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Modeling and Simulations of Polymers: A Roadmap

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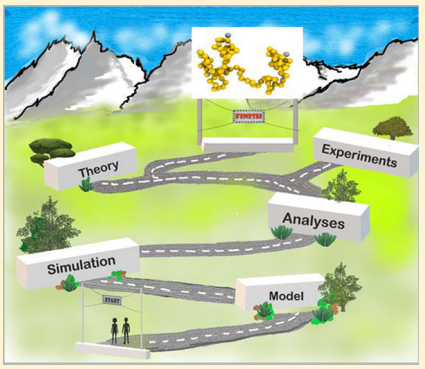
ABSTRACT: Molecular modeling and simulations are invaluable tools for the polymer science and engineering community. These computational approaches enable predictions and provide explanations of experimentally observed macromolecular structure, dynamics, thermodynamics, and microscopic and macroscopic material properties. With recent advances in computing power, polymer simulations can synergistically inform, guide, and complement *in vitro* macromolecular materials design and discovery efforts. To ensure that this growing power of simulations is harnessed correctly, and meaningful results are achieved, care must be taken to ensure the validity and reproducibility of these simulations. With these considerations in mind, in this Perspective we discuss our philosophy for carefully developing or selecting appropriate models, performing, and analyzing polymer simulations. We highlight best practices, key challenges, and important advances in model development/selection, computational method choices, advanced sampling methods, and data analysis, with the goal of educating potential polymer simulators about ways to improve the validity, usefulness, and impact of their polymer computational research.



I. INTRODUCTION

Polymers are a class of complex fluids that present unique challenges to a computational scientist, as they exhibit interesting and important phenomena over a broad range of length scales starting from monomer (angstroms) to the polymer radius of gyration (nanometers) and time scales ranging from femtoseconds to seconds/minutes or even years (in the case of glasses). Many, but not all, of these computational challenges have been addressed over the years with numerous developments in software and algorithms as well as through significant improvements in computer hardware. It is not surprising that with these advances we have reached a point where molecular simulations of polymers can be done significantly faster than some of the earliest simulations of polymers[1] and on a device as small as a smartphone! Perhaps it is not an exaggeration to say that the power to do polymer simulations is at our fingertips. With these software and hardware advances, a growing number of simulation studies of polymers provide valuable insight into new as well as existing macromolecular materials and through predictions inspire polymer chemists to find synthetic routes to design new materials that show tremendous promise. Yet, we sometimes hear skeptics label simulations as an "easy" and/or "unreal" tool in contrast to (more difficult) theory and (real) experiments. We believe that part of this skepticism stems from a non-negligible number of peer-reviewed articles in reputable journals that present incorrectly/hastily done computational studies and/or predict phenomena that prove to be wrong by follow-up simulations/theory/experiments. Nonetheless, from our perspective, for every one of those incorrect simulation studies, there are many more carefully and correctly done, creative, powerful, and insightful simulations (or *in silico* experiments) whose predictions have been proven correct by *in vitro* experiments and/or whose insights have inspired novel experiments.

With this optimistic view of the growing power of polymer modeling and simulations, we feel it is more important now than ever to educate the researchers—new students at undergraduate and graduate levels or experts in other fields who choose to use simulations for the first time to complement their work—of the *right/correct* ways to design and perform polymer simulations. In our opinion a central challenge with simulations is that incorrect results often do not *look* unrealistic or incorrect, and therefore care must be taken to validate that the results of a polymer simulation are meaningful. In this Perspective, we highlight some (not all) of the best practices and common pitfalls a researcher should keep in mind as they choose the model and simulation method appropriate for the problem at hand and how they should correctly analyze the simulation trajectories to reach meaningful conclusions. We note that there are other well-written perspective articles, like Frenkel's "Simulations: the dark side", which is a must-read for experienced and beginner simulators alike.[2] Another short perspective article from a few editors of *Langmuir*[3] guides the readers on the qualities of a good theory or simulation paper/study from the perspective of the *Langmuir* readership. These articles from Frenkel and the *Langmuir* editors focus broadly on simulations in general, yet many of the guidelines listed in these perspectives are definitely applicable and useful for polymer simulations. In contrast to these articles, we focus this

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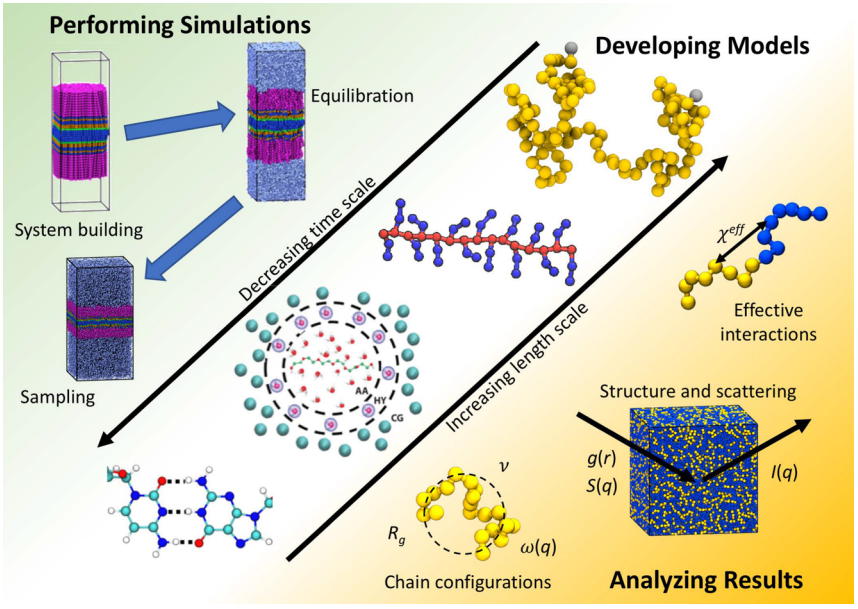

Figure 1. Schematic illustrating many of the key steps in performing a polymer simulation. This Perspective will discuss important considerations and best practices when developing appropriate polymer models, building and running polymer simulations, and analyzing and communicating the results. Parts of this image were adapted with permission from refs 56 and 57.

Perspective specifically on modeling and simulations of polymers/macromolecules. We provide examples from our group and other groups from around the world who, like us, work in the areas of polymer nanocomposites, solvent processing of polymers, conducting polymers for organic photovoltaics, and polymers complexing/conjugating with nucleic acids/peptides for biomaterial design—subjects of our past and current research interests. This Perspective is written from a multidisciplinary view because of our philosophy about polymer models and simulations which lies somewhere between that of a chemist (who prefers to maintain atomistic detail) and a physicist (who prefers to design general models for universal behavior).

We emphasize that this Perspective in no way is meant to be a comprehensive review or a substitute for outstanding textbooks on simulations[4−8] or past review articles on polymer simulations,[9−22] all of which are excellent resources for novices and experts alike. We realize that because of our specific areas of interest and expertise, we have not discussed many currently trending or classical topics within the polymer field that are important and deserve the same attention as those that we cover here. For example, we have excluded detailed discussions of the models, simulations, and analyses that correctly capture polymer dynamics,[23−33] nonequilibrium simulation methods that are used to study effects of mechanical shear and/or other external field effects,[34−44] specific challenges related to polarizable models and simulations of polarizable macromolecular systems,[45−55] quantum mechanical simulation methods that are relevant to understanding/developing polymer reactions, and so forth.

We have organized the flow of information in this Perspective like a roadmap for performing simulations of polymers, with the sequence of the sections mirroring the workflow of polymer computational research. Figure 1 demonstrates some of the key steps along that workflow, including developing a suitable model (and appropriate model resolution/length scale), building and running the simulation, and analyzing the simulation trajectory to produce useful data. As we present our opinions and views along the various steps in the workflow, we cite and highlight some new and exciting modeling and simulation work in the areas listed above and mention, briefly, some yet-to-be-solved challenges/problems.

II. "WHAT MODEL SHOULD I USE FOR THE PROBLEM AT HAND?"

It is vital that those who are thinking of using modeling and simulation as a potential tool for their scientific/technical polymer-related problem first ask the question, "what do I want the modeling and simulation exercise to accomplish?" Only with a clear answer to the above question should one proceed to identify the appropriate model to accompany the simulation approach. The "best model" depends on the system one wishes to study and/or the question(s) that one wishes to answer. Broadly, for classical molecular simulations of polymers most models fall into one of two classes—atomistic or coarse-grained—the latter containing either generic models or models that are parametrized/optimized for specific chemistries.

In general, if the problem at hand asks for an understanding of the local, monomer-level (re)arrangements, fluctuations, or interactions, within a disordered or ordered polymer system, then atomistic models are the appropriate choice. For example, atomistic models can enable study of local monomer-level fluctuations or monomer−monomer contacts/interactions at interfaces of domains within a block copolymer system that is known to phase separate into a specific morphology.[58−61] Atomistic models have also shown how monomers and segments of polymers arrange near a specific nanoparticle surface within a polymer nanocomposite.[13,62−75] Another example where atomistic simulations are useful is in studying gas/small molecule solubility/absorption/diffusion within pores of a polymer membrane, where the specific chemistry and size of the gas/small molecules impact its interactions with and solubilities in preassembled (glassy) polymers.[76] In the case of charged polymer systems, electrostatic interactions and/or entropic driving forces (e.g., translational entropy related to counterions) are critical, and in these cases, atomistic

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