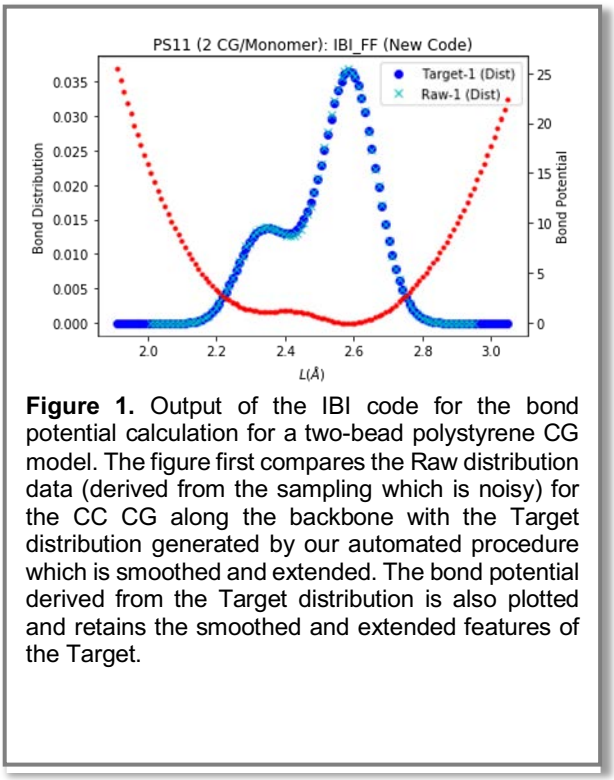

Figure 1. Output of the IBI code for the bond potential calculation for a two-bead polystyrene CG model. The figure first compares the Raw distribution data (derived from the sampling which is noisy) for the CC CG along the backbone with the Target distribution generated by our automated procedure which is smoothed and extended. The bond potential derived from the Target distribution is also plotted and retains the smoothed and extended features of the Target.

Relevance to MGI

Computation at mesoscopic length scales between the atomistic and continuum for polymeric and similar soft materials requires coarse-graining techniques. These techniques enable computational access to the greater length and time scales inherent to these materials by subsuming atoms associated with monomers or other chemical moieties into "coarse-grained" sites and then describing the physics by means of a potential parametrized for the coarse-grained description of the material. Bottom-up methods such as IBI, in which the CGFF is directly derived from atomistic simulation data, have the advantage of retaining a high degree of chemical specificity, and thus, can typically capture equilibrium structure quite well. However, bottom-up methods retain a Hamiltonian description of the force-field potential but with reduced degrees of freedom (or configurational entropy). This results in accelerated dynamics and a softer mechanical response due to a smoothed free-energy landscape arising from a reduction in topological constraints and fluctuations associated with the fine-grained atomistic details, which are averaged out. We employ an approach to correct the accelerated dynamics of CG models based on the statistical mechanics of coarse-graining by the addition and parameterization of a nonconservative (or dissipative) potential to the material description as represented by a Hamiltonian potential. The dissipative potential typically involves a friction parameter whose parametrization is fundamentally related to the integrals of autocorrelation functions of the atomistic system, making the entire approach derivative of atomistic reference simulations. Our approach combines these two methods and supports the NIST role in the MGI to create techniques and standards for the interoperation of modeling systems at multiple length and time scales.

Technical Progress

- **Iterative Boltzmann Inversion**: We have developed a new software code based on the Iterative Boltzmann Inversion (IBI) method which automates the development of conservative potentials for coarse-grained molecular dynamics (MD) calculations of soft materials.
- **Dissipative Potentials**: We are developing tools and approaches for parametrizing friction based on different measures of translational and rotational motion, and thermomechanical properties of molecular systems, as well as investigating the temperature dependence of the friction.
- **COMSOFT-Tools**: Our code is built on a series of reusable Python modules called COMSOFT Tools which are designed to enable data handling, data interoperability and molecular analysis functions for applications involving multiscale MD data.

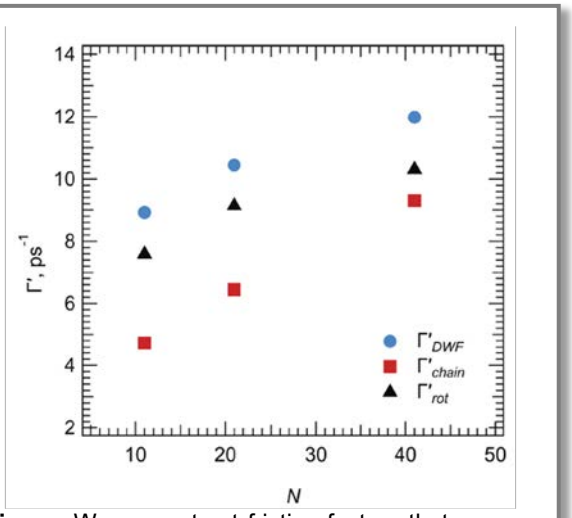

Figure. We can extract friction factors that recover specific measures of dynamics shown here for polystyrene oligomers with varying number of monomers, N. Dynamics here include the Debye-Waller factor, chain diffusivity, and chain rotational relaxation time. From reference 1, not subject to copyright in the US.

Future Plans

Our immediate plans are to publish the IBI code through the COMSOFT-Tools GitHub repository along with documentation on usage. The first step of future plans will be to integrate tools for parametrizing friction into the repo which we anticipate will be driven by a process of continuous improvement as we develop practical implementations of theoretical concepts. We also anticipate the development of better tools for mapping all-atom systems into coarse-grains and machine learning approaches based on COMSOFT-Tools for the better description of bonded potentials.

Broader Impacts and Workforce Development

Training in the usage of our software tools will be accomplished through online manuals, tutorials, videos and possibly workshops. We anticipate that as the tools mature and achieve greater usage, their knowledge will naturally be carried into the workforce by undergraduates and especially graduate students working in molecular simulation of soft materials.

Data Management and Open Access

As mentioned above, the IBI code and related tools will be published through an open access GitHub repository. Data derived from the software will be published through various auspices, including publications, the NIST Science Data portal, and through the companion Web Force-Field Project (WebFF) which will provide an online platform for publishing force-field data for soft materials.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Accurate force-fields for coarse-grained MD are very important to future materials discovery but remain very difficult to develop for quantitative (rather than qualitative) materials calculations. We anticipate that the development and maturation of these tools will greatly accelerate the development of CGFF, which will directly aid the MGI approach to materials development wherever it is being employed. We have had some early discussion with a commercial software company about the implementation of the IBI code in their package.

Publications and References

1. Lilian C. Johnson and Frederick R. Phelan, Jr., "Dynamically consistent coarse-grain simulation model of chemically specific polymer melts via friction parameterization," J. Chem. Phys. 154 (8), 084114 (2021). DOI: 10.1063/5.0034910