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Project Title

The role of nucleation in melt memory effects in semi-crystalline polymers

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Scope and Purpose

While semi-crystalline polymers are ubiquitous and have been studied for decades, many mysteries remain regarding the kinetics of crystallization. One especially perplexing phenomena is the so-called melt memory effect in polymer re-crystallization experiments, where properties such as the nucleation rate and crystal thickness are observed to depend strongly on process history. It is widely suspected that melt memory effects are tied to the primary nucleation event in polymer crystallization, however the community is divided between two fundamental explanations. Traditionally it was believed that slow dynamics (i.e. entanglements) were the root cause of memory effects. However, driven by a number of intriguing experimental results, researchers have recently suggested that melt memory effects are better explained by a more sophisticated theory of primary nucleation that includes one or more intermediate mesomorphic phases.

We are using advanced sampling Monte Carlo techniques to explore the free energy surface of coarse-grained and atomistic polymer models proximate to the primary nucleation transition state to search for these phases. Specifically, our project scope includes three tasks:

1. Perform Wang-Landau sampling of the free energy surface of a coarse-grained polymer model undergoing crystallization.
2. Perform Wang-Landau sampling of more detailed atomistic models.
3. Use information from Tasks 1 and 2 to investigate dynamics on the relevant free energy surfaces using molecular dynamics simulations.

Our calculation of the free energy surface will provide decisive evidence (for at least the theoretical models we consider) of the existence or absence of mesomorphic states, while avoiding some key numerical challenges inherent to simulations of dense polymer systems, thereby bringing us one step closer to a complete picture of polymer crystallization kinetics.

Project Progress

At the beginning of the project, we had preexisting codes for performing Wang-Landau simulations of small scale dense polymer melts in Python. However, further software development was needed in order to reach the system size necessary to observe crystallization. As such we built a GPU accelerated, C++ code capable of running the desired calculations. Note that while software development was necessary, we were not developing new methods as is required by the scope of the PRF DNI.

Our software development proceeded in two phases. First, we built and tested a GPU-accelerated Metropolis Monte Carlo (MMC) simulation following the work of Anderson et al [1]. Building a MMC code first allowed us to stage and test both the GPU acceleration and the bond-breaking polymer moves necessary for efficiently simulating dense melts. Following the development of the MMC code, we adapted it to run the Wang-Landau (WL) algorithm, allowing for calculations of the free energy surface.

Results from both modes (MMC and WL) of our GPU-accelerated code are shown in Figure 1. Figure 1(a) shows the total internal energy of 10^2 polymers, each with 10^2 Lennard-Jones beads as a function of temperature at a dimensionless density $\rho\sigma^3 = 0.15$ compared to a serial open source MMC code, Simpatico [2]. The agreement is very good. Figure 1(b) shows the relative speedup of the GPU-accelerated code versus a serial MMC simulation as a function of the number of particles for the same conditions (10^2 beads/polymer, $\rho\sigma^3 = 0.15$, $k_BT/\epsilon = 5$). The speedup is substantial for large systems, approaching two orders of magnitude for 2×10^4 chains. The combined results in Figures 1(a) and 1(b) demonstrate that our GPU-accelerated MMC code is accurate and fast enough to simulate the system sizes necessary to capture crystallization.

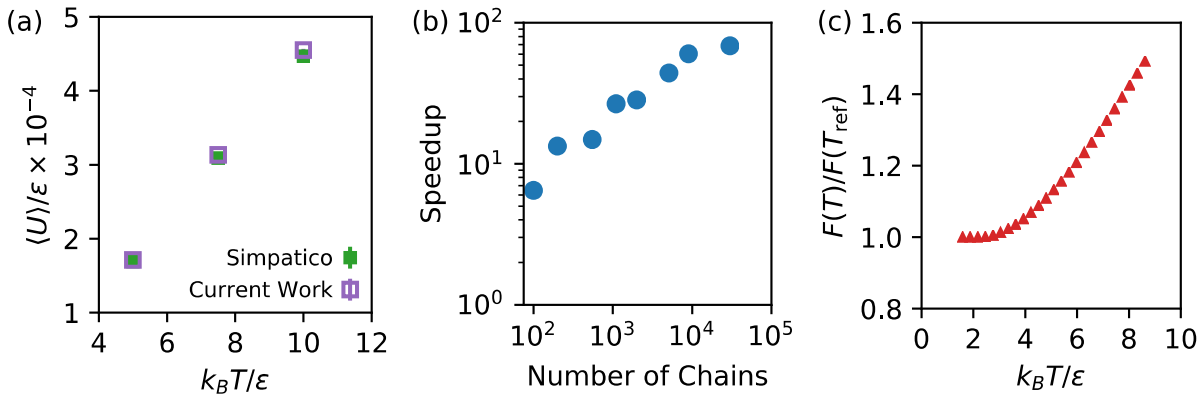

Figure 1. (a) Total internal energy of our MMC code for a chain of Lennard-Jones Spheres (well depth, ϵ; length scale, σ) versus temperature compared to an equivalent calculation using the open-source MMC code Simpatico [2]. (b) Relative speedup for a single Monte Carlo step of a GPU accelerated MMC simulation versus a serial MMC simulation. (c) The free energy (relative to the free energy at $k_B T_{\mathrm{ref}}/\epsilon = 1.586$) as a function of temperature for a square-well chain (well depth, ϵ; well size, σ) generated by a Wang-Landau simulation.

Moving to the desired WL simulations, Figure 1(c) shows a preliminary calculation of the relative free energy as a function of temperature for a system of 2×10^3 square-well chains with 100 beads each at $\rho\sigma^3 = 0.85$. Note that this simulation is significantly larger than systems we were previously able to model, but is well below the maximum system size we can reasonably simulate. The free energy shown here is the primary quantity we desire to examine for mesomorphic and crystallization phase transitions. To complete the search for these transitions we require calculations that span a larger temperature range and an analysis of various order parameters that characterize the change of phase from a melt to a crystalline and to various mesomorphic phases. Further simulations and the calculation of these order parameters is currently in progress.

Impact

This project has been significant for both my career and that of several of my students. As my first funded grant, this project is a significant step towards an independent research trajectory and provides our lab with data, experience, and funded students. This grant provides the primary funding for a PhD student, and it provided him with an opportunity to attend a summer school on High Performance Computing this year at UC San Diego. We have also had three undergraduate students involved in the project, one of whom was paid using grant funds. This latter student subsequently graduated and secured employment as an engineer at a company producing polymer composites.

References

[1] J. A. Anderson, E. Jankowski, T. L. Grubb, M. Engel and S. C. Glotzer, "Massively parallel Monte Carlo for many-particle simulations on GPUs", J. Comput. Phys. 254 (2013) 27–38.

[2] David C. Morse, University of Minnesota. https://github.com/dmorse/simpatico