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**An Integrated Multiscale Approach to Simulate Amorphous Porous Polymer Networks**

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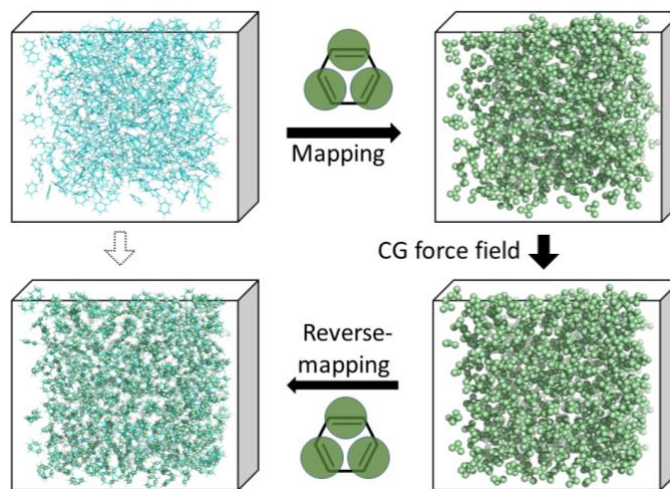
Our research team (the PI, a postdoctoral researcher, and an undergraduate researcher) started working on this project in September 2017, with two major aims in mind: (1) the development of integrated multiscale approach, and (2) the application to amorphous porous polymer networks simulations. At the current stage, we have accomplished most of the first aim, with the success to develop a systematic mapping/reverse-mapping method for the polymer building blocks described in the proposal. We have also developed the potentials and parameters for the non-reactive coarse-grained (CG) sites, while making good progresses towards the potentials for the reactive CG sites. We are also well prepared to integrate the mapping/reverse-mapping method and the CG potentials for the multiscale simulations of porous polymer networks.

In general, we are preparing a manuscript to describe the methodology to develop the non-reactive CG sites, in addition to a relevant paper recently under review by *Angew. Chem. Int. Ed.* (in collaboration with Prof. Severin Schneebeli at UVM). This research and the support from the ACS PRF have multiple profound impacts on the PI and her team, particularly to enhance the career development: (1) The PI (Prof. Jianing Li) is able to expand her research into a new area, accumulate preliminary data, and establish new collaborations. The support was also used to add new equipment and improve the research infrastructure in her lab. (2) The postdoctoral researcher (Dr. Yong-Tao Ma) received valuable training opportunities as well as support to travel to the 256th ACS national meeting in Boston. (3) The undergraduate researcher (Marlo Zorman), indirectly supported by the grant, has gained research experience with mentorship from both the PI and senior researchers in the PI's lab. Major findings under this grant support are described as follows.

**I. The mapping/reverse-mapping tool development.**

Our multiscale approach is based on the interconvertible all-atom (AA) and CG models. The mapping/reverse-mapping method play a main role in the model transformation. After obtaining the position vectors of AA and CG sites, the mapping and reverse-mapping matrices can be calculated with Singular Value Decomposition (SVD) algorithm. This algorithm is based on the general reverse theory. We have proven that the mapping and reverse-mapping matrices are unique for each building block, regardless of rotation and translation in the three-dimensional space. Therefore, they only need to be calculated once before application to transformations. Currently, we have determined the matrices needed for the interconversion of AA and CG models for all the building blocks in our research project, with a Python program.

Herein, we use the benzene system to demonstrate our proof of concept. To use the minimal CG sites while keeping the planar structure, three CG sites (2 heavy atoms to 1 CG sites) are designed to represent one benzene molecule. Each CG site is placed at the center-of-mass (COM) of its corresponding atoms. With the AA and CG coordinates, we can readily derive the mapping and reverse mapping matrices. With these matrices, we have built an AA model with 600 benzene molecules at a constant-temperature and



**Figure 1.** The system of 600 benzene molecules was simulated for 5-ns with the AA model (final snapshot, upper left) at 298 K and 1 atm. With the mapping matrix, the CG model (upper right) was generated for a 20-ns simulation (final snapshot, lower right) under the same condition. The final AA model (lower left) was recovered with the reverse mapping matrix. All the AA and CG models demonstrate similar equilibrium properties.

constant-pressure condition (298 K and 1 atm). A 5-ns AA simulation was carried out to achieve equilibrium. The final AA model was transformed to the three-site CG model, with the aid from the mapping matrix, followed by a 20-ns CG simulation under the same condition. The final CG model was recovered to the AA model with the reverse mapping matrix. These two AA models (the original one and the recovered one) show very similar properties like the density and the radial distribution functions.

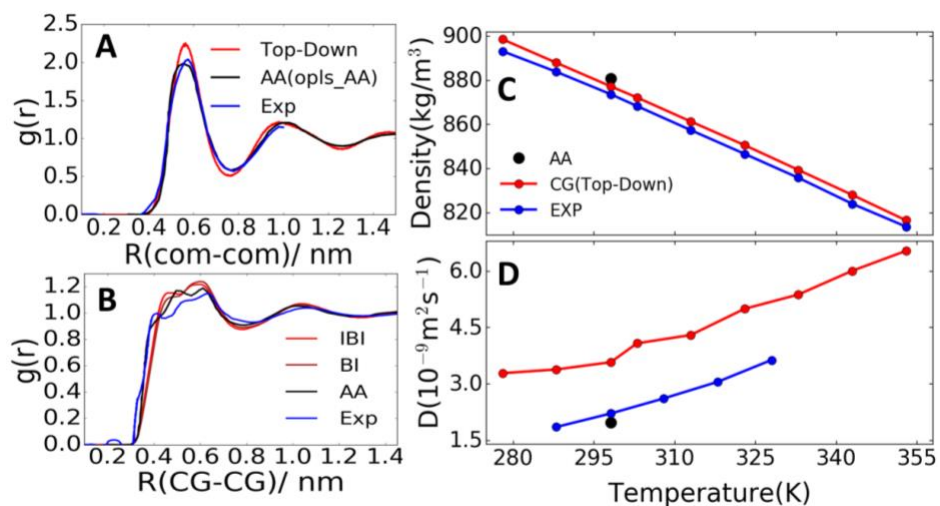
In addition, we also compare our method with an earlier geometric approach (*i.e.* Tieleman et al. *J. Chem. Theory Comput.* **2014**, *10*, 676). For rigid molecules like benzene as well as the building blocks for the polymer networks in our study, these two methods obtain almost identical results with only difference in the fourth decimal place of the recovered AA coordinates. However, our mapping/reverse mapping method is more straightforward to implement and faster in execution.

## II. The non-reactive coarse-grained (CG) parameter development.

There are three terms in the CG potential function of our proposed reactive CG force field: the bonded or connection term, the reactive term, and the non-reactive term. The bonded terms are described by harmonic potentials, while the non-reactive terms are represented by the Lennard-Jones (LJ) potentials. We first targeted to develop the non-reactive parameters, using the top-down and bottom-up systematic coarse graining methods. Again, we use the three-site CG model of benzene to show the proof of concept, and we can readily extend the methods to develop the parameter set for the building blocks of the conjugated microporous polymers.

For the top-down method, we used density as the target thermodynamic function to modify the CG force parameters and the radial distribution function  $g(r)$  to compare the overall features of the benzene liquid structure under different models. As shown in Fig. 2A, the COM-COM  $g(r)$  of our top-down model is comparable to the ones from experiments and an AA model (the OPLS-AA force field). Our CG model with parameters from the top-down method reproduces the first peak of  $g(r)$  at 0.55 nm. Next, we tested the transferability of our CG model under a range of temperature for the liquid state. While the CG model reproduces the experimentally observed densities (Fig. 2C), it shows a speedup of diffusion at a factor of 2 (Fig. 2D), which is consistent with the mapping level (2 heavy atoms/CG site). These results show that using the top-down method, we can obtain the accurate and transferable non-reactive parameters.

In addition, we also tested several bottom-up methods, including the Bozeman Inversion (BI), Iterative Bozeman Inversion (IBI) methods. We are also working on the Force Match (FM) and Relative Entropy (RE) methods. In short, the CG models with parameters from the bottom-up methods generate good approximation to experimental observations and the AA model, with the site-to-site  $g(r)$  reproducing the overall trend of the ones from the AA model and experimental measurement (Fig. 2B). However, these CG models seem to be less transferable than one from the top-down method. Thus, we used the top-down method to generate the non-reactive parameters for the proposed building blocks of our conjugated polymers. We are also working on the derivation of the reactive parameters with a similar strategy. In the next funding period, we will combine all the parameters to complete our proposed force field, followed by the application to the simulations of porous polymer networks. We will analyze the simulation data with experimental data as references, which will inform us to further improve these non-reactive and reactive parameters from systematic coarse graining.



**Figure 2.** (A) Comparison of radial distribution functions of the top-down CG and AA benzene models. (B) Comparison of radial distribution functions of two bottom-up CG and AA benzene models. The simulated (C) densities and (D) diffusion coefficients from 270 to 350 K.