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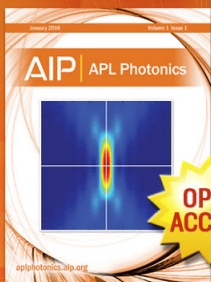
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Fast convergence to equilibrium for long-chain polymer melts using a MD/continuum hybrid method

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Effective and fast convergence toward an equilibrium state for long-chain polymer melts is realized by a hybrid method coupling molecular dynamics and the elastic continuum. The required simulation time to achieve the equilibrium state is reduced compared with conventional equilibration methods. The polymers move on a wide range phase space due to large-scale fluctuation generated by the elastic continuum. A variety of chain structures is generated in the polymer melt which results in the fast convergence to the equilibrium state. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4759036>]

I. INTRODUCTION

Atomistic simulations for polymers have been studied intensively. Especially molecular dynamics (MD) calculations for polymers in order to reveal the dynamical behavior of the chain structure have been carried out. MD calculations for long-chain polymers, however, have been limited by the massive computational costs due to the very long relaxation times of entangled long-chain polymer melts. According to reptation theory, the relaxation time of an entangled polymer melt consisting of chains with N monomers scales as N^3 . This means that a prohibitively long simulation time is needed to relax a dense polymer melt. Moreover, a complex system such as an entangled polymer melt exhibits a huge number of local-minimum energy states in the free energy surface. Energetic barriers much larger than the thermal energies separate the initial configurations from the final equilibrium states, which leads to relaxation times far greater than currently accessible computational resources allow.

The coarse-grained (CG) approach for polymer molecules, in which multiple atoms are combined into a large bead, enable us to extend the spatial and time scales of the simulation. In particular, the time scales up to several orders of magnitude from the atomistic level.¹ The length of the chain polymer is, however, limited to the order of 10^4 monomers even with the CG approach.²

A variety of method has been proposed for obtaining well-equilibrated CG polymer. Auhl *et al.* used the initial configuration reducing the density fluctuation and a double-bridging algorithm⁴ for a MD calculation.³ They demonstrated the effectiveness of their method in long-chain polymer simulations. Gao proposed a method of polymer chain generation by connecting the polymer to monomers, combining with the relaxation of polymer conformations by MD step.⁵ Perez *et al.* confirmed that the relaxation is performed while the chains are generated and showed an applicability of this method to complex polymers such as nanostruc-

tured polymer.⁶ Subramanian generated the well-equilibrated polymer by affinely scaling the simulation box and adding the beads along the contour of the chain, and applied it to the cyclic polymers.⁷ Methods for overcoming the local energy minimum on the energy surface have been intensively studied.^{8–12} The multicanonical MD method¹³ enables sampling over a much larger phase space, and was applied to a CG model of protein folding.¹⁴

In the present paper, MD simulations for long-chain polymer melts are performed by a hybrid MD/continuum method, in which the dynamics of the atoms is coupled with those of the continuum degrees of freedom concurrently. This hybrid method was originally proposed by our group, and it has been applied to a simple one-dimensional system,^{15,16} in which the spring force of the continuum acts on the atomic chain system and generates large-scale fluctuations and a variety of atomic phonon modes in the atomic chain. In the present paper, the hybrid method is applied to a polymer melt consisting of long-chain polymers. We demonstrate that the large-scale fluctuation induces a large number of states of the long-chain polymers and leads to the fast convergence toward the final equilibrium state. Our purpose is to show the result of accelerating MD calculations using the MD/continuum hybrid method and the effectiveness of this method for long-chain polymer simulations.

II. METHOD

We describe a single polymer as a bead-spring chain in which monomers of the polymer are represented by spherical beads. The beads have an excluded volume described by the repulsive force of the 12-6 Lennard Jones potential

$$U_{LJ}(r) = \begin{cases} 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4}\right\} & r \leq r_c \\ 0 & r > r_c \end{cases}, \quad (1)$$

where the cutoff radius r_c is set as $2^{1/6}\sigma$. Each bead is connected with the neighboring beads in the polymer chain via a finite extensible nonlinear elastic (FENE) potential as

$$U_{\text{FENE}}(r) = \begin{cases} -0.5kR_0^2 \ln(1 - (r/R_0)^2) & r \leq R_0 \\ \infty & r > R_0 \end{cases}, \quad (2)$$

where $k = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$. The calculation is performed using the software package ESPResSo.¹⁷

The above CG polymer model is connected with the elastic continuum. Details of the MD/continuum hybrid method are explained in Ref. 15, and here the procedure of the hybrid method is only briefly explained. The elastic continuum surrounds the MD cell including the CG polymer model and the elastic stress acts on the MD cell. In the case of a constant-pressure MD method,¹⁸ the constant pressure acts on the MD cell. The constant pressure is replaced by the elastic stress of the continuum in the hybrid method as shown in Fig. 1. Since the present system is considered to be isotropic, the cubic MD cell is under isotropic stress of the elastic continuum, which is described by the springs as shown in Fig. 1. According to the procedure of the MD/continuum hybrid method,¹⁵ we can describe the Lagrangian functional L of the present hybrid model consisting of N particles in the MD cell with the volume V and the N_s springs as

$$\begin{aligned} L(\{s_i, \dot{s}_i\}, V, \dot{V}, \{u_\mu, \dot{u}_\mu\}) \\ = \sum_{i=1}^N \frac{mV^{2/3} \dot{s}_i \cdot \dot{s}_i}{2} - \phi(\{s_i\}, V) \end{aligned}$$

In the equation of motion (5) for the volume V , the first two terms on the right correspond to the internal pressure of the CG polymer system, and the last term is the elastic force caused by the adjacent spring ($\mu = 1$). This equation plays a role for connecting the CG polymer system of the MD cell to the springs. The simultaneous equation of the degrees of $\{s_i\}$, V and $\{u_\mu\}$ is integrated numerically and we obtain the time convolution of the coordinations of the polymer, the volume of the MD cell, and the displacement of the springs.

In this hybrid model, the springs are used as an elastic bulk polymer. Five springs are used in the present model, where each spring has the same elastic property as that of the CG polymers in the MD cell. We derive the bulk modulus of the polymer melt by using the constant-pressure MD method and use this value as the spring constant K . Since each spring is equivalent to the bulk polymer, the spring's mass M should be the total mass of all the polymers in the MD cell. The value of M is, however, set to a considerably lighter value than the total mass (about one tenth of the total mass) in the present

$$\begin{aligned} + \frac{Q\dot{V}^2}{2} - \frac{K}{2}(V - V_0 - u_1)^2 + \frac{Mu_1^2}{2} \\ + \sum_{\mu=2}^{N_s} \frac{Mu_\mu^2}{2} - \frac{K(u_{\mu-1} - u_\mu)^2}{2}, \quad (3) \end{aligned}$$

where s_i are the scaled coordinates of the particles, such that the Cartesian positions \mathbf{r}_i are $\mathbf{r}_i = V^{1/3}\mathbf{s}_i$. u_μ are displacements of the springs in volume units. m and M are the masses of the particles and the springs, and Q is the inertial mass for the motion of the volume V , which is also presented in the standard constant-pressure MD method.¹⁸ ϕ is the potential energy between the particles of the CG polymer model. The fourth term $\frac{K}{2}(V - V_0 - u_1)^2$ corresponds to the elastic potential energy of the first spring ($\mu = 1$) as is illustrated in Fig. 1(c). This energy depends on the volume V and the displacement of this spring u_1 , in which K is the spring constant. V_0 corresponds to the volume under no displacement applied on springs. The initial displacements and their velocities of the springs u_μ, \dot{u}_μ are set so as to apply the pressure on the CG model. The displacement of terminal spring u_{N_s} is fixed. The equations of the motion for the particles, volume, and the springs are derived easily from the above Lagrangian

$$m \frac{d\dot{s}_i}{dt} = -V^{-2/3} \frac{\partial \phi}{\partial s_i} - \frac{2}{3} \frac{\dot{V}}{V} m \dot{s}_i, \quad (4)$$

$$Q \frac{d\dot{V}}{dt} = \frac{1}{3V} \sum_{i=1}^N \left(mV^{2/3} \dot{s}_i^2 - s_i \cdot \frac{\partial \phi}{\partial s_i} \right) - K(V - V_0 - u_1), \quad (5)$$

$$M \frac{d\dot{u}_\mu}{dt} = \begin{cases} K(V - V_0 - u_\mu) - K(u_\mu - u_{\mu+1}), & (\mu = 1) \\ K(u_{\mu-1} - u_\mu) - K(u_\mu - u_{\mu+1}), & (\mu = 2, 3, \dots, N_s - 1). \end{cases} \quad (6)$$

calculations. As will be mentioned in Sec. IV, the choice of parameters such as mass and an initial velocity of the spring is important to improve the convergence toward the equilibrium. We choose a suitable value of M by doing several attempts to get the best convergence.

We perform two different MD calculations starting from a stretched polymer and from Gaussian chain with close to correct end-to-end distance of polymer. For the case of initially stretched polymer, 10 CG polymer consisting of 400 beads are placed in the MD cell. In this case, we adopt a bending potential for the CG polymer defined by

$$U_{\text{bend}}(\theta) = k_\theta(1 - \cos \theta), \quad (7)$$

where θ is the angle between the neighboring bonds within the polymer chain. We adopt small bending potential of $k_\theta = 0.25\epsilon$. The stretched chain structure has low potential energy (for a fully stretched chain, $U_{\text{bend}}(0) = 0$) and we use it as an initial configuration. It will be demonstrated that such a stretched polymer with small bending potential relaxes dur-

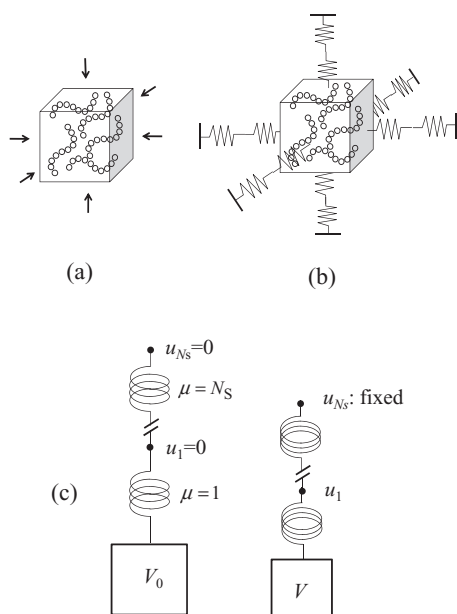


FIG. 1. Schematic views of (a) a standard constant-pressure MD model and (b) and (c) the hybrid model. (a) The polymer system consists of monomers (open circle) in a cubic MD cell under an external constant pressure. (b) The springs enclose the cubic MD cell and isotropic forces by the springs act on the polymer system. (c) Schematic image of the hybrid model. On left-hand side, no displacement is applied on springs, while on the right-hand, MD cell is compressed by the springs. The displacement of the terminal spring (u_{N_s}) is fixed.

ing finite temperature MD. Using this bending potential and the average bond length $\langle b \rangle = 0.97 \sigma$, the square root of end-to-end distance of equilibrated polymer is derived to be 26.9σ . For the case of initially Gaussian chains, 50 CG polymer consisting of 500 beads are placed in the MD cell. In this case, no bending potential in CG polymer is applied. The number density of the CG polymer liquid is set to $0.85 \sigma^{-3}$ and the temperature is set to $1.0 \epsilon/k_B$ for both cases. The time unit of the calculation is $\tau = \sigma(m/\epsilon)^{1/2}$. The integration of the equation of the motion is performed using a time step 0.006τ .

To show the effectiveness of the hybrid method, we investigate the required simulation time to achieve the equilibrium state. Conventional Andersen constant-pressure MD is performed using the same initial configuration for the both cases in order to compare it to the result of the hybrid method.

III. RESULTS

The single-chain structure is characterized by the end-to-end distance R . The time convolutions of the calculated R in the present MD calculations are monitored in Fig. 2 for the case of the initially stretched chains, where the result obtained by the conventional method is compared with that from the hybrid method. In the conventional MD method, considerably longer simulation time ($t \sim 1.0 \times 10^6 \tau$) is needed to obtain a stable value of R , which is in good agreement with the analytical value $R = 26.9\sigma$. The long-chain polymer such as the present model has very slow diffusion time and requires a long simulation time to reach the relaxation using a conventional MD method. In contrast, the R of the hybrid method is fluctuating widely and rapidly converges toward the equilib-

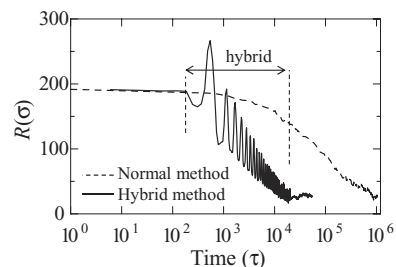


FIG. 2. Time convolutions of the end-to-end distance R of polymer melts obtained by the conventional method (broken line) and hybrid method (solid line) for the case of initially stretched polymers. The calculation with the hybrid method stops at $t = 2.0 \times 10^4 \tau$, and the constant-pressure MD calculation is continued after that.

rium value. After a simulation with the hybrid method until $t = 2.0 \times 10^4 \tau$, the calculation is continued with the conventional MD method. The required time to reach stable value of R using the hybrid method is $t \sim 10^4 \tau$, which is about one hundredth of the time required using the conventional method.

Snapshots of a single polymer obtained by the conventional method and by the hybrid method are shown in Fig. 3. We start the MD calculations using the same initial configuration of a long stretched polymer as shown in Fig. 3 ($t = 0$). At $t = 4.5 \times 10^4 \tau$, the polymer configuration of the conventional method still has a stretched chain structure, while that of the hybrid method has a entangled structure. In general, a flexible polymer such as the present polymer model has an entangled structure in the equilibrium state. This entangled structure can be obtained at $t = 4.5 \times 10^4 \tau$ by the hybrid method, while we manage to obtain it only at $t \sim 10^6 \tau$ by the conventional method.

For the case of initially stretched polymers, we derive the mean square internal distance $\langle R(n)^2 \rangle$, averaged over all internal distances $n = |i - j|$ along all the polymer chains, where $i < j \in [1, M]$ are the monomer indices. It is shown in Fig. 4

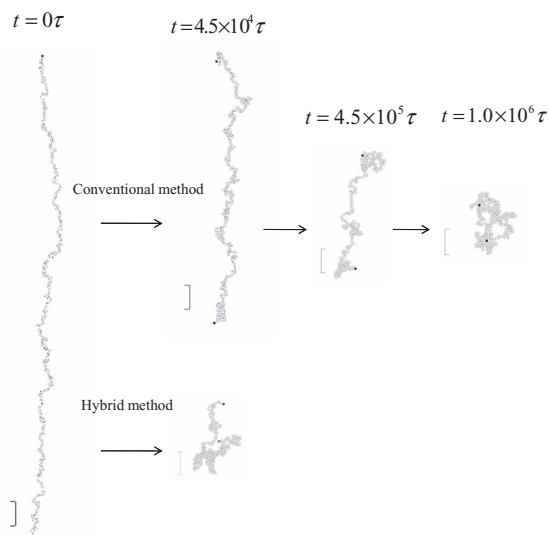


FIG. 3. Time convolution of a single polymer configuration obtained by the conventional method and hybrid method for the case of initially stretched polymers. This is one polymer chosen from ten polymers in the simulation system. Guides in figure indicate the length of 10σ .

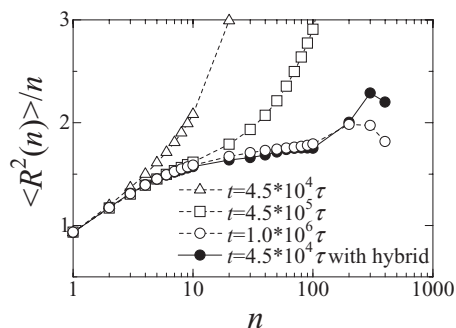


FIG. 4. Mean square internal distances obtained by the conventional method (broken lines) and hybrid method (solid line) for the case of initially stretched polymers. For the conventional method, results at three different times ($t = 4.5 \times 10^4 \tau$, $4.5 \times 10^5 \tau$, and $1.0 \times 10^6 \tau$) are shown.

that the curve of $\langle R(n)^2 \rangle / n$ obtained by the hybrid method at $t = 4.5 \times 10^4 \tau$ already reaches to that at final stage $t = 1.0 \times 10^6 \tau$ by the conventional method. The curve obtained by the conventional method at $t = 4.5 \times 10^4 \tau$ reflects from the initial stretched structure, and even at $t = 4.5 \times 10^5 \tau$, it remains in the polymer chain structure. This initial structure still remains even after long-time MD run and it leads to small deformations of polymer for long distance ($n > 200$) at final stages of the conventional method and hybrid method (open circles and solid circles in Fig. 4). It is, however, clearly shown from the time convolution of polymer configuration and $\langle R(n)^2 \rangle$ that the polymer melts go to the equilibrium and that convergence toward the equilibrium is accelerated by our hybrid method.

In order to compare our method with the method developed by Auhl *et al.*, we also studied a system in which the starting state consists of Gaussian chains with close to the correct end-to-end distance as determined from short chain simulations. Here, we studied the same model as Auhl *et al.* performed, 50 fully flexible chains of length $N = 500$. Initial configuration for the CG polymers with correct end-to-end distance is generated according to so-called “fast push-off” method.³ As is seen in Fig. 5, initial polymer has deformation at intermediate and long distance ($n = 10$ –500), and it remains at $t = 2.4 \times 10^5 \tau$ performed by a conventional MD calculation. Auhl *et al.* mentioned that order of $10^6 \tau$ time are

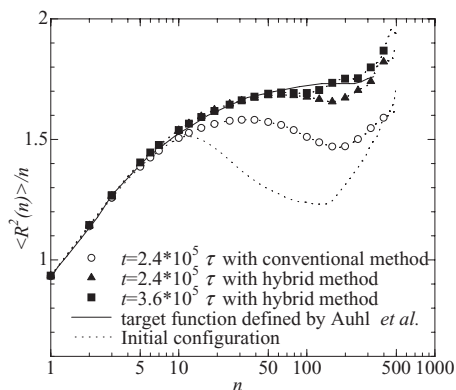


FIG. 5. Mean square internal distances obtained using correct end-to-end distance of polymer as an initial configuration.

required to obtain equilibrium states for such long polymers by normal MD method.

Using the above initial configuration with correct end-to-end distance, we perform the hybrid calculation. We use the hybrid method till $t = 1.0 \times 10^5 \tau$ and the calculation is continued with a standard constant-pressure MD method. It is seen from Fig. 5 that at $t = 2.4 \times 10^5 \tau$, the initial deformation becomes relax rapidly, and after additional $1.2 \times 10^5 \tau$ MD run, $\langle R(n)^2 \rangle / n$ fits nicely with the “target function” defined by Auhl *et al.* as the signature of well-equilibrated polymer melts. We can obtain a fully equilibrium state for a long-chain polymer with MD run for order of $10^5 \tau$ time. It is again shown from this result that the convergence toward the equilibrium is improved by the hybrid calculation. Auhl reported that the order of $10^5 \tau$ was taken to obtain the equilibrium states for the same length polymers using the double-bridging method. Effectiveness for the convergence by our hybrid method is comparable to that calculated by the double-bridging method.

IV. DISCUSSION

The fluctuation of the end-to-end distance R of the hybrid method means that the chain structure of the polymer is fluctuating widely during the simulation. The time convolution of the internal pressure of the CG polymer system and the volume of the MD cell is shown in Fig. 6. It can be seen in Fig. 6 that the internal pressure and the system volume are widely fluctuating. It can also be seen that the time convolution of the volume is out of phase with the internal pressure. These large-scale fluctuations arise in the polymer system; low pressure induces a large expansion of the volume, and a large pressure compresses the system. Hence, the number density of the system is also widely fluctuating. This situation is different from that in the calculation by constant-pressure MD method, in which the constant pressure applies on the atomic system and the system is fluctuated so as to balance the internal pressure with the external constant pressure. The difference between our hybrid model and the Andersen’s model has been discussed in our previous study.¹⁵

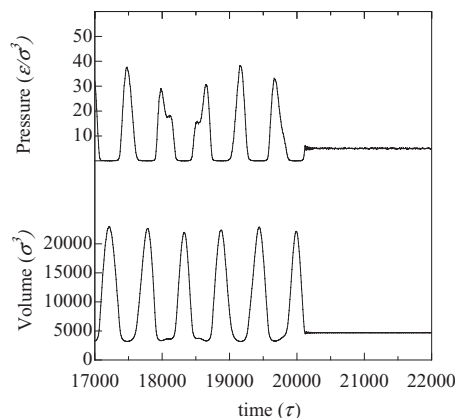


FIG. 6. Time convolution of the internal pressure and the volume of the MD cell for the case of initially stretched polymers. The calculation by the hybrid method stops at $t = 20000\tau$, and the constant-pressure MD calculation is continued after that.

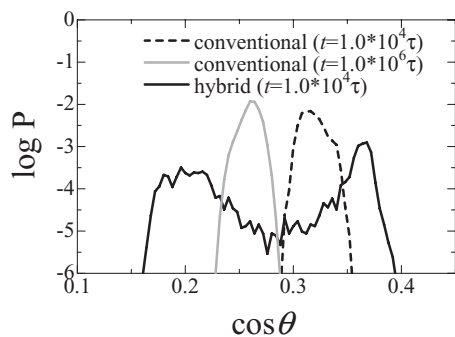


FIG. 7. The probability distribution functions of $\cos \theta$ for the hybrid method together with the conventional method for the case of initially stretched polymers.

Due to the large-scale fluctuations, a large variety of chain structures are generated and the trajectory of the polymer spreads over a wide phase space. For the case of the initially stretched polymers, the CG polymer has a bending potential, which is associated with the chain structure and bond angle θ of polymer as shown in Eq. (7). The averaged $\cos \theta$ among all polymers is derived from the bending potential and its probability distribution is obtained by sampling from the MD ensemble over a time period of 1000τ . The probability distribution function (PDF) of $\cos \theta$ is shown in Fig. 7. In the conventional method, the PDF of bond angle for polymers is limited in narrow range, which means that few variety of chain structure of polymer is generated. In contrast, a much wider range of PDF is covered by the hybrid method. The wide range of the bond angle indicates a generation of a large variety of chain structures and its trajectory is over a much wider phase space than that of the conventional method. This situation also occurs for the case of initially Gaussian chains with no bending potential.

The fluctuations in the polymer system are generated by the vibrations of the springs. The motion of the springs is connected with that of the MD cell as is described by Eq. (5). The large-scale dynamics of the elastic continuum leads to the fluctuation of the CG polymer system, large variety of chain structure and results in the fast convergence to the equilibrium. If only small stress of the elastic continuum acts on the CG polymer system, the convergence is not improved. We reduce initial velocities of springs in the hybrid calculation. It is confirmed in Fig. 8 that a small vibration of the springs induces small fluctuations in the polymer system, and the convergence is not improved compared to the conventional method in this case.

The convergence depends not only on the amplitude of the fluctuations as just mentioned, but also on the time scale of the fluctuations. The heavy weight of the springs introduces slow dynamics of the springs and redundant fluctuation in the polymers, and it does not lead to effective convergence toward the equilibrium state. Light weight springs induce quick fluctuation in the polymers, which avoids structural relaxation of the polymers. In the present calculations, we set the mass of springs so as to get best convergence as mentioned in Sec. II. The effectiveness of the convergence is closely associated with the time scale of fluctuation as well as its amplitude.

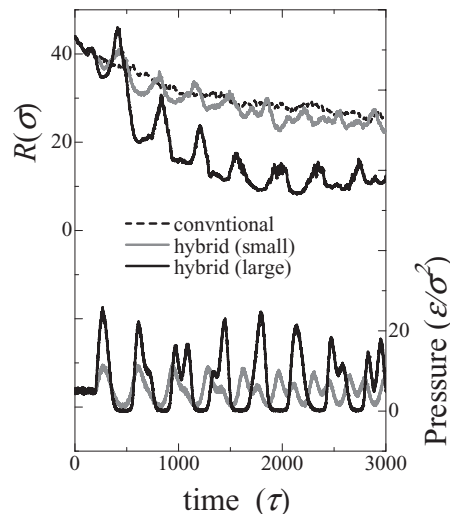


FIG. 8. Time convolution of the end-to-end distance R and the internal pressure. The results are obtained with a smaller system than in the present calculations, where a single polymer consists of 100 coarse-grain monomers and stretched polymers are used as a initial configuration. The gray line indicates the result obtained in the case of a small fluctuation by the hybrid method, while the solid line indicates the result in the case of large-scale fluctuations.

The relation between fluctuation and convergence is of interest and an interesting topic for further research.

We use two different initial states for the polymer systems, the stretched polymers and the Gaussian chains with correct end-to-end distance. The end-to-end distance for the case of initially stretched polymer clearly shows fast convergence, however, this initial structure remains even after long-time MD calculations using the hybrid method. Though many varieties of chain structure are generated under the large-scale fluctuations, the initially stretched structures survives for a long time and considerably affects the convergence toward the fully equilibrated state.

The initially Gaussian chain has the end-to-end distance of an equilibrated polymer. For this case, the initial deformations in polymers relax rapidly with the hybrid method and a fully equilibrated state was achieved at the end of the simulations. The fully equilibrated state can be obtained effectively using both a proper initial configuration and the hybrid method, in which the effectiveness of the convergence is comparable to the double-bridging method³ as mentioned in Sec. III. In the double-bridging method, a variety of chain structures are generated by using artificial treatments such as cutting chain polymer and switching partial chains. In the hybrid method, polymer chains are not cut nor is there any partial chain exchange, but large-scale fluctuations are introduced via the coupled spring system, which generate a variety of chain structure, as just mentioned.

V. CONCLUSION

We couple a CG polymer model and an elastic continuum using the hybrid method. The polymer melt consisting of the CG polymers is simulated and it is shown that fast convergence toward the equilibrium state of the polymer melt is achieved. The elastic continuum of the hybrid model acts

on the polymer system and produces large-scale fluctuations. The fluctuations allow the polymer system to sample over a much wider phase space than the conventional method, inducing a variety of polymer states, and leads to fast convergence toward the equilibrium. For both the studied initial configurations, stretched chains and Gaussian chains with the correct end-to-end distance, the hybrid method enables significantly quicker equilibration compared to classical MD. For the second case starting with chains of the correct end-to-end distance, the performance of the hybrid method is comparable to the double-bridging method of Auhl *et al.*³

In our previous studies,^{15,16} a one-dimensional model was calculated by the hybrid method and the large-scale fluctuation causes the generation of a variety of phonons in the particle system. The phonons obtained by the hybrid model reproduced those by large-scale all-atom calculations. It was shown that the hybrid model enables us to extend the *spatial scale* to much larger values. In the present study, the hybrid method is applied to the long-chain polymer that has very slow diffusion dynamics. The required simulation time to reach the equilibrium state of the polymer melt is reduced. The present hybrid model thus enables us to reach a much wider *time scale* than that by the conventional MD method.

Although the present model is simple, the hybrid method can be applied to more realistic and complex systems such as polycarbonate¹⁹ and protein molecules. The equilibrium structure and various properties at finite temperatures can be obtained with reasonable computational cost.

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