

Developing Coarse-Grained Force Fields for Polystyrene with Different Chain Lengths from Atomistic Simulation

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Abstract: We developed a coarse-grained force field and have extended it to polystyrene with longer chain length. A systematic method was introduced and was utilized to explain how the coarse-grained force field for polystyrene could be developed from the atomistic simulation in the paper. We elected to use polystyrene with different chain lengths of 20, 40 and 80 monomers in this study. In three cases, we utilized the same new mapping scheme. The coarse-grained force field does reproduce the bond, angle, and radial distribution of the atomistic model. The coarse-grained model proved successful, as shown by analyses of the static and dynamic properties of different chain lengths.

Keywords: coarse-grained, atomistic simulation, polystyrene.

Introduction

Although computational power increases largely every year, the huge number of degrees of freedom limits full-atomistic simulation when it comes to investigating long polymer chains. To circumvent this problem, we need to feasibly simplify the polymer system. Therefore we reduce the degrees of freedom by mapping atomistic model onto coarse-grained structures and keeping only those degrees of freedom that are relevant for the specific range of our interest.

As a matter of fact, some simple models for studying meso- and macroscale phenomena in polymer systems have been used extensively.^{1,2} The typical examples are "time coarse graining",³ dissipative particle dynamics (DPD) and smoothed particle dynamics (SPD).⁴⁻⁷ Because these methods are connected with their generic nature, they mostly don't distinguish between chemically different polymers.

Recently, various so-called CG models have been developed to enhance polymer simulations such as bond fluctuation model,⁸⁻¹⁵ and the high-coordination lattice.¹⁶⁻¹⁸ Guerrault built a potential of mean force and used it in the system of polyethylene and cis-polybutadiene.¹⁹ Clancy defined a long range interaction energy and estimated a continuous effective potential energy between beads.²⁰ Murat mapped bead-spring type polymer chains in a melt to a soft-core liquid with fluctuating ellipsoidal particles modeled by an anisotropic Gaussian potential.²¹ Louis *et al.* used a similar way to coarsen polymer chains in dilute to semi-dilute solu-

tions.^{22,23} Tschöp and successors²⁴⁻²⁶ and Akkermans *et al.*²⁷ did systematic studies of polymer melt coarse graining, and developed a hierarchy of methods to bridge the gap from microscopic to mesoscopic simulation. Müller-Plathe developed the ways, which are similar to us, to automatically adjust force fields to specific systems on mesoscale phenomena for polymer.²⁸⁻³¹ The crucial point of this kind of methods is to choose suitable mapping scheme, use corresponding optimization strategy and construct feasible intra- and intermolecular potential terms.

In our lab we have developed coarse-grained force field for a cis-poly(1,4-butadiene) homopolymer chain with 10 monomers³² and successfully extended it to diblock copolymer.³³ Due to wide application of polystyrene in the industry, we select it here. In this paper we make a different mapping scheme. In order to compare, we choose polystyrene with different chain lengths of 20, 40 and 80 monomers. In this paper we call them st-20, st-40 and st-80 respectively.

Methods

Conceptual Points. Atomistic force fields of polymers usually comprise two major parts: bonded and non-bonded potential term in Ref 28. For both parts, there are several different contributions to describe the energy. Generally the total force field energy can be expressed as follows:

$$\begin{aligned} V_{tot} &= V_{bonded} + V_{non-bonded} \\ &= (V_{str} + V_{bend} + V_{tors}) + (V_{vdw} + V_{es} + \dots) \end{aligned} \quad (1)$$

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V_{tot} is the total energy of the system; V_{str} is the potential of the bond stretching between pairs of bonded atoms and V_{bend} represents the potential of the angle bending between three atoms; V_{tors} is a torsional potential needed for the change of the energy as bonds rotate; V_{vdw} accounts for the excluded volume repulsive as well as the intermolecular attractive forces between atoms in different polymer chains or in the same polymer chains but at least three bonds apart; V_{es} describes the potential of the electrostatic interactions.³⁴ The coarse-grained force field will be constructed in the same way. With so many potential terms, i.e. V_{str} , V_{bend} , V_{tors} , and $V_{non-bonded}$, it's meaningless to make the adjustment of all the terms at the same time. Therefore we will make successive adjustment of the terms in the order of their relative strength. According to the experience of Müller-Plathe *et al.* in Ref.28, we will also start with the stretching energy, working on the way systematically down to the non-bonded energy in the order as,

$$V_{str} \rightarrow V_{bend} \rightarrow V_{non-bonded} \quad (2)$$

Details of the Simulation. To build the coarse-grained models, we obtained the distributions of bonds, angles, and radial distribution functions (RDFs) from the full atomistic simulations. The molecular dynamic simulations of polystyrene were performed with the program Tinker³⁵⁻⁴⁰ in an orthorhombic cubic box with the standard periodic boundary conditions. The parameters of the all-atom force field for the polymer directly come from the MM2⁴¹⁻⁴³ force field. The runs are performed in the NVT ensemble and the temperature is set to 300 K corresponding to $k_B T = 2.49$ kJ/mol.

In the molecular simulation, The Langevin equations of motion are used at a constant temperature as follows:

$$m_i \frac{d^2 r_i}{dt^2} = -m_i \zeta_i \frac{dr_i}{dt} + \sum_j F_{ij} + \xi_i \quad (3)$$

Where r_i is the position of the i th bead and $\sum_j F_{ij}$ and ξ_i are the systematic and random forces, respectively, on the i th bead. The white and Gaussian random force ξ_i satisfies $\langle \xi_i \rangle = 0$ and its variance is $\langle \xi_i(t) \xi_j(t) \rangle = 2 \zeta_i k_B T \delta_{ij} \delta I$, where the bracket denotes the ensemble average and I is a 3×3 unit matrix. The term ζ_i represents the friction coefficient of i th bead; we used $\zeta_i = 0.91$ in the simulations. The Langevin equations of motion are integrated via the Velocity Verlet algorithm^{44,45} with a time step $\Delta t = 0.2 \tau$.⁴⁶ A pre-equilibration procedure is run in a higher temperature at first. The equilibration runs are performed until the distributions of bonds, angles and RDFs are steady. It's proved that run a more lengths about 10^7 integration steps turns out to be enough to determine smooth RDFs.

Coarse Grained Force Field Development

Mapping. At first we choose the center of the coarse-grained beads. The mapping is illustrated in Figure 1. As sketched

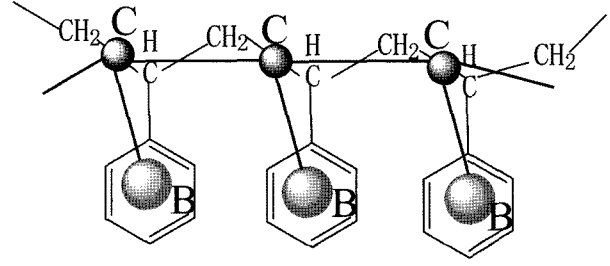


Figure 1. Illustration of the mapping of polystyrene from the atomistic to the mesoscopic level.

in Figure 1, every C strand and B strand are replaced by one bead respectively, centered at the mass' center of the unit.

Therefore, the force field will have two types of coarse-grained beads corresponding to C or B strand, two different bond types corresponding to two kinds of bond distributions (C-C, C-B), two angle types corresponding to two kinds of angle distributions (C-C-C, C-C-B).

Bonded Potential. A multi-peaked distribution of a structural parameter,³¹ say a bond distance l , can be approximated by a sum of n Gaussian functions characterized by their centers (l_{ci}), total areas (A_i), and width (ω_i):

$$P(l) = \sum_{i=1}^n \frac{A_i}{\omega_i \sqrt{\pi/2}} \exp^{-2(l-l_{ci})^2/\omega_i^2} \quad (4)$$

If we define, $g_i(l) = \frac{A_i}{\omega_i \sqrt{\pi/2}} \exp^{-2(l-l_{ci})^2/\omega_i^2}$, the distribution

can be written as $P(l) = \sum_{i=1}^n g_i(l)$, The corresponding potential can be obtained by Boltzmann inversion. It's written as:

$$V(l) = -kT \ln \sum_{i=1}^n g_i(l) \quad (5)$$

The force can be written as: $F(l) = -4kT \frac{1}{l} \frac{\sum_{i=1}^n g_i(l) (l-l_{ci})}{\sum_{i=1}^n g_i(l)}$ (6)

For the angle potentials, the equations for potentials and

Table I. Parameters of Bond Potential Represented by Eq. (6)

| Polystyrene | Bond Type | n | i | A_i | ω_i | l_{ci} |
|-------------|-----------|-----|-----|--------|------------|----------|
| st-20 | C-C | 2 | 1 | 0.0039 | 0.1351 | 2.36 |
| | | | 2 | 0.0055 | 0.1485 | 2.59 |
| st-40 | C-C | 2 | 1 | 0.0063 | 0.1567 | 2.36 |
| | | | 2 | 0.0037 | 0.1159 | 2.59 |
| st-80 | C-C | 2 | 1 | 0.0040 | 0.1954 | 2.37 |
| | | | 2 | 0.0046 | 0.1345 | 2.60 |
| | B-C | 1 | 1 | 0.0010 | 0.1466 | 3.25 |

forces can be obtained in the similar way:

$$V(\theta) = -kT \ln \sum_{i=1}^n g_i(\theta) \quad (7)$$

$$F(\theta) = -4kT \frac{\sum_{i=1}^n g_i(\theta) \frac{(\theta - \theta_{ci})}{w_i^2}}{\sum_{i=1}^n g_i(\theta)} \quad (8)$$

Here n is equal to the number of the peaks. The values of the parameters for bonds and angles of polystyrene with 20, 40 and 80 monomers are listed in Table I and Table II. The optimized efforts for them are shown in Figure 2 and Figure 3.

Non-bonded Potential. For the non-bonded part of the potential, we derive an effective non-bonded potential from a given target radial distribution function $g(r)$. We suppose

Table II. Parameters of Angle Potential Represented by Eq. (8)

| Polystyrene | Angle Type | n | i | A_i | ω_i | θ_{ci} |
|-------------|------------|-----|-----|--------|------------|---------------|
| st-20 | C-C-C | 2 | 1 | 0.0051 | 0.4151 | 123.2 |
| | | | 2 | 0.0149 | 0.9305 | 164.8 |
| | B-C-C | 3 | 1 | 0.0069 | 0.3083 | 82.5 |
| | | | 2 | 0.0060 | 0.3089 | 102.6 |
| | | | 3 | 0.0053 | 0.3239 | 148.9 |
| st-40 | C-C-C | 2 | 1 | 0.0083 | 0.7027 | 130.8 |
| | | | 2 | 0.0138 | 0.5231 | 164.2 |
| | B-C-C | 3 | 1 | 0.0022 | 0.2574 | 82.2 |
| | | | 2 | 0.0054 | 0.4781 | 103.1 |
| | | | 3 | 0.0031 | 0.3190 | 150.1 |
| st-80 | C-C-C | 2 | 1 | 0.0051 | 0.4303 | 126.9 |
| | | | 2 | 0.0122 | 0.4564 | 163.9 |
| | B-C-C | 3 | 1 | 0.0047 | 0.2351 | 82.6 |
| | | | 2 | 0.0093 | 0.4442 | 105.0 |
| | | | 3 | 0.0087 | 0.2798 | 150.5 |

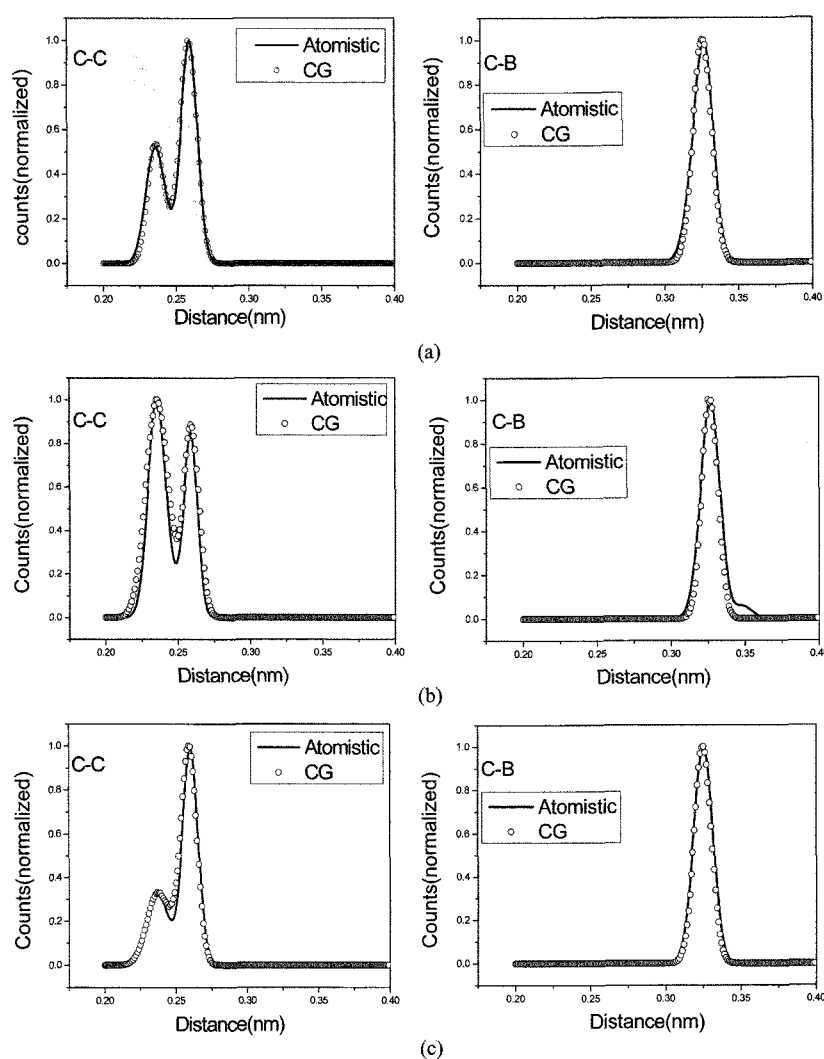


Figure 2. Histogram of C-C, C-B bond length of polystyrene with 20 (a), 40 (b) and 80 (c) monomers from atomistic simulation (solid lines) and from coarse-grained simulations (empty circles) at 300 K.

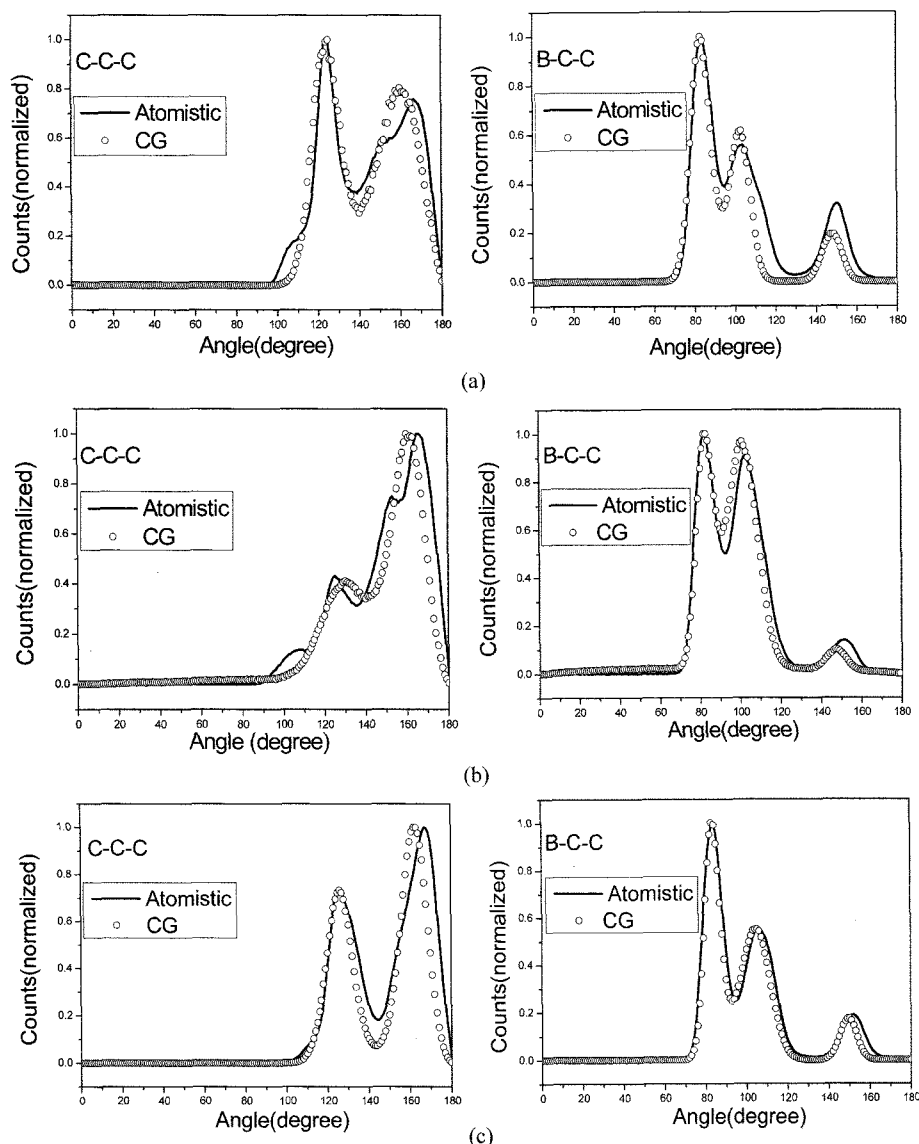


Figure 3. Histogram of C-C-C, B-C-C angle of polystyrene with 20 (a), 40 (b), and 80 (c) monomers from atomistic simulation (solid lines) and from coarse-grained simulations (empty circles) at 300 K.

to start from a tabulated initial potential $V_0(r)$. It has been proposed to invert RDFs for one-component simple liquid systems by taking a simple Boltzmann inverse of $g(r)$.⁴⁷ But it is exact only in the limit of infinitely dilute systems. We use the potential of mean force,

$$F(r) = -k_B T \ln g(r) \quad (9)$$

which is a free energy and not a potential energy (except for the case of zero density). However, $F(r)$ is usually sufficient to serve as the initial guess $V_0(r)$ for an iterative procedure. The potential needs to be improved, which is done by a correction term. This step can be iterated as follows by:

$$V_{i+1}(r) = V_i(r) + k_B T \ln \frac{g_i(r)}{g(r)} \quad (10)$$

$$\text{Until } f_{\text{target}} = \int \omega(r)(g(r) - g_f(r))^2 dr \quad (11)$$

arrives below an initial threshold. We apply $\omega(r) = \exp(-r)$ as a weighting function to penalize deviations at small distances. Because of the mapping scheme used in the paper, we get a good agreement of radial distribution functions between atomistic and coarse-grained simulation through zero iteration. In three iterations, the merit function f_{target} stays below 0.048. In Figure 4, the distribution of RDFs obtained from atomistic simulation is compared with CG simulations.

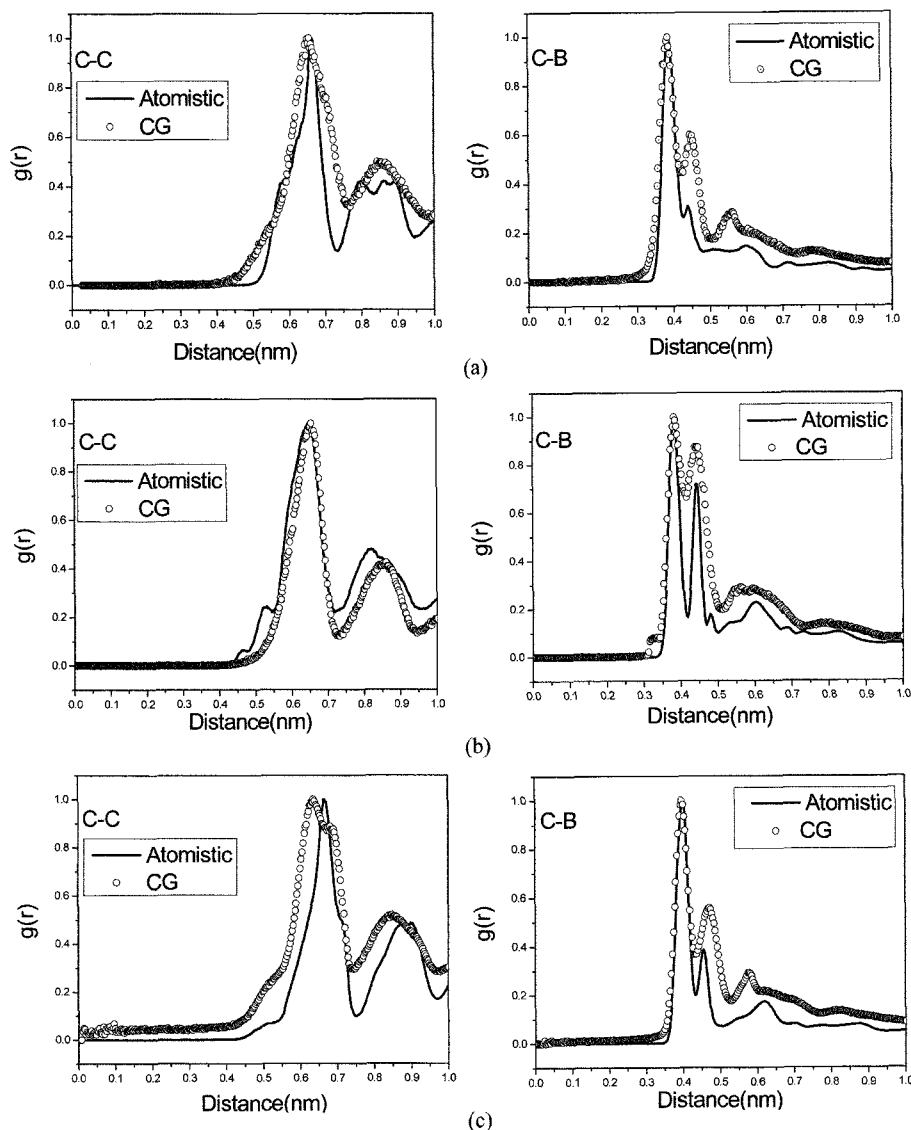


Figure 4. Interchain C-C, C-B radial distribution functions (RDFs) of polystyrene with 20 (a), 40 (b) and 80 (c) monomers from atomistic simulation (solid lines) and from coarse-grained simulations (empty circles) at 300 K.

Static and Dynamic Properties of Polystyrene

Now we discuss static and dynamic properties from atomistic simulations and coarse-grained simulations. We analyze the results obtained from the coarse-grained model and demonstrate that this model does reproduce the results from the atomistic simulations.

First, values of the mean-square end-to-end distance ($\langle R_G^2 \rangle$) and the mean-square radius of gyration ($\langle S_G^2 \rangle$) are calculated. The statistical results of the main chain (C-C) are shown in Table III. The coarse-grained force field reproduces the properties of the atomistic model very well.

It's found that the diffusion of the coarse-grained molecular dynamics simulation shows the same characteristics as that obtained from an atomistic molecular dynamics simula-

Table III. The Mean-Square End-to-End Distance and the Mean-Square Radius of Gyration for the Atomistic and Coarse-Grained Simulation of Polystyrene with 20, 40 and 80 Monomers

| Polystyrene | | $\langle R_G^2 \rangle / \text{nm}^2$ | $\langle S_G^2 \rangle / \text{nm}^2$ | $\langle R_G^2 \rangle / \langle S_G^2 \rangle$ |
|-------------|-----------|---------------------------------------|---------------------------------------|-------------------------------------------------|
| st-20 | Atomistic | 0.150347 | 0.013575 | 11.08 |
| | CG | 0.156545 | 0.14177 | 11.04 |
| st-40 | Atomistic | 0.606492 | 0.53781 | 11.27 |
| | CG | 0.609668 | 0.54866 | 11.11 |
| st-80 | Atomistic | 2.971119 | 2.60099 | 11.42 |
| | CG | 3.009242 | 2.68448 | 11.21 |

tion for C-C. The diffusion coefficient could be measured by monitoring the mean-square displacement (MSD) of the

center of gravity of the chains^{48,49}

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{g_{CG}(t)}{t} = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{\partial}{\partial t} \langle (r_i(t) - r_i(0))^2 \rangle \quad (12)$$

where the quantity in braces is the ensemble-averaged mean

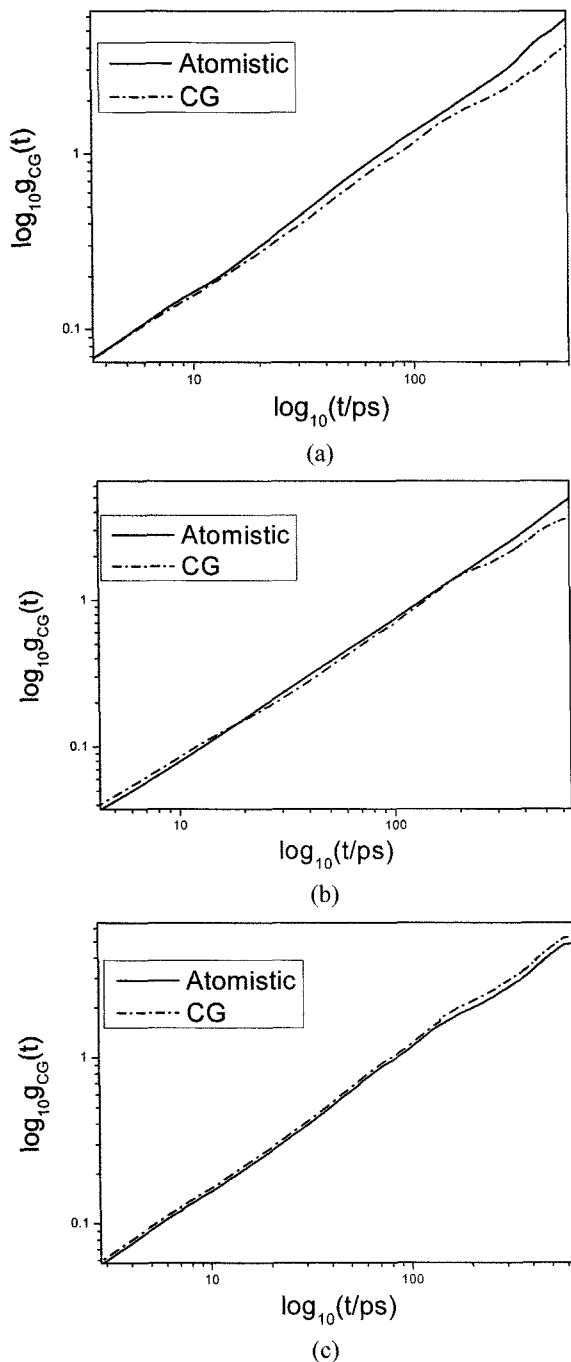


Figure 5. Mean-square displacement of the center mass of polystyrene with 20 (a), 40 (b) and 80 (c) monomers at 300 K and 103.1 KPa. The solid line and the broken line represent atomistic simulation and coarse-grained simulation separately, after shifting in long time to bring both sets of curves into coincidence.

square displacement of the molecules and $r_i(t)$ is the vector coordinate of the center of mass of bead i . The mean square displacements of the atomistic and coarse-grained simulations at 300 K and 101.3 KPa are shown in Figure 5. As you can see, the diffusion coefficient of the coarse-grained simulations agreed very well with atomistic simulations.

Discussion and Conclusions

This work introduces a systematic procedure to coarse grain atomistic model of polystyrene with different chain lengths of 20, 40 and 80 monomers. The results are reported above. As you can see, the three kinds of polystyrene have similar bond and angle distribution functions including the number of peaks n and peak position l_{cl}/θ_{cl} . Although there exists a little variation in the angle (C-C-C) distribution of st-40, it's proved to be effective to ignore the variation.

Coarse-grained models ignore some detailed information of atomistic models. Therefore we could see some discrepancies between atomistic models and coarse-grained models in Figure 3 and Figure 4. However in Figure 4, $f_{target} \leq 0.048$. It's acceptable.

It's demonstrated that the optimization algorithm m is powerful. Our reasonable mapping scheme extends the method from cis-poly with 10 monomers in Ref.32 to polystyrene with 80 monomers. Our final analysis of static and dynamic properties testifies the coarse-grained model is effective.

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