COMMUNICATIONS

Exploration of conformational phase space in polymer melts: A comparison of parallel tempering and conventional molecular dynamics simulations

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Parallel tempering molecular dynamics simulations have been performed for 1,4-polybutadiene polymer melts in the 323 K–473 K temperature domain at atmospheric pressure. The parallel tempering approach provides a vast improvement in the equilibration and sampling of conformational phase space for the atomistic melt chains in comparison with conventional molecular dynamics simulations even for molecular weights and temperatures considered to be routinely accessible via the latter technique. © *2001 American Institute of Physics.*
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I. INTRODUCTION

Sampling of chain conformations in polymer melts and solutions using molecular dynamics (MD) and Monte Carlo (MC) simulations is a challenging problem. Well away from the glass transition temperature, local conformational properties in these systems typically relax on times scales that allow for accurate sampling from relatively short simulation trajectories. However, with increasing molecular weight, sampling of chain conformations quickly becomes intractable for conventional simulation techniques, even in systems without entanglements. Hence, despite tremendous improvements in computational hardware that allow routine performance of multi-nanosecond simulations of polymeric systems,[1–6] the mean-square radius of gyration $\overline{R_g^2}$ and end-to-end distance $\overline{R_e^2}$ obtained from these simulations often have quite large error bars. Since many properties of polymer melts and solutions depend upon chain conformations, the predictive capabilities of simulations for these systems can be severely impacted by this limitation. The situation becomes even worse for systems with rough energy landscapes (e.g., melts near the glass transition temperature, heterogeneous systems) where systems can easily become locked in one region of phase space during the entire length of a simulation.

In recent years, simulation techniques that involve expanded ensembles have been developed to provide an effective way to overcome problems associated with sampling of properties in systems with intrinsically slow relaxations and highly heterogeneous phase space. Parallel tempering (PT) is one of these techniques.[7,8] Yamamoto and Kob[9] found that PT simulations provide orders-of-magnitude faster sampling of phase space in comparison with conventional MD simulations in applications to a super-cooled Lennard-Jones liquid. Yan and de Pablo[10,11] have shown that the PT approach combined with open-ensemble simulations (''hyper-parallel''

tempering) allows prediction of phase equilibrium in a coarse-grained polymer blend much faster and for a wider range of thermodynamic conditions than conventional open-ensemble simulations. The question we wish to address in this work is the applicability of the extremely promising PT method to realistic models of polymer melts well-removed from the glass transition temperature. For unentangled polymer melts, it has been widely assumed that conventional MD simulations can provide efficient equilibration and sufficient sampling of phase space in this temperature regime. We concentrate specifically on chain conformations of the polymer using an atomistically detailed model, comparing PT results with those obtained from conventional MD simulations.

II. MOLECULAR DYNAMICS SIMULATION METHODOLOGY

We conducted MD simulations of a 1,4-polybudadiene melt consisting of 40 chains of 30 repeat units (10% vinyl, 40% cis, 50% trans)[12] using a well-validated[13,14] quantum-chemistry based atomistic potential described elsewhere.[12,13] Simulations were carried out over the temperature domain $323 \leqslant T \leqslant 473$ K in 5 K increments. The glass transition temperature of PBD is estimated to be around 180 K,[14] hence, the lowest melt temperature corresponds to $T \approx 1.8 T_g$. Simulations performed using the *NPT* and *NVT* MD simulation methodologies described in detail in our previous work.[14] The 31 PBD melt systems were initially equilibrated in the *NPT* ensemble for 4–10 ns to obtain equilibrium density at atmospheric pressure. In this work, we focus our attention on the analysis of chain conformations at 323 and 353 K, for which extensive conventional MD simulations have been previously performed. For these systems *NPT* simulations were followed by *NVT* equilibration simulations

of approximately a Rouse time (30 and 15 ns, respectively for 323 and 353 K) followed by *NVT* simulations of 90 and 45 ns, respectively.[12,14]

III. PARALLEL TEMPERING METHODOLOGY

A comprehensive derivation of the statistical mechanical foundation of the PT method can be found elsewhere.[10,11] Unlike previous applications of PT simulations to Lennard-Jones liquids[9,10] and polymer mixtures,[11] where temperature tempering was performed isochorically, we performed PT simulations isobarically. For atomistically detailed systems such as PBD, where comparison with experimental data or prediction of properties is potentially of great interest, the isobaric data generated for all 31 systems can be useful. Constant pressure conditions for each replica can be maintained by either performing the simulations of each replica in the *NPT* ensemble or by employing *NVT* conditions with each replica being simulated at the predetermined density that yields the desired pressure. We chose the latter approach using densities obtained from the conventional *NPT* simulations described previously. It is important to note that in this case the energy change associated with the volume change that occurs during a replica swapping attempt *must* be taken into account in determination of the acceptance criteria. The acceptance probability (p_{acc}) for exchanging coordinates x_i and x_j that, prior to the attempt, were simulated at temperatures T_i and T_j in simulation boxes of volumes V_i and V_j, respectively, is given by Eq. (1):

$$P_{acc}(x_i \leftrightarrow x_j) = \min\left[1, \exp\left\{\begin{array}{l} \beta_i(U(x_i)^{V_i} - U(x_j)^{V_i}) - \\ \beta_j(U(x_i)^{V_j} - U(x_j)^{V_j}) \end{array}\right\}\right],$$

(1)

where $U(x)^V$ is the potential energy corresponding to the set of coordinates x in a volume V, and β is the corresponding Boltzmann factor $\beta = 1/kT$. The additional energy calculations before each swapping attempt increase the computational costs of such isobaric simulations relative to isochoric PT, but because replica swapping is attempted only occasionally, this effect is minor. More important is the decrease in exchange probability that results from the energy difference due to volume changes. Fortunately, this effect is offset by a greater increase in dynamics with increasing temperature along the isobaric path compared to the isochoric path.

The 31 PBD systems evenly distributed over the temperature domain 323 K$\leq T \leq$473 K provided a 5 K difference between neighboring thermodynamic states. After determination of density for each system from conventional *NPT* simulations, 2 ns PT *NVT* equilibration was carried out. The PT simulations were performed on a parallel architecture, where each system was assigned to a single node, communication between which was organized using standard MPI libraries. During the PT simulation, exchange of coordinates was attempted only between systems at T_i and T_{i+1} alternatively for $i=1,3,5...$or $i=2,4,6...$ every $\Delta t_{ex} = 0.4$ ps. The coordinates of systems i and $i+1$ were temporarily scaled by V_{i+1}/V_i and V_i/V_{i+1}, respectively, and the energies of the systems were determined. If the exchange attempt was accepted, the coordinates of systems i and $i+1$ were perma-
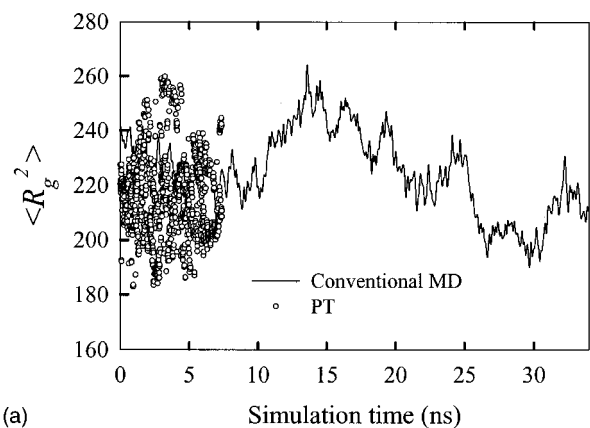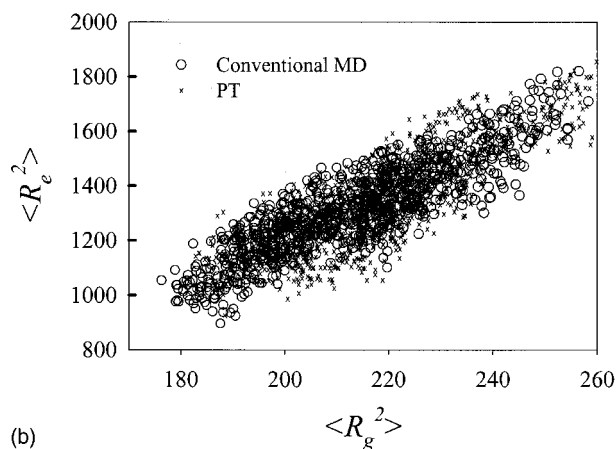
FIG. 1. Comparison of conformational space sampling obtained from PT and conventional MD simulations at 353 K. (a) Evolution of the $\langle R_g^2 \rangle$ as a function of simulation time; (b) $\langle R_e^2 \rangle$ vs $\langle R_g^2 \rangle$.

nently scaled by V_{i+1}/V_i and V_i/V_{i+1}, respectively, and instantaneous velocities of atoms in systems i and $i+1$ were scaled by $(T_{i+1}/T_i)^{1/2}$ and $(T_i/T_{i+1})^{1/2}$, respectively. The overall acceptance probability for attempted exchanges was approximately 0.06, with values ranging from 0.08 at 473 K to 0.04 at 323 K. A PT simulation with appropriate *NVT* conditions for each replica was performed over 9.0 ns. It was confirmed that during the PT simulation each system visited each temperature many times. A comparison of the density of states (potential energy distribution) at 353 K from parallel tempering with that obtained from the 45 ns *NVT* conventional MD simulation confirmed that phase space was correctly sampled in the PT simulation.

IV. RESULTS AND DISCUSSION

In the discussion of PT simulation results, we will concentrate our attention on two temperatures (323 and 353 K) for which results from extensive conventional MD simulations are available for comparison.

T=353 K. We begin our analysis by comparing the evolution of the average square radius of gyration, $\langle R_g^2 \rangle$, obtained as the instantaneous average over all chains in the systems. In Fig. 1, $\langle R_g^2 \rangle$ is shown as a function of simulation time for PT and conventional MD simulations. For conventional MD simulations long-time oscillations in $\langle R_g^2 \rangle$ can be

observed indicating that, in order to obtain an accurate over-all average value of $\langle R_g^2 \rangle$, a simulation much longer than the Rouse time (15 ns) is required. In contrast, PT simulations provide a thorough sampling of $\langle R_g^2 \rangle$ over a much shorter trajectory length. In Fig. 1(b), we compare the exploration of conformational phase space for the two methods by plotting the average square end-to-end distance $\langle R_e^2 \rangle$ versus $\langle R_g^2 \rangle$. This figure illustrates that the methods exhibit a quite similar sampling of conformational phase space.

The resulting overall average value of $\langle R_g^2 \rangle$, $\overline{R_g^2}$, obtained from the PT simulation (216.8±3.6 Å^2) is in good agreement with the value obtained from conventional MD simulations (220.2±8.7 Å^2). The error bars were calculated as the variance in $\overline{R_g^2}$ for individual chains. The uncertainty obtained from the 45 ns conventional MD run is twice that obtained from the 9 ns PT simulation. A conventional MD simulation trajectory of approximately 275 ns would be needed in order to provide the same accuracy as the 9 ns PT simulation for chain conformations. This indicates that even if we are only interested in chain statistics for a single system (353 K), we save nothing by performing conventional MD simulation (275 ns) at that temperature compared to the PT simulation (31 systems × 9 ns=279 ns), which provides data for all 31 systems. Realizing that the relative efficiency of the PT approach will likely be even greater at lower temperatures (slower dynamics), the utility of the PT method in obtaining chain statistics in atomistic polymer melt simulations is clear.

T=323 K. Figure 2 shows plots equivalent to those in Fig. 1 but for the lowest temperature in the PT simulation (323 K). The oscillations of $\langle R_g^2 \rangle$ from conventional MD have a much larger period than at 353 K. It appears that the 90 ns run, more than 3 Rouse times, does not provide accurate sampling of chain conformations. Comparing $\langle R_g^2 \rangle$ obtained from PT simulation with that from conventional MD simulations further strengthens this suspicion. Figure 2(a) clearly illustrates that the much shorter PT simulation explores a much wider range of $\langle R_g^2 \rangle$ than conventional MD simulations. Figure 2(b) further illustrates the discrepancy between sampling of conformational phase space from PT and conventional MD simulations. The value of $\overline{R_g^2}$ obtained from conventional MD simulation is 200.9±6.0 Å^2. This implies that $\overline{R_g^2}$ changes by as much as 10% upon cooling from 353 to 323 K, which is inconsistent with experimental values and predictions of a rotational isomeric state (RIS) model based upon the same quantum chemistry studies used in parametrizing the PBD force field,[13] where a change of less than 1% in this temperature domain is observed. The relatively small error bars of ±6.0 Å^2 estimated for $\overline{R_g^2}$ based on deviation of individual chains properties from the ensemble average are misleading in this case because the ensemble average value itself was not sampled accurately during this run. At this temperature, in conventional MD simulations the system is locked in a particular region of phase space and did not have a chance to explore other regions during the length of the simulation. In contrast, the PT simulation was able to provide sampling over a significantly wider range of $\langle R_g^2 \rangle$ values and the resulting $\overline{R_g^2}$, 216.7±3.8 Å^2, is in much better agreement with RIS predictions.
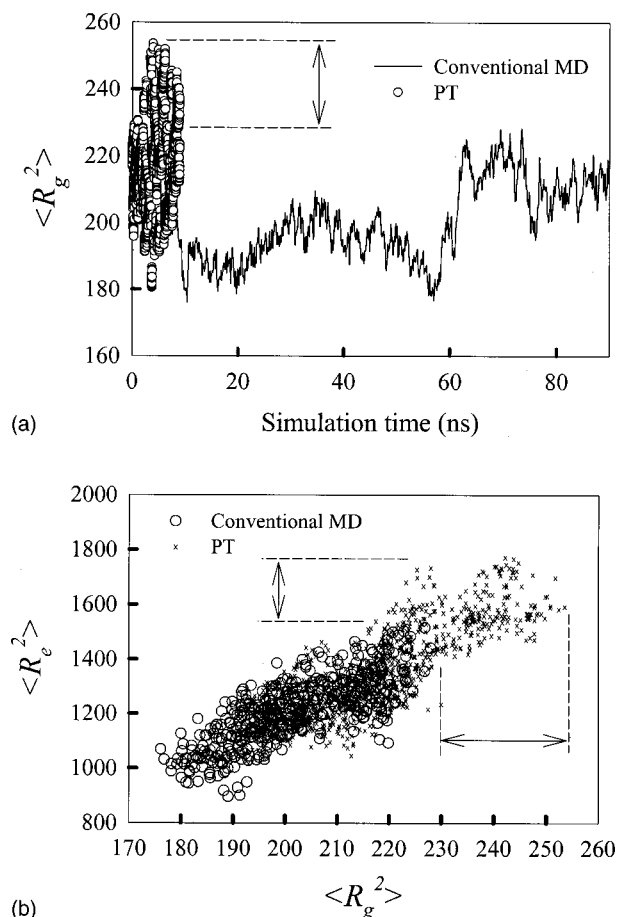

FIG. 2. Comparison of conformational space sampling obtained from PT and conventional MD simulations at 323 K. (a) Evolution of the $\langle R_g^2 \rangle$ as a function of simulation time; (b) $\langle R_e^2 \rangle$ vs $\langle R_g^2 \rangle$. Dashed lines denote the region of $\langle R_g^2 \rangle$ and $\langle R_e^2 \rangle$ that has not been sampled in conventional MD simulations.

System relaxation. There are two effects responsible for the relatively fast sampling of phase space in PT simulations compared to conventional MD simulations: (1) Each replica in PT simulations is able to relax faster as a consequence of spending time at higher temperatures during the simulation; and (2) The statistics at any particular temperature are improved by contributions from N uncorrelated systems. The importance of the former effect is illustrated in Fig. 3
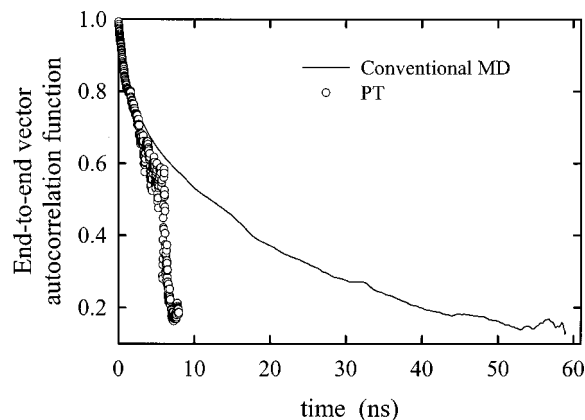

FIG. 3. Chain end-to-end vector auto-correlation functions calculated from PT and MD simulations at 323 K.

which shows the end-to-end vector auto-correlation function for PBD chains at 323 K obtained from conventional MD and PT simulations. For the PT simulation, this function was calculated as follows: When system i visits 323 K (at some time t_0) the clock starts. Upon return of that same system to 323 K, after visiting other temperatures (at some time t_1), the correlation between chain end-to-end vectors in this system is calculated and attributed to statistics for the time interval $\Delta t = t_1 - t_0$. Hence the auto-correlation function shown in Fig. 3 for the PT simulation does not reflect any reversible dynamical process, but simply quantifies how quickly the end-to-end vectors decorrelate. It is clear from the figure that the PT simulation provides significantly faster relaxation of chain end-to-end vectors in comparison with conventional MD simulations. Figure 3 reveals that short PT and long conventional MD simulation runs have resulted in approximately the same relaxation of the polymer chains in the systems. However, while conventional MD simulations only provide statistics for one set of coordinates, the PT simulation has contributions from N independent systems. Therefore, we believe that $\overline{R_g^2}$ prediction at 323 K from the PT simulation is more accurate than the value obtained from the conventional MD simulation because during the PT simulation run, 31 independent systems contributed statistics for this temperature and most of these systems were able to completely decorrelate by the time they visited the 323 K temperature again. It is necessary to note that PT MD simulations do not allow us to examine any underlying dynamics of the system (except for very short time intervals between accepted replica swaps when there is no artificial perturbation introduced in the system) and therefore can be used only for sampling static properties and acceleration of equilibration.

V. CONCLUSIONS

We believe this work constitutes the first application of parallel tempering in molecular dynamics simulations of chain properties of an atomistic polymer melt. We have shown that the PT approach, which has clearly demonstrated advantages for coarse-grained polymer systems, can enhance simulations of atomistically detailed polymeric systems and substantially expand the time and length scales accessible by these simulations. Even for a polymer melt well above the glass transition temperature and below the entanglement molecular weight, a system generally considered to be well-suited for conventional MD simulations, application of the PT simulation method has clear advantages over conventional MD simulations. The PT method provides thorough sampling of conformational space more expediently than conventional MD simulations and significantly faster relaxation of large length-scale correlations, resulting in much faster equilibration in comparison with conventional MD simulations.

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