



# Developing structure and thermodynamic properties-consistent coarse-grained model for random copolymer systems



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## ABSTRACT

Molecular characterizing of random copolymer systems at large timescales is significantly important in prediction and advancing understanding of materials properties and phenomena. In this paper, we present a hybrid structure and thermodynamic properties-consistent method to develop a quantitative coarse-grained (CG) model for perfluoropolyethers (PFPEs). The bonded potentials were derived via iterative Boltzmann inversion by reproducing the distributions of bond distances and angles from the reference atomistic simulations. A novel analytical form based on multi-centered Gaussians was then introduced for the first time to represent the resultant tabulated bonded potentials well. Moreover, the non-bonded potentials were denoted by the Lennard-Jones potentials and the parameters were devised by directly matching the temperature-dependent density and surface tension of the CG models and the experiments. The transferability of the CG potentials to target PFPEs with higher molecular weights was also validated. The hybrid method in this work is of particular value and provides a guideline in developing analytical and quantitative CG potentials for random copolymers rationally.

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## 1. Introduction

Polymers have been widely utilized in engineering fields such as dendritic polymers for smart drug delivery [1], shape memory polymer composites for optics and electronics [2,3], carbazole-containing polymers for photovoltaic devices [4], and fluorinated polymers for nano-imprinting and lubrication [5,6]. Among them, perfluoropolyethers (PFPEs) are playing significant roles as high performance lubricants for specific use in the photonic, electronic, aerospace, and data processing industries [7–11]. However, due to the intrinsic complexity and versatility of polymers, incomplete understanding of and the lack of knowledge related to the physical, mechanical, and dynamic properties retard the rate of optimizing existing polymers and designing new ones rationally. Particularly, how the polydispersity effect and the nanostructure of a random copolymer system (e.g., PFPE) influences its properties has not yet been quantitatively clarified. This critical issue is laborious to investigate experimentally as it is difficult to synthesize polymers

with arbitrary chain length and sequence distributions of two or more different monomers along the chains.

Molecular simulations, on the other hand, are becoming significantly important in predicting properties and examining phenomena in biological and materials science. For instance, molecular dynamics (MD) simulation is capable of describing polymeric systems at an atomic scale, but it can only handle time scales of up to a few hundred nanoseconds [12–17]. It is reported that the relaxation time  $t$  increases with the chain length  $L$  as  $t \sim L^{3.4}$  for polymer melts [18]. Therefore, the large time and length scales required to precisely represent the structure and dynamics of polymeric systems in full detailed atomistic models are incredibly expensive and challenging in classical MD simulations. Although computer resources and simulation algorithms have advanced tremendously, the extensive number of degrees of freedom of versatile polymers limits atomistic approaches for exploring phenomena at mesoscopic and macroscopic time and length scales.

One effective way to circumvent this problem is to reduce the number of degrees of freedom within atomistic models through the representation of successive multiple atoms as one coarse-grained (CG) interaction site or bead with a specified mass and charge, depending on the atoms represented. The new CG bead interacts

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through more computationally efficient intra- and inter-molecular interactions that are optimized from the realistic replaced super-atoms. The number of simulated particles of interest is thus greatly reduced to allow for a significant jump in the accessible spatial/temporal scale. In general, to derive a reliable CG model usually consists of two critical steps: mapping atomistic coordinates of molecules into corresponding CG bead positions, and developing suitable force field for intra- and inter-molecular interactions between CG beads. The mapping scheme mainly depends on the structure and interactions of the molecules as well as the intended end-usage of the CG model. Taking polystyrene for example, there is not yet complete agreement on the choice of the bead mapping scheme due to its bulky phenyl ring substitutes and the kind and amount of tacticity involved [19–22]. Nevertheless, once the mapping scheme is determined, the next crucial issue is to devise effective CG force field parameters by reproducing target properties from the reference simulations of underlying atomistic model. According to the reproduced properties, various coarse-graining approaches can be classified into structure-based [23–26] (distributions of structural properties, i.e., the bond length, bending angle and dihedral angle), force-based [27–30] (effective interactions between the CG beads), and thermodynamic properties-based [31–34] (density, entropy, surface tension, or partitioning free energy, etc.) techniques. Apparently, we cannot expect that one parameterization method is capable of reproducing all the properties of the system accurately even at the thermodynamic state of calibration. In most cases of the structure-based coarse-graining methods such as iterative Boltzmann inversion [35] or inverse Monte Carlo [36], additional optimization of thermodynamic properties such as the pressure of the CG system needs to be taken into consideration [37,38]. Similarly, the force matching method that aims to preserve the forces of the CG model and the reference atomistic system may not represent the local conformational properties sufficiently [26,39]. On the other hand, the MARTINI force field [31–33], which has been widely employed in the CG simulations of biomolecules and polymers, makes use of partitioning free energy profiles as targets in the parameterization and corrections have to be made to capture underlying local structure adequately for specific polymeric models [40,41]. Undoubtedly, these would lead to the pursuit of hybrid approaches that enable both structural and thermodynamic consistency in the same CG model.

Furthermore, two kinds of force field forms, namely, analytical and numeric potentials, are often used to describe the interactions between CG beads. In atomistic simulations, the structural properties such as the probability distributions of the distance between two adjacent atoms can be well reproduced by a simple analytical potential. However, in CG models, the reduced degrees of freedom and the intrinsic complex nature of polymer connectivity complicate the matter significantly. It is prevalent to observe multiple and interweaved peaks in the probability distribution functions of the bond length and bending angle for coarsened CG beads in polymers. Consequently, numerical potentials or tabulated potentials have been frequently used to replace complicated analytical potentials. Although numerical potentials exhibit good reproduction of targeted distribution functions, the price of their higher accuracy is the loss of computational efficiency, physical interpretation of adjustable parameters, and mathematical-transferability of the potential form.

Therefore, in this work, we aim to develop computationally efficient and analytical CG model for random copolymer PFPEs by using a hybrid structure and thermodynamic properties-based approach. The PFPEs have been chosen as our model systems since they are commonly used as nanostructured lubricants in micro- and nano-devices due to their desirable properties such as

low surface tension, chemical and thermal stability, good lubricity, and low volatility. In the CG model, the bonded potentials are iteratively derived via the structure-based iterative Boltzmann inversion method. Their analytical expressions are derived based on sums of Gaussians to reproduce the distributions of bond lengths and angles of the reference atomistic simulations. The analytical non-bonded potentials are devised and tuned by matching the thermodynamic properties such as density and surface tension of the CG model and the experiments. Both the CG bonded and non-bonded potentials are refined to preserve the local structure and thermodynamic properties accurately at the thermodynamic state of calibration. A full description of the simulation details including the mapping scheme, the atomistic and CG MD models is outlined in Section 2. The optimization procedure and validation of the CG force field for PFPEs are reported in Sections 3 and 4. Finally, we present the summary and conclusions in Section 5.

## 2. Simulation details

### 2.1. The need of a novel CG model for PFPEs

Earlier CG models used in polymeric systems usually predicted general properties. Kremer and Grest proposed the bead-spring model coupled with a finitely extensible nonlinear elastic (FENE) potential for the simulations of entangled linear polymer melts [42]. They used the simple model to study systems with varying chain lengths covering from Rouse behavior into the reputation regime. This CG bead-spring model has also been extended to study nanostructures and dynamic behaviors of PFPEs such as surface morphology [43], nano-mechanics [44], and thermal depletion under rapid laser heating [45–50], in a qualitative manner. In addition to this, a CG bead-breakable model has been proposed as well by us to investigate the depletion kinetics of PFPEs under heat treatment [51,52]. However, in both CG bead-spring and bead-breakable models, the PFPE molecule was expressed by a sequence of identical beads and the bead number represents the molecular weight. For instance, a PFPE chain with a molecular weight of 2000 g/mol is usually characterized by a number of 10 identical beads, with each bead simply possessing a mass of around 200 g/mol and a bead diameter of 0.7 nm. Obviously, these CG models cannot provide sufficient physiochemical intra-molecular details when PFPEs approach to molecular dimensions. The stochastic chain length and sequence distributions of different monomers of PFPEs are also not preserved and have never been paid attention to in the traditional models. In addition, for functional PFPEs, only a short-range exponential decay potential is incorporated into the models to distinguish the functional end groups from the nonfunctional backbone groups, without considering different bead mass and size effects on the two atom groups. Critically, the potential parameters in the traditional models in most MD simulations are chosen in a way to reflect the energy and length scales qualitatively. In view of these, a novel coarse-graining method needs to be proposed to improve the details of intra- and inter-molecular interactions for PFPEs, and more importantly, to provide a potential for describing the PFPE model quantitatively and more precisely.

### 2.2. Mapping scheme from atomistic to CG model

We mainly develop a hybrid structural and thermodynamic properties-based CG model for PFPE Z, which is commonly used as nanostructured lubricant in magnetic hard disk drives and has a random linear chemical structure of  $\text{CF}_3\text{--O--}(\text{CF}_2\text{--CF}_2\text{--O})_p\text{--}(\text{CF}_2\text{--O})_q\text{--CF}_3$  with  $p/q = 0.5 \sim 2$ . Nevertheless, the coarse-

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