



# Bulk modulus of poly(ethylene oxide) simulated using the systematically coarse-grained model

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## ABSTRACT

In this work, the bulk modulus of the poly(ethylene oxide) (PEO) has been simulated using the dynamical stepwise compression procedure, for which the coarse-grained (CG) potentials are systematically parameterized by the multiscale scheme. It is demonstrated that the simulated bulk modulus and its temperature dependence compare well with the empirically calculated results, validating the CG potentials. Moreover, it is confirmed that the bulk modulus is closely related to the glass transition temperature ( $T_g$ ), and thus the reliability in simulating the bulk modulus significantly depends upon the reliability in reproducing the  $T_g$ . Furthermore, good agreement is attributed to the adequate representability and transferability of the CG potentials, which are generally hard to be achieved at the same time. This work highlights that both can be simultaneously achieved by simply reproducing the pressure-volume-temperature properties. Together with great gains in computational efficiency, the multiscale scheme can find a wide application in simulating various polymer systems.

## 1. Introduction

Mechanical properties (including modulus, strength, Poisson's ratio, etc.) are of great importance for a variety of engineering applications of polymeric materials [1]. Accordingly, many experimental methods (i.e. tension, bending and impacting) are available for measuring the mechanical properties and relating them to various factors (i.e. temperature). While the experimental methods are quite valuable to obtain these macroscopic properties, they have great difficulty in tracking the evolution in the microscopic structure and mesoscopic morphology during mechanical deformation. Alternatively, molecular simulations are a kind of promising methods on this aspect because they can provide a wealth of information on structure, dynamics and interactions of model systems dictating the macroscopic phenomena.

At the early age, both static and dynamic approaches were developed to simulate the elastic mechanical constants of polymers by deforming the unit cell models [2,3]. Even at the latest time, some of these methods are being applied to complex polymer systems (i.e. polymer nanocomposite) [4]. As reported, the static approach was less time-consuming and could sometimes yield results closer to the experimental data than the dynamic approach [5]. However, the static approach does not take into account the entropy effects, and thus cannot examine the temperature dependence. On this aspect, the hybrid all-atomistic (AA) molecular mechanics (MM)–molecular dynamics (MD) method recently

reported by Sahputra et al. [6] seems to be quite promising. For either method, two ways can be used to deform the unit cell models, namely stress-driven and strain-driven. Among the two, the strain-driven way is less realistic but be easier be brought into convergence than the stress-driven way so that it has been more widely used [7]. With the rapid development of the computational power, more realistic simulation by the dynamic stress-driven method will be the inevitable trend.

One of important challenges in simulating polymers is so-called spatiotemporal scale problem. For AA MD simulations, the accessible strain rate is much higher than that in experiments. As one general consequence, the simulated temperature dependences of mechanical properties (i.e. Young's modulus and bulk modulus) significantly deviate from the experimental one [6,8–10]. With respect to the space scale, crazy and shear band by the mechanical deformation occur at the order of micron ( $\mu\text{m}$ ), for which the state-of-art AA simulations cannot be used. On this aspect, coarse-grained (CG) simulation is one method that is closest to this scale [11–14]. However, the CG potentials parameterized so far are so soft that the simulations with them cannot well reproduce the compressibility [15–17]. Consequently, only few simulation works obtained the mechanical properties that could be compared to the experimental values [18–22]. It is not clear about how to parameterize the CG potentials if not against the mechanical properties to reproduce them by the simulations.

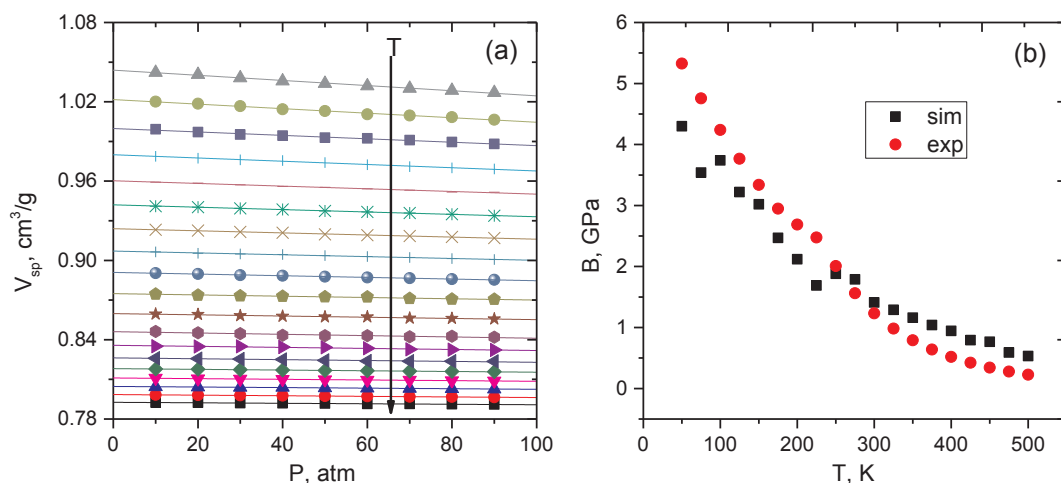
Recently, I have developed a multiscale modeling scheme in which

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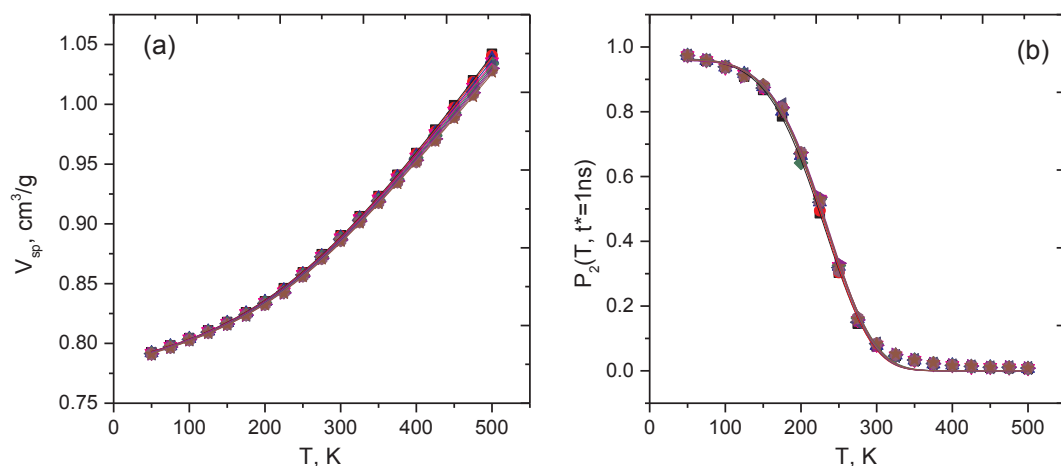
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**Fig. 1.** The specific volumes versus the pressure at various temperatures (a) and the bulk modulus versus the temperature (b) for the studied PEO bulk, where the vertical solid line in (a) points towards the direction the temperature decreases, and the oblique solid lines in (a) are the linearly fitted ones to the data, and both the simulated and experimental values are presented in (b).



**Fig. 2.** The specific volumes (a) and the reorientation functions (b) as functions of temperature for the studied PEO bulk at various pressures.

the structural and volumetric properties obtained from the AA simulations of an oligomer melt are used as target ones for parametrizing the CG potentials [23]. As demonstrated, the so-obtained CG potentials are versatile: they can be used to reasonably reproduce the volumetric properties while capturing the essential features of structure and dynamics of polymer chains; with an aid of the pre-built scaling relation, they can be reliably used to simulate the glass transition temperature ( $T_g$ ) of polymer bulks with various degrees of polymerization and films with various thicknesses [24]. In this work, I examine whether the CG potentials can be used to reliably simulate the mechanical properties of polymers, which is expected since the mechanical properties are closely related to the volumetric properties that can be well reproduced.

More specifically, the bulk modulus of poly(ethylene oxide) (PEO) melt is studied as a typical example for its versatile applications in many fields. The bulk modulus characterizes compressibility of a system, which is regarded to be the mechanical property that can be more readily to achieve success using the equilibrium MD because of small one-dimensional deformations involved in the procedure unlike shearing or uniaxial tension [8]. For this purpose, the stress-drive dynamic method is employed for realistic simulations as detailed in Section 2. In Section 3, it is demonstrated that the CG potentials are promising in simulating both thermal and mechanical properties of polymers by the MD method. Finally, the reason for this success is discussed in terms of the representability and transferability of the CG

potentials.

## 2. Computational details

The model system comprised of 27 PEO chains of 250 monomers per chain has been simulated using the CG MD method. As suggested by the density and the solubility parameter [25], this chain is long enough to represent the realistic polymer. According to the 1:1 mapping scheme in which each monomer  $-\text{CH}_2-\text{O}-\text{CH}_2-$  was reduced to one CG bead at the center of mass (COM), the single CG chain model was first built from the last configuration of the AA MD simulations at 450 K in the previous work [26]. Using the genconf tool of GROMACS-4.5.4 [27,28], 27 of such chains were generated by multiplying the given coordinate file of the single chain. Along each dimension of the three, three chains were packed, in which the conformations were allowed to be randomly rotated. The so-obtained model was then subjected to the energy minimizations (EM) and MD simulations. The VOTCA [29] was employed to facilitate the CG procedure, and the GROMACS [27,28] was used to implement all simulations.

For these simulations, the inter-bead interactions were described by the previously developed CG potentials, which were parametrized using the multiscale modeling scheme [23]. The initial model system was equilibrated for 100 ns ( $1 \text{ ns} = 10^{-9} \text{ s}$ ) at 500 K at 1 atm ( $1 \text{ atm} = 0.1 \text{ MPa}$ ), which is found to be long enough to obtain the

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