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Developing coarse-grained force fields for *cis*-poly(1,4-butadiene) from the atomistic simulation

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Abstract

Computational methods are described and applied to study how to develop coarse-grained force fields for *cis*-poly(1,4-butadiene) from the atomistic simulation. We developed an iterative method for potential inversion from distribution functions for the polymer systems. Then, we analyzed the static character and dynamic character from atomistic simulation and coarse-grained (CG) simulation as a simple application, the results also testified the coarse-grained modeling is effective.

Keywords: Atomistic simulation; Coarse-grained; Poly(1,4-butadiene)

1. Introduction

With the increase of computer power, simulations in a complex system such as polymer might be realized in future. However, quantitatively modeling a polymer chain in fully atomistic details at the meso- or macroscopic length scale is nowadays difficult because of the huge number degree of freedoms in the system. A possible way to solve this problem is to reduce the number of degree of freedoms through mapping atomistic model onto coarse-grained structures. In fact, some simple coarse-grained models for polymer system have been extensively used for understanding of problem such as relaxation of a polymeric chain or the thermodynamics of a complex polymer system in melt or in solution [1–3]. However, due to their generic natures, they do not distinguish between chemically different polymers. Thus, the meso- or macroscale phenomena for polymer have mostly been qualitatively investigated. Up to data, there is still a great challenge to get a meaningful potential function that may exactly map the atomistic force field. Recently, several groups have developed their potential functions. Reinier et al. [4] explored a systematic procedure to coarsen a microscopic model towards a mesoscopic model. Murat and Kremer [5] mapped bead-spring type polymer chains in a melt to a soft-core liquid with fluctuating ellipsoidal particles modeled by an anisotropic Gaussian potential. A similar way to coarsen polymer chains in dilute to semi-dilute solutions was found by Louis et al. [6,7]. A potential of mean force was built and used in the system of polyethylene and *cis*-polybutadiene by Guerrault et al. [8]. Clancy defined a long range interaction energy and estimated a continuous effective potential energy between beads [9]. Straub obtained an anisotropic potential for protein simulations extracted from the continually growing databases of protein structures [10]. Of the models currently developed, the way to obtain effective mesoscale potentials going from iterative optimization procedures from atomistic simulations by Müller-Plathe et al. [11–13] is close to us. However, the analytical potentials and the manual process of selecting a good functional form of the potential are developed in this paper.

To map atomistic structure to coarse-grained models, several atoms are usually considered as a single 'super-atom'. The interaction energies between two super-atoms are obtained in an optimization procedure that reproduces

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the structural distributions between the super-atom which is obtained from the atomistic simulations. In this paper, we are to set up a coarse-grained model of a *cis*-poly(1,4-butadiene) homopolymer chain. We select it because of its wide applications as in industry. It does not take a great of degree of imagination to come up with, as its very similar to natural rubber, polyisoprene. It is good for uses, which require exposure to low temperatures. Tires treads are often made of polybutadiene copolymers. Belts, hoses, gaskets and other automobile parts are made from *cis*-poly(1,4-butadiene), because it stands up to cold temperatures better than other elastomers. Thus, investigations of *cis*-poly(1,4-butadiene) polymer is obviously necessary.

2. Method

Atomistic polymer force fields are usually divided into two major parts, i.e. bonded and non-bonded potential term, refer to Ref. [11]. In each part, there involves several different contributions. Thus, the total force field energy can be described as follows:

$$V_{\mathrm{tot}} = V_{\mathrm{bonded}} + V_{\mathrm{non-bonded}} = (V_{\mathrm{str}} + V_{\mathrm{bend}} + V_{\mathrm{tors}}) + (V_{\mathrm{vdw}} + V_{\mathrm{es}} + \ldots) \tag{1}$$

here, V_{tot} is the total energy of the system; V_{str} and V_{bend} are the potentials which are contributions of the bond stretching between pairs of bonded atoms and the angle bending between three atoms, respectively; V_{tors} is a torsional potential accounting 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} is the potential of the electrostatic interactions [14]. The coarse-grained force field will be built in the same way. Being a neutral polymer for the *cis*-poly(1,4-butadiene), the electrostatic interactions among unbonded atoms are reasonably ignored. However, having still totally four potential terms, i.e. V_{str}, V_{bend}, V_{tors}, and V_{vdw}, we do not intend to make the adjustment of all the terms at the same time, but the successive adjustment of the terms in the order of their relative strength. According to the experience of Müller-Plathe et al. in Ref. [11], we will also start with the stretching energy, working on the way systematically down to the torsional energy in the order as,

$$V_{\mathrm{str}} \rightarrow V_{\mathrm{bend}} \rightarrow V_{\mathrm{non-bonded}} \rightarrow V_{\mathrm{tors}} \tag{2}$$

To set-up the coarse-grained models, we started from the atomistic simulations from which the distributions of bonds, bond angles, dihedral angles and radial distribution function (RDF) could be obtained. The molecular dynamic simulations of 10 monomers *cis*-poly(1,4-butadiene) were performed with the program Tinker—a free software tools for molecular design—in an orthorhombic cubic box with the standard periodic boundary conditions. The parameters of the all-atom force field for the polymer were taken directly from the MM3 [15–17] force field and used without modification. The runs are performed in the NVT ensemble and the temperature is set to 500 K corresponding to $k_{\mathrm{B}}T = 4.15$ kJ/mol. The Langevin equations of motion were integrated by the Velocity Verlet algorithm with a time step $\Delta t = 0.01\tau$ [18].

Initial configurations were generated according to the given parameters of bonds, bond angles, dihedral angles and van der Waals interactions (VDW) by MM3 force field. Then we optimized the system's energy to relax overlapping monomers, in which case the excluded volume problems could be avoided. And then, the chains were randomly placed into the simulation box with periodic boundary conditions.

A pre-equilibration procedure is run in a higher temperature at first. And it was until the distributions of bonds, bond angles, dihedral angles and RDF were stabilized (or could be reproduced in different part of time) that the equilibration runs were performed. After that, ran a more lengths about 10^5 integration steps turned out to be enough to determine smooth RDFs.

The first step of the coarse-graining procedure is to choose a center of the super-atom. Natural choices were (i) the center of the mass' center of each monomer. In view of the particularity of *cis*-poly(1,4-butadiene), we centered the double bond of the monomer, (ii) every second carbon atom on the backbone. With respect to both mapping points, the bond length and angular distributions were obtained from the atomistic simulations. The distributions looked quite similar for both cases. However, for choice i, they were slightly sharper (not shown). Moreover, the super-atom centered at the double bond is flat all carbon atoms of one monomer lied in one plane. For this reason, we finally chose the double bond's center of the monomer as the mapping point for the super-atom. The mapping to the mesoscale was sketched in Fig. 1. Each monomer was replaced by one super-atom, centered at the double bond's center of the monomer.

The distribution of distances between two successive coarse-grained beads along the chain is shown in Fig. 2,

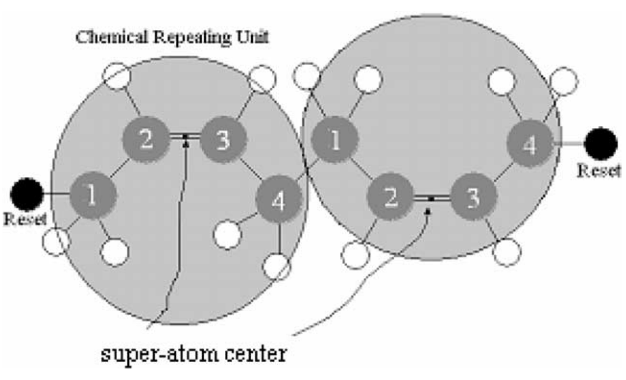

Fig. 1. Illustration of the mapping of *cis*-poly(1,4-butadiene) from the atomistic to the mesoscopic level.

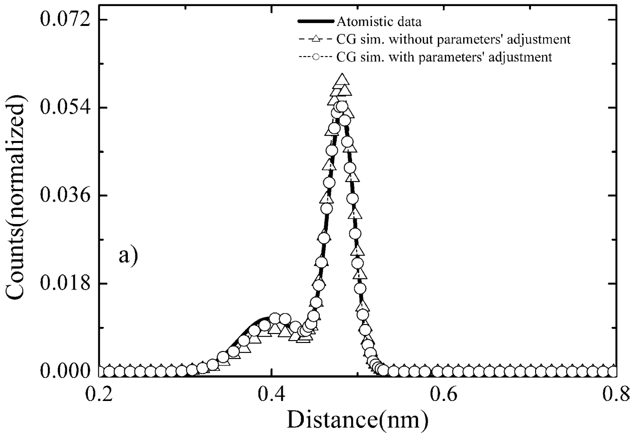

Fig. 2. Bond parametrization for the *cis*-poly(1,4-butadiene) atomistic sim. and CG model. The atomistic data could be fitted by two Gaussians. The relative amplitudes are optimized.

which has the feature of two peaks. The two-peak distribution is represent by the two Gaussian functions, which is Boltzmann-inverted for obtaining the $V_{\rm str}$. Here, Boltzmann-inverted is a method that can always for potential inversion from a distribution to yield a potential of mean force. For details on the Boltzmann-inverted as we used, we refer to Ref. [19].

To get the effective potential based on the distribution, let first find a function for fitting the distribution, and then Boltzmann-inverted on it. Of many functions available to fit this curve, two Gaussian functions are chosen here, as expressed in Eq. (3),

$$P(x) = \frac{A_1}{\omega_1} e^{\frac{-2(x-x_{c1})^2}{\omega_1^2}} + \frac{A_2}{\omega_2} e^{\frac{-2(x-x_{c2})^2}{\omega_2^2}} \tag{3}$$

Here, A_1, A_2, x_{c1}, x_{c2}, ω_1, ω_2 are the parameters obtained through two Gaussian function fitting, respectively. Then, taking the logarithm at the both sides is considered.

$$\begin{aligned} -\ln P(x) = {} & -\ln \frac{A_1}{\omega_1} + \frac{2(x-x_{c1})^2}{\omega_1^2} \\ & - \ln\left\{ 1 + \frac{A_2\omega_1}{A_1\omega_2} e^{\left[\frac{2(x-x_{c1})^2}{\omega_1^2} - \frac{2(x-x_{c2})^2}{\omega_2^2}\right]} \right\} \end{aligned} \tag{4}$$

and the Boltzmann-inverted is used in the end,

$$\begin{aligned} V_{\rm str}(x) = {} & k_{\rm B}T\Big\{k_1(x-x_{c1})^2 \\ & - \ln\Big\{1 + k_3 e^{[k1(x-x_{c1})^2 - k_2(x-x_{c2})^2]}\Big\}\Big\} \end{aligned} \tag{5}$$

Here, $k_1 = 2/\omega_1^2$, $k_2 = 2/\omega_2^2$, $k_3 = \omega_1 A_2/\omega_2 A_1$. To lower the number of parameters, we freeze all of the parameters except one—the value of the parameter k_3—as the relative changes of two peaks, which can be needed adjusting to be reproduced specifically for each bond, the values of the parameters are listed in Table 1 and the optimized effort for it as shown in Fig. 2, too.

The angular distribution of three successive super-atoms along the chain is well approximated by a Gaussian bell function, and then the Boltzmann-inverted distribution is applied to obtain a harmonic potential, as stated in Eq. (6).

$$V_{\rm bend}(\alpha) = -k_{\rm B}T \ln\left(\frac{p(\alpha)}{\sin \alpha}\right) \tag{6}$$

It turns out to be sufficiently reproduced without further optimization. The result is shown in Fig. 3. The atomistic data (solid line) is well mapped by the coarse-grained model (squares).

We illustrate the procedure with the example of deriving an effective non-bonded potential $V_0(r)$ from a given target radial distribution function $g(r)$. Suppose, we start from a tabulated initial potential $V_0(r)$. It has been proposed [20] to invert RDFs for one-component simple liquid systems by taking a simple Boltzmann-inverse of $g(r)$. But it is exact only in the limit of infinitely dilute systems. We use the potential of mean force

$$F(r) = -k_{\rm B}T \ln g(r) \tag{7}$$

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. Simulating our system with $V_0(r)$ will yield a corresponding $g_0(r)$, which is different from $g(r)$. The potential needs to be improved, which is done by a correction term. This step can be iterated:

$$V_{i+1}(r) = V_i(r) + k_{\rm B}T \ln \frac{g_i(r)}{g(r)} \tag{8}$$

Clearly a potential that reproduces $g(r)$ is a fixed point of the iteration. Thus, if the series converges, we have a valid solution. Therefore, in the iterative process, we quote the

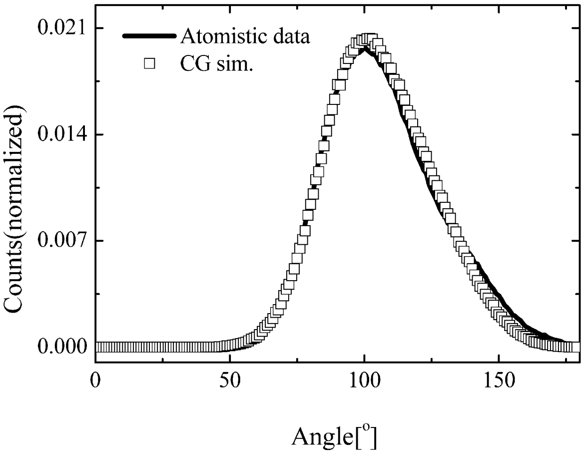

Fig. 3. Angular distribution for the *cis*-poly(1,4-butadiene).

Table 1
The initial values of parameters (of two Gaussians to the data) for the atomistic bond distribution as well optimized parameters for the CG model of the *cis*-poly(1,4-butadiene)

Parameters	k_1	x_{c1}	k_2	x_{c2}	k_3
The initial values of parameters from the atomistic sim.					
Values	5.907	4.014	17.40	4.807	4.740
The CG sim. with the parameters' adjustment					
Values	5.907	4.014	17.40	4.807	3.667

merit function

$$f_{\text{target}} = \int \omega(r)(g(r) - g_j(r))^2 \mathrm{d}r \tag{9}$$

to measure the curve convergence quantitatively (Table 2).

As a weighting function, we applied $\omega(r) = \exp(-r)$, in order to make more strongly deviations at small distances. The results are as follows:

#	f_target
Step 1	0.17020973
Step 2	0.07162240
Step 3	0.02199232
Step 4	0.00338895
Step 5	0.00271357
Step 6	0.00432713
Step 7	0.00279188
Step 8	0.00448853
Step 9	0.00290504

Looking at the merit function, we can see that the RDF converged after about four iterations. After that, the deviations can be regarded as pure noise within our statistical accuracy, which is introduced in Ref. [11]. A close looking at Fig. 4 also reveals that the curves converge from short distances to large distances: areas that are mimicked very accurately in an earlier iteration could be off in a subsequent one. And it is visualized for RDF in Fig. 5. Compared with the target RDF from the atomistic simulation, the RDF from coarse-grained simulation can both reproduce the rise of the main peak and the convergence. The coarse-grained RDF agrees well to the target RDF obtained from the atomistic simulation.

For the distribution of the dihedral angle, first, the Boltzmann-inverted distribution was applied first, which is

$$V_{\text{dihedral}}(\theta) = -k_{\text{B}}T \ln p(\theta) \tag{10}$$

However, the curves of the atomistic simulations could not be reproduced well by the coarse grained simulations. But we can obtain the coarse-grained simulations potential function of torsion by non-linear curve fitting method, and the function was used the Fourier progression forms, i.e.

$$V_{\text{dihedral}}(\theta) = \sum_{n=1}^{6} \frac{V_n}{2}(1 + \cos(n\theta - \gamma_n)) \tag{11}$$

here series of γ_n ($n = 1, 2, \ldots, 6$) were fixed. Compared to the distribution of the dihedral angle from atomistic simulation, we adjusted the values of V_n ($n = 1, 2, \ldots, 6$) in proper,

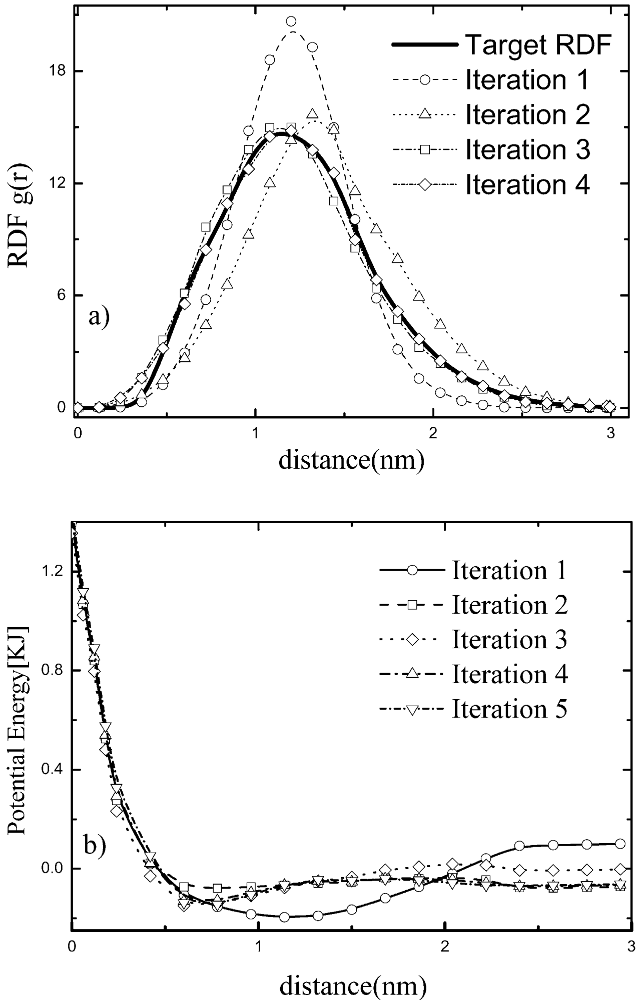

Fig. 4. Optimization of the intermolecular (a) RDF for *cis*-poly(1,4-butadiene) by way of the iterative Boltzmann-inverted method and the potential energy (b) correspond to it. The RDF of iteration 1 corresponds to the initial potential guess, the direct Boltzmann inversion of the intermolecular target RDF. The quality of the trial RDFs improves very fast. After the fourth iteration (shown), the trial RDFs matches the target within line thickness (not shown any more).

Table 2
The mean-square end-to-end distance and the mean-square radius of gyration for the atomistic and coarse-grained simulations of the *cis*-poly(1,4-butadiene)

	$\langle R_G^2 \rangle$/nm^2	$\langle S_G^2 \rangle$/nm^2	$\langle R_G^2 \rangle / \langle S_G^2 \rangle$
Atomistic sim	2.8206	0.4857	5.8073
CG sim	2.8255	0.4852	5.8234

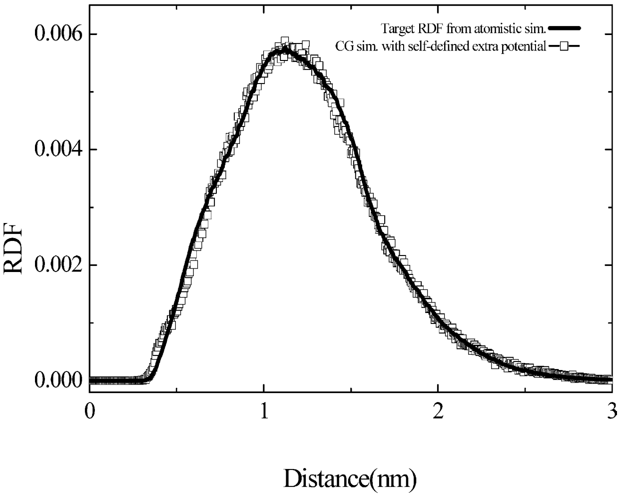

Fig. 5. Interchain radial distribution function (RDF) for super-atoms as obtained from atomistic simulation of *cis*-poly(1,4-butadiene) and for the optimized potential of coarse-grained. To the latter, after smoothed for the potential, we also cut-off the potential before $r<0.38$ nm ($4\% \times g(r)_{\max}$). Compared with the target RDF from the atomistic simulations, the latter can both reproduce the rise of the main peak and the convergence.

especially the values of V_1 and V_2, according to the distribution of the dihedral angle from coarse-grained simulation. The result is shown in Fig. 6. From the figure, the atomistic data (solid line) is symmetrized and five-point smoothed. The coarse-grained data is obtained for the force fields with (circles) torsional potential. Qualitatively, they reproduce the atomistic curve.

2.1. Static and dynamic properties of homopolymers

For analytical potentials, it is relatively straightforward to automatically adjust the parameters not only to structural but simultaneously also to chains properties like static and dynamic properties. We now briefly explain some of the results that have been obtained for the coarse-grained model described to demonstrate that this model does in fact reproduce the results from the atomistic simulation.

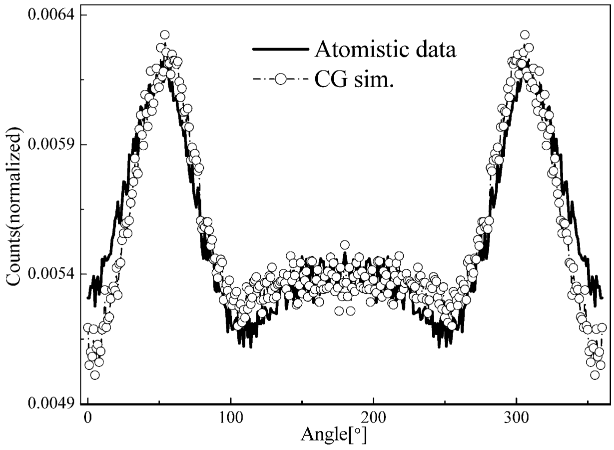

Fig. 6. Normalized distribution of the dihedral angles for *cis*-poly(1,4-butadiene), obtained from the simulation. The parameters γ_n ($n=1, 2,\ldots, 6$) are fixed, and the initial values of them are 0° except γ_2 is 180°. And the initial values of parameters V_n ($n=1, 2,\ldots, 6$) are -0.033, -0.009, 0.054, 0.034, 0.004, -0.006, respectively.

First, we obtained some of the measurements of chain properties, the mean-square end-to-end distance ($\langle R_G^2\rangle$) and the mean-square radius of gyration ($\langle S_G^2\rangle$). The values of the statistical results are given in Table 2. The coarse-grained force field reproduced the properties of the atomistic model.

More interesting is that the diffusion of the coarse-grained molecular dynamics simulation shows the same characteristics as that obtained from an atomistic molecular dynamics simulation for *cis*-poly(1,4-butadiene). The mean-square displacement (MSD) of the linear (Einstein) regime of the coarse-grained model was used to obtain a diffusion coefficient [21,22].

$$D = \frac{1}{6}\lim \frac{g_{\mathrm{CG}}(t)}{t} = \frac{1}{6}\lim \frac{\partial}{\partial t}\langle (r_i(t) - r_i(0))^2\rangle \qquad (12)$$

where the quantity in braces is the ensemble-averaged mean 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 500 K and 101.3 kPa are shown in Fig. 7. The MSDs are linear-up to 3.0 ps, followed by another liner regime. The diffusion coefficient of the coarse-grained simulations agreed well with atomistic simulations.

3. Conclusions

Results of a molecular dynamic simulation of *cis*-poly(1,4-butadiene) are reported. An all-atom force field for the polybutadiene is developed using MM3 force field's parameters, and the coarse-grained models is developed by

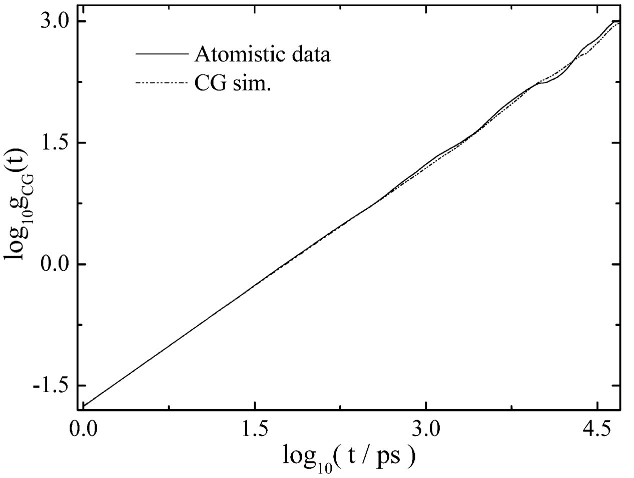

Fig. 7. Mean-square displacement of the center mass of *cis*-poly(1,4-butadiene) chain at 500 K and 101.3 kPa. The solid line denotes results from atomistic molecular dynamic simulation and the broken line denote results from coarse-grained molecular dynamic simulation, after shifting in log *t* to bring both sets of curves into coincidence.

our own new force field, which are designed to match structural properties such as radial distribution functions of various kinds derived by atomistic simulations of *cis*-poly(1,4-butadiene). We developed an iterative method for potential inversion from distribution functions for the polymer of the *cis*-poly(1,4-butadiene). However, the iterative method could be used for the polymer systems. What's more, it could also be utilized for other chemical systems, in which intramolecular connectivity had to be taken into account.

The optimization algorithm was proved powerful. However, for the distribution of the dihedral angle, the CG simulation's data reproduce the atomistic curve, but the efficiency of the simulation of it was poor. We wanted to obtain the effective potential of this term through the iterative method, but the results proved it ineffectually. This work will be continued. At last, we analyzed the static character and dynamic character from atomistic simulation and coarse-grained simulation, the results also testified the coarse-grained modeling is effective.

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