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Project Title: Multiscale Modeling of Real Polymer Melts

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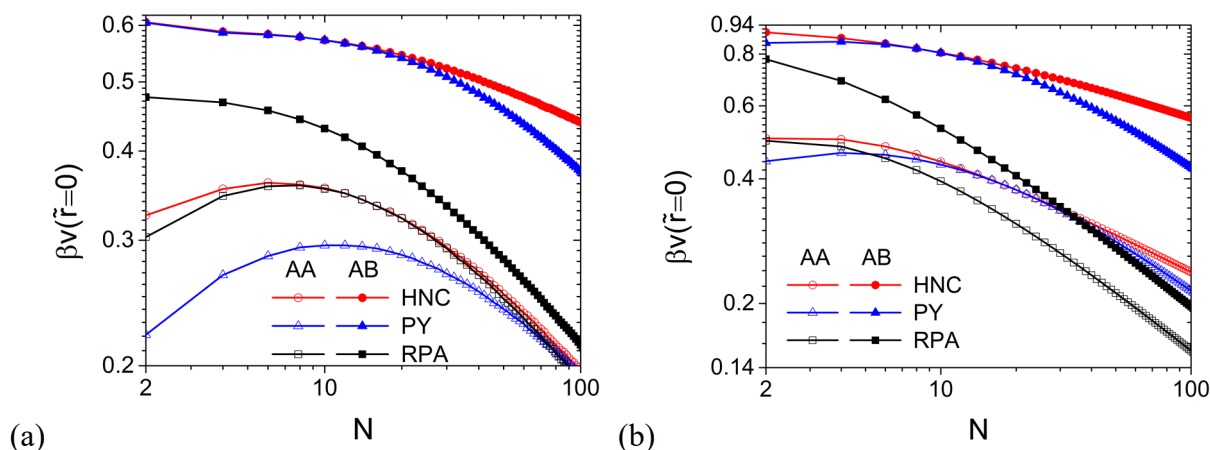
1. Progress of the Research

During the project period of 1/1/18 to 8/31/19, we have made the following progress: (1) Applied the systematic and simulation-free strategy for coarse graining of multicomponent polymeric systems proposed by the PI (Wang, Q., *Polymer* **2017**, *117*, 315) to the structure-based coarse graining of diblock copolymer melts. (2) Developed a general code for performing the self-consistent polymer reference interaction site model (SC-PRISM) calculations of various models of polymer melts. These are briefly described below.

(1) Structure-based coarse graining of diblock copolymer melts

Although block copolymer melts have been investigated in many experimental, simulation, and theoretical studies due to their both fundamental and practical importance in polymer science and engineering, their coarse graining has been performed only by a few groups, all of which used only a few (fixed) number of coarse-grained (CG) segments to represent each copolymer chain and simple analytical expressions for the CG potentials that require additional approximations. We therefore applied our recently proposed systematic and simulation-free strategy for the structure-based coarse graining of multicomponent polymeric systems (Wang, Q., *Polymer* **2017**, *117*, 315) to diblock copolymer melts, where we used the well-developed PRISM theory, instead of the commonly used many-chain molecular simulations, to obtain the structural and thermodynamic properties of both the original and CG systems, and to quantitatively examine how the effective non-bonded pair potentials between CG segments and the thermodynamic properties of CG systems vary with the coarse-graining level.

We proved that our coarse-graining strategy does not change the spinodal curve of diblock copolymers, regardless of the original model system, closures, and coarse-graining levels for the two blocks. Using a simple original model system for symmetric diblock copolymer melts, which consists of continuous Gaussian chains with the Dirac δ -function interactions and is solved with the ideal-chain conformations and the Percus-Yevick (PY) closure, we coarse-grained each block as $N/2$ segments and examined CG systems with $2 \leq N \leq 100$. We found that coarse graining (i.e., decreasing N) increases both the peak value and peak location of the partial structure factor characterizing the composition fluctuations in the CG system. Contrary to the common practice in the literature, the CG potentials obtained from short-chain systems cannot be directly used for long-chain systems; this is in fact the transferability problem in coarse graining (Louis, A. A., *J. Phys.: Condens. Matter* **2002**, *14*, 9187). We also found that the structure-based coarse graining cannot give thermodynamic consistency at any coarse-graining level, consistent with our previous work on homopolymer melts (Yang, D. L.; Wang, Q., *J. Chem. Phys.* **2015**, *142*, 054905; Wang, Q.; Yang, D. L., *Polymer* **2017**, *111*, 103) and binary polymer blends (Wang, Q., *Polymer* **2017**, *117*, 315).



The figure above, for example, compares the strength of the non-bonded CG pair potentials $\beta_V(\tilde{r}=0)$ between AA and AB segments, obtained with the random-phase approximation (RPA), PY, and hypernetted chain (HNC) closures for the CG system, for symmetric diblock copolymer A-B melts at the invariant degree of polymerization $\bar{N}=10^4$ (a) and 10^3 (b), where \bar{N} is proportional to (and has about the same order of magnitude as) the number of monomers on each chain for real polymer melts used in experiments, and $\beta=1/k_B T$ with k_B being the

Boltzmann constant and T the thermodynamic temperature. We therefore see that the CG potentials obtained from short-chain systems (having small \bar{N}) cannot be directly used for long-chain systems (having large \bar{N}). For more details and/or results, we refer the readers to our published paper (Wang, Y.; Wang, Q., *Polymer* **2019**, *160*, 303).

(2) Code development for SC-PRISM calculations

Chain conformations described by the intrachain pair correlation function, or equivalently its 3D Fourier transform $\hat{w}(q)$, are needed as an input to the PRISM calculations but depend on the system parameters such as the polymer density and interaction potentials. Approximating the interchain interactions by an intrachain pairwise solvation potential, the SC-PRISM calculations combine the PRISM calculations with single-chain simulations to determine $\hat{w}(q)$ self-consistently. We have developed a general SC-PRISM code for various models of polymer melts, where our C code for highly accurate PRISM calculations is combined with our parallel FORTRAN 90 code for efficient single-chain Monte Carlo (SCMC) simulations. Following the method outlined by Mendez et al. (*J. Chem. Phys.* **2001**, *115*, 5669), we adjusted the strength of the solvation potential such that the SCMC simulations reproduce the mean-square chain end-to-end distance, and used the histogram reweighting to reduce the need of SCMC simulations in each iteration. This enables our subsequent coarse graining of polymer melts using the SC-PRISM theory as planned.

2. Impact of the Research on PI's Career and That of Participating Students

The PI's group combine advanced theories and computer simulation techniques to study at nano- to meso-scales (i.e., from sub-nanometers to micrometers) the behavior of nanostructured polymeric materials. We use a suite of computational tools, ranging from particle-based molecular simulations to molecular-level theories, to investigate both thermodynamic and dynamic behavior of polymeric systems. Since established at Colorado State University in 2004, we have been using Monte Carlo simulations and self-consistent field calculations to study inhomogeneous polymeric systems at surfaces and interfaces. Our most recent focus before this project was on developing a novel class of fast Monte Carlo simulation techniques and applying them to polymer melts in bulk and confined films, grafted polymers, polymer blends, block copolymers, and liquid crystals. The research being carried out in this New Directions (ND) project fits well with the PI's group. In particular, the general code for performing the SC-PRISM calculations of various models of polymer melts developed here greatly expands the toolbox used in the PI's group; with further extension to multicomponent polymeric systems such as polymer solutions and polyelectrolytes, this stimulates a new research direction (i.e., multiscale modeling of polymeric systems) being actively pursued by the PI.

This ND project also supports the careers of participating graduate students. In particular, a PhD student (Ms. Yan Wang) published her very first peer-reviewed journal article based on her research of (1) above, and is preparing for another manuscript to be submitted for publication based on (2) above. Yan also disseminated her research results by giving well-organized presentations at several professional conferences, including the American Physical Society (APS) March meetings in 2018 and 2019, the American Institute of Chemical Engineers (AIChE) annual meeting in 2018, and the 20th Symposium on Thermophysical Properties in 2018. Most importantly, participation in this project has trained her with combined theoretical and computational skills to independently address fundamentally important and challenging problems in soft materials, and has fostered her strong interest and curiosity in acquiring new knowledge and conducting scientific research. As a result, Yan is planning to pursue an academic career after obtaining her PhD degree.