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An Integrated Multiscale Approach to Simulate Amorphous Porous Polymer Networks

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Our research team (the PI, a postdoctoral researcher, a graduate researcher, and an undergraduate researcher) continued to advance this project in 2018-2019, with two major aims in mind: (1) the development of an integrated multiscale approach, and (2) its application to polymer networks simulations. Since September 2017, we have published two research papers related to the proposed project and one educational paper (Fig. 1). In addition, this grant provided excellent training opportunities for students/scholars, leading to a successful placement of a postdoctoral fellow to a faculty position and the support of two students toward their degrees. At the current stage, we have accomplished and extended the first aim into organic and non-organic systems, while we are still making efforts to solve major challenges in developing and validating the potentials and parameters for the reactive coarse-grained (CG) sites of the proposed building blocks. As an alternative approach to the traditional systematic coarse-graining approach in the original proposal, we are pursuing a machine-learning approach which will allow us to study more general building blocks for porous polymer networks (PPNs).



Figure 1. Cover arts from reported publications (*J. Chem. Theory Comput.* **2019**, *15*, 1514–1522, *Front Cover*; *Angew. Chem. Int. Ed.* **2019**, *58*, 1035–1052, *Inside Back Cover*; *J. Chem. Ed.* **2019**, *96*, 1961–1966, *Supplementary Cover*). The ACS-PRF grant was acknowledged in all three publications.

1. Research Progress.

Mapping and Backmapping. Our multiscale approach is based on the interconvertible all-atom (AA) and CG models. We have derived the mapping and reverse-mapping matrices that can be calculated from a Singular Value Decomposition (SVD) algorithm. While we obtained the proof-of-concept with rigid model systems of benzene, naphthene, and anthracene, we have generalized the methodology to the building blocks in our original proposal (which are also fairly rigid). This allows us to accurately interconvert the model resolutions. Furthermore, we are extending/validating this concept to more building blocks, which were discovered in recent PPN synthesis (*Adv. Mater.* **2018**, *30*, 1705710; *Prog. Polym. Sci.* **2018**, *79*, 121; *Polym. Rev.* **2018**, *58*, 1). In comparison with the geometric approach of Tieleman *et al.* (*J. Chem. Theory Comput.* **2014**, *10*, 676), our approach generated comparably accurate backmapping results at slightly higher efficiency. We are also comparing our approach with the graph approaches by Pablo *et al.* (*J. Chem. Theory Comput.* **2019**, *15*, 1191)

CG Potential Development. Our design of the CG potential function contains three terms: the bonded or connection term, the reactive term, and the non-reactive term. While the bonded term adopts the form of the harmonic potential, we learned from recent progress that the Lennard-Jones (LJ) potential is an accurate representation of the non-reactive term for homogeneous and heterogenous model systems of benzene and naphthene in the condensed phases. However, in terms of many physiochemical properties, the accuracy to anthracene remains to be improved. To improve the accuracy for our PPN building blocks which are more polar and complex than the model systems, we have made attempts to use available tools VOTCA and BOCS by Noid *et al.* (*J. Phys. Chem. B* **2018**, *122*, 3363) for systematic bottom-up CG potential development. We successfully improved the non-reactive CG potentials using the Bozeman Inversion (BI), Iterative Bozeman Inversion (IBI), Force Match (FM), and Relative Entropy (RE) methods. We are currently assessing the results yielded from these bottom-up CG methods as well as the transferability to more general systems. Moreover, from many attempts of using analytical functions for the reactive CG potentials (as originally proposed), we learned that they are difficult to derive explicitly. To overcome this problem, we are developing a feedforward neural network (FNN) to generate the

reactive CG potentials based on *ab initio* MD simulations. Overall, we are making steady progress to combine top-down, bottom-up, and machine-learning approaches to develop the reactive CG force field for PPNs.

Integrated Simulation Approaches. With current success in non-reactive systems, we are extending our tests for supermolecular self-assembly systems. Modeling manmade or natural polymer assembly from disperse chains to the nanostructure is often intractable at the atomistic resolution, mainly due to the large time and length scales. To address this challenge, we have developed a new approach which integrates CG, mixed-resolution, and AA modeling in a single simulation. We are able to simulate the initial encounter stage with the CG model, while the further assembly and reorganization stages are simulated with the mixed-resolution and AA models. We have implemented this top-down approach (Fig. 2) with new tools to automate model transformations and to monitor oligomer formations. We have successfully applied this top-down approach to natural polymers. Extensive validations and tests are being performed with manmade polymer systems including some typical PPNs. Additional to the serial integrated simulation approach, we are also developing resolution exchange, a new approach to carry out parallel simulations at different resolutions while attempting the transfer of configurations on a regular time interval (Fig. 2). In general, these two approaches will help advance our capacity to study and predict the structure-property relationships of PPNs and other polymers.

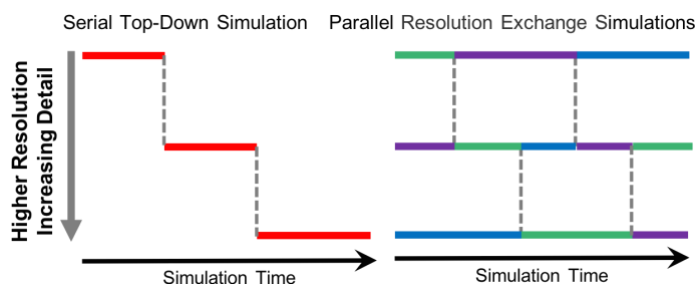


Figure 2. Schematic of integrated simulation approaches at three resolutions. Dash lines indicate transformation or swap of configurations.

2. Impacts on the PI's career and student/scholar training.

Support to the PI's career development. This research and the support from this award have profound impacts on the PI's career development. At first, the PI (Jianing Li) is able to advance her research program and enter a new area of nanostructure design. While two research papers have been published as the proof-of-concept, more preliminary data are being collected, and the collaboration with synthetic chemists is further advanced, which result in two more papers (under review by *Chem* and *Angew. Chem. Int. Ed.*) and one joint federal grant (USDA-NIFA 2018-07583). The PI was also recognized by a number of awards including the 2019 ACS OpenEye Junior Faculty Award. Moreover, the PI is able to integrate her research and teaching to enhance student engagement and learning experience. Specifically, the PI with and her team have evaluated the application of Virtual Reality (VR) in chemical education, findings of which have been published recently in *J. Chem. Ed.* Further, the PI also received support from this award to organize and participate scholar activities. The PI organized a symposium "Advances in Multiscale Modeling" with 23 speakers at the ACS meeting in San Diego, CA in Fall 2019. All these impacts contribute to the PI's scholar-teacher development and preparation for her tenure evaluation.

Support to the student/scholar career development. This award has supported three excellent students/scholars. (1) A postdoctoral researcher (Dr. Yong-Tao Ma) received valuable training opportunities in multiscale modeling. In March 2019, Dr. Ma finished his postdoctoral training and successfully started his independent career as a faculty member. (2) A graduate student (Xiaochuan Zhao) was supported with a research assistantship. Xiaochuan who took over this project from Dr. Ma continues to work on the reactive CG potential and integration of multiscale approaches. With a number of papers in preparation, Xiaochuan is making steady progress toward his PhD thesis in 2020. (3) An undergraduate researcher (Marlo Zorman), indirectly supported by the grant, has gained research experience with mentorship from both the PI and senior researchers in the lab. Marlo recently won a highly selective award from UVM (the 2019 APLE summer research award). While he is summarizing his discovery in top-down simulations of self-assembly, Marlo is working on his honors thesis and preparing for his applications to graduate schools.