A Novel Monte Carlo Scheme for the Rapid Equilibration of Atomistic Model Polymer Systems of Precisely Defined Molecular Architecture

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Two novel connectivity-altering atomistic Monte Carlo moves are presented for the fast equilibration of condensed phases of long-chain systems with a variety of chain architectures. With the new moves, isotropic or oriented melts of linear or long-chain branched polymers, dense brushes of terminally grafted macromolecules, and cyclic peptides can be simulated. Results concerning the structural, conformational, and volumetric properties of linear, monodisperse polyethylene melts, simulated with a new united-atom molecular model, are in excellent agreement with experimental data.

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In recent years, computer simulations have developed into a powerful tool for studying the dynamic, structural, and topological features of macromolecular systems. A major challenge in these studies is the large spectrum of length and time scales characterizing molecular structure and motion, particularly when the molecular weight (MW) of the constituent chains exceeds the characteristic value for the formation of entanglements. Heretofore, molecular dynamics simulation studies of macromolecular systems have been limited to relatively short chains (up to C_{120}) [1], and short time spans, rarely exceeding a few decades of nanoseconds. However, a robust sampling of the configuration space of truly polymeric substances is a prerequisite for the reliable prediction of their physical properties and the development of computer-aided materials design strategies.

The Monte Carlo (MC) method offers an excellent alternative to molecular dynamics (MD) for the simulation of dense polymer systems. Through the design of clever moves, configurational sampling can be dramatically enhanced. MC moves such as concerted rotation [2], configurational bias [3,4], and internal configurational bias [5] have thus successfully addressed the problem of equilibrating polymer systems of moderate chain lengths. However, even these moves prove incapable of providing equilibration when applied to polymer melts of molecular length exceeding about C_{100}. A solution to this problem was given by the development and efficient implementation of a chain-connectivity altering MC move, end-bridging (EB) [6,7]. Using EB, atomistic systems consisting of a large number of long chains, up to C_{1000}, have been simulated in full atomistic detail [7]. Similar efforts, employing chain-connectivity altering segmental rearrangements, include the cooperative motion algorithm (CMA) [8] used in lattice-based simulations of complex polymer systems and an off-lattice MC study of the interphase between crystals with freely rotating chains [9].

Despite its remarkable efficiency in equilibrating long-chain polymer melts, EB suffers from three shortcomings: (a) It cannot equilibrate monodisperse polymer melts; a finite degree of polydispersity is necessary for the move to function. While this is not a drawback in modeling industrial polymers, which are typically polydisperse, an ability to equilibrate strictly monodisperse polymers is highly desirable for comparing against theory or experiments on anionically synthesized model systems. (b) It relies on the presence of chain ends. Thus, it does not offer itself for dense phases of chains with nonlinear architectures containing long strands between branch points such as H-shaped polymers, for cyclic molecules, or for model polymer systems of infinite chain length. (c) Its performance drops considerably as the stiffness of chains increases or in the presence of chain orientation.

All of these disadvantages are overcome by the introduction of two new connectivity-altering moves proposed in this Letter. The key innovation of the two new moves is the construction of two bridging trimers among four properly chosen mers along one or two chains in the system. When the four mers are chosen along the backbones of two different chains, the move is termed *double bridging* (DB); when they are chosen along the same chain, it is termed *intramolecular double rebridging* (IDR). The two moves are shown schematically in Figs. 1 and 2.

Figure 1a presents the original conformations of two chains, ich and jch, involved in a DB move. The move is realized by allowing an internal mer i of chain ich attack a mer j of chain jch. Then a trimer (j_a, j_b, j_c) adjacent to mer j is excised from jch and a new bridge, the trimer (j'_a, j'_b, j'_c), is formed between mers i and j. To complete the move, a second trimer bridge needs to be constructed: mer j_2 of jch attacks mer i_2 of ich. The trimer (i_a, i_b, i_c) adjacent to mer i_2 is excised from ich, and atoms i_2 and j_2 are connected through the new trimer bridge (i'_a, i'_b, i'_c). In the new system configuration, after the move has been accepted, the two chains ich and jch have become ich' and jch', possessing completely different conformations from those of ich and jch. Given two mers i and j along the backbones of chains ich and jch, respectively, there

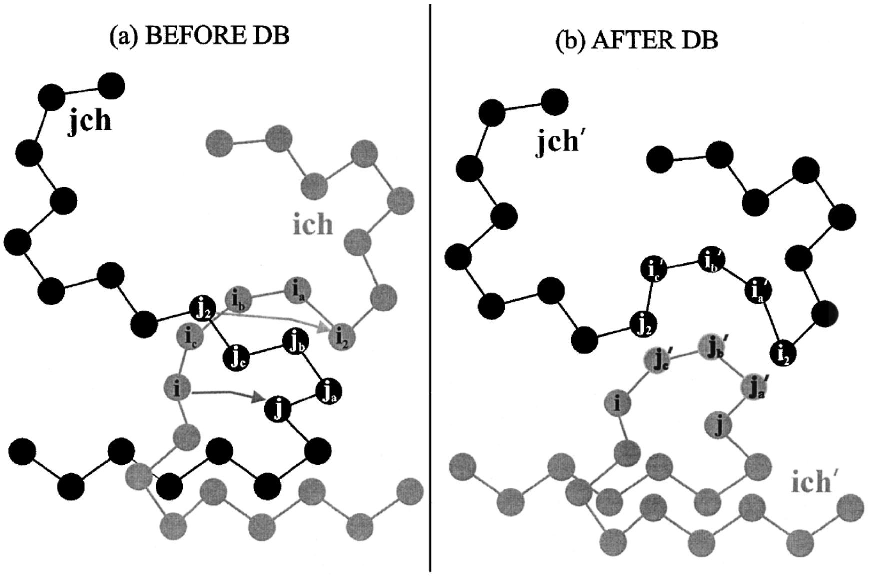

FIG. 1. Schematic of the double bridging (DB) move. (a) Local configuration of the two chains prior to the DB move. Trimer (j_a, j_b, j_c) is to be excised from jch, and trimer (i_a, i_b, i_c) from ich. (b) Local configurations of the two new chains after the DB move. Trimer (j_a', j_b', j_c') connects i and j in ich'. Trimer (i_a', i_b', i_c') connects i_2 and j_2 in jch'.

exist in general four different ways in which DB can be performed, depending on which two of the four trimers adjacent to mers i and j are excised. In a monodisperse system, if i and j are appropriately positioned relative to the ends of ich and jch, one of these four DB moves always preserves monodispersity (see Fig. 1).

The IDR move is shown schematically in Fig. 2. Here, both the primary and secondary bridgings are performed on mers belonging to the same chain. In this case, given the two mers along the backbone of the chain, there exist two possible ways in which IDR can be attempted.

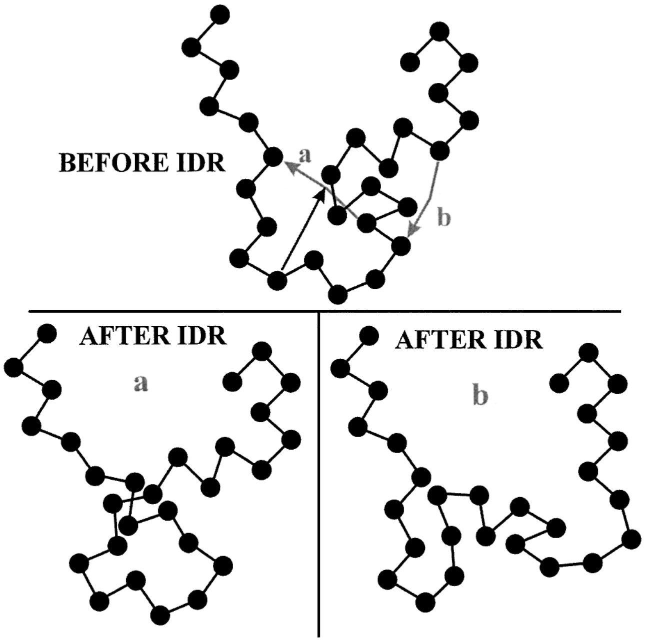

FIG. 2. Schematic of the intramolecular double rebridging (IDR) move. Top: Local configuration of the chain prior to the IDR move. The attack shown as a dark grey arrow is combined with either of the attacks (a, b) represented by light grey arrows. Bottom: Trial configurations of the chain after attacks a and b, respectively.

Geometrically, DB and IDR entail the construction of a trimer, bridging two dimers in space with prescribed bond lengths and angles. This problem has been addressed by the methods developed initially by Pant and Theodorou [6] and Mavrantzas *et al.* [7], and more recently by Wu and Deem [10]. The solutions obtained are weighted based on their total potential energies. The acceptance criterion of the new moves takes into account the probability of selection of the two sites for bridging, the probability of selecting one of the multiple solutions at each site, the Jacobians of transformation from constraint to Cartesian coordinates for the solution pair [6], and the composite energies of the initial and final states [11]. The evaluation of the acceptance criterion requires attempting also the reverse move, subject to the same weighting procedure. This symmetry guarantees microscopic reversibility [11].

The two new moves are particularly attractive for modeling macromolecular systems of complex architectures, most of which cannot be equilibrated with existing MC moves. Grafted polymer melts, star polymers, long-chain branched molecules, particularly those consisting of a main chain backbone from the two ends of which emanate a number of arms, cyclic peptides and ring polymers, rigid and/or oriented chain systems, and model systems of infinite molecular weight, with no ends, are a few examples (see Fig. 3).

Long-chain branched (LCB) polymers, in particular, have attracted considerable attention in recent years. Despite extensive experimental and theoretical studies of these systems, detailed molecular simulations with model LCB systems have not appeared in the literature. The main reason for this is the inability of all MC moves developed so far to rearrange configurations rigorously, while respecting the complex chemical architecture of

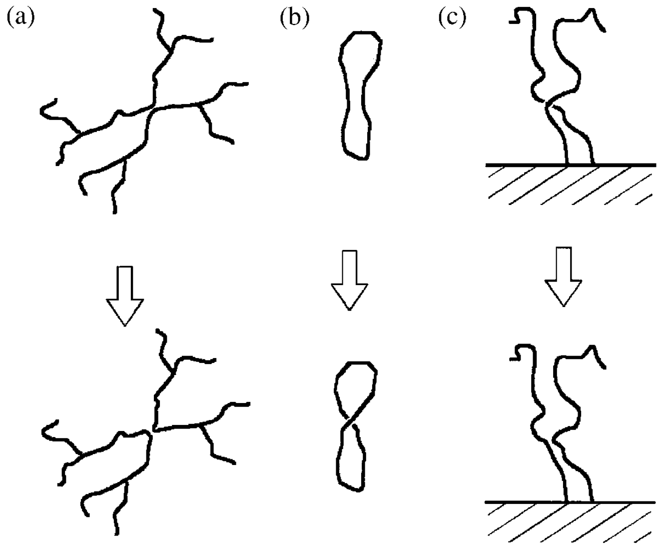

FIG. 3. Application of the DB and/or IDR moves to model polymer systems of complex architecture. (a) H-shaped molecules, (b) cyclic molecules, and (c) monodisperse grafted polymer brush.

these molecules. Here, the two new moves offer an excellent opportunity: both are straightforwardly applicable to LCB molecules if the double trimer bridging is attempted between the main backbones of two such chain molecules.

In the following, results are presented from atomistic MC simulations utilizing the two new moves for two linear, strictly monodisperse, polyethylene (PE) melt systems: a 16-chain C_{500} and an 8-chain C_{1000} PE melt (both containing a total of 8000 interacting sites) at $T = 450$ K and $P = 1$ atm. The simulations have been executed with the *polybead* molecular model, which makes use of the united atom description, according to which methylene (CH_2) and methyl (CH_3) groups are treated as equivalent, spherically symmetric united atoms. These are connected by fixed bonds of length 1.54 Å and interact via a 12-6 Lennard-Jones nonbonded potential with collision diameter $\sigma = 3.95$ Å and well depth $\epsilon = 0.0914$ kcal/mol. The atomistic model used in the simulations is a hybrid of the asymmetric united-atom (AUA) model of Toxvaerd [12] and the TraPPE model of Martin and Siepmann [13]. Three-body interactions are specified by the Van der Ploeg and Berendsen [14] bending potential, while the torsional energy follows the Toxvaerd [12] functional form. A typical mix of the moves utilized in the simulations consists of 19% reptations, 35% concerted rotations, 35% DB, 10% IDR, and 1% volume fluctuation moves, with one accepted DB or IDR move every 50 000 attempted DB or IDR moves. Despite the small acceptance rate of the moves, the conformational changes induced are so drastic that the performance of the algorithm is astonishingly high.

Figure 4 shows the rate at which the autocorrelation function of a unit vector directed along the end-to-end vector of chains, $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$, drops to zero for both the C_{500} and C_{1000} monodisperse PE melts simulated. Figure 4 shows that, for both systems, less than about 3×10^5 s are needed for $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ to decay completely. Remarkably, the decay rate of $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ increases somewhat with chain length: For the longer C_{1000} system, the $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ drops to zero faster than for the shorter C_{500} PE melt. This demonstrates that the efficiency of the new moves remains unaltered with increasing molecular length, in clear contrast to conventional chain-connectivity preserving MC

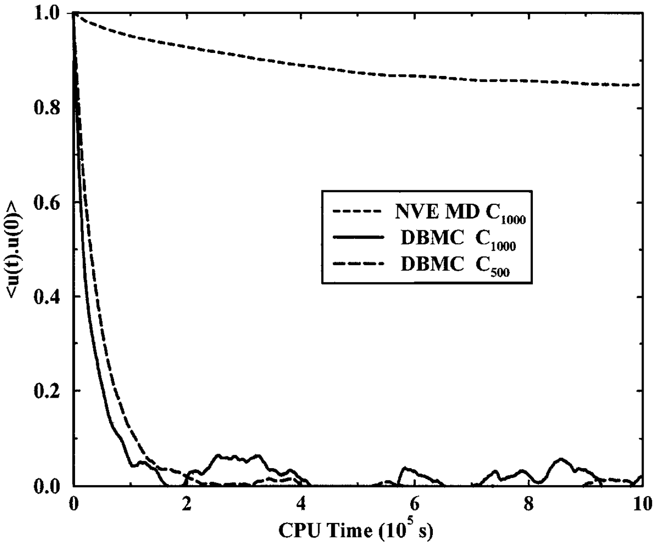

FIG. 4. Decay of the chain end-to-end vector autocorrelation function $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ at $T = 450$ K and $P = 1$ atm, for the monodisperse C_{500} (long-dashed line) and C_{1000} (solid line) linear PE melts, consisting of the same number of interacting sites (= 8000). Also shown is the curve (short-dashed line) obtained for a monodisperse C_{1000} PE melt with the NVE MD method. All CPU times are on a DEC Alpha single-processor system at 667 MHz.

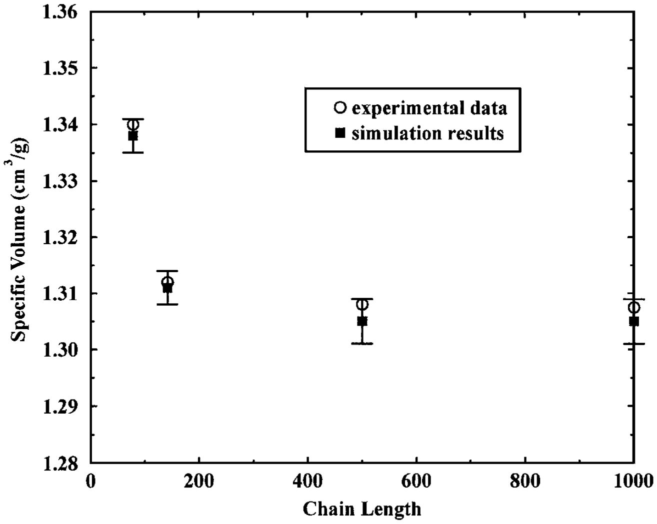

FIG. 5. Dependence of the specific volume on chain length, as predicted by the present method with the newly adopted model and as measured experimentally ($T = 450$ K and $P = 1$ atm).

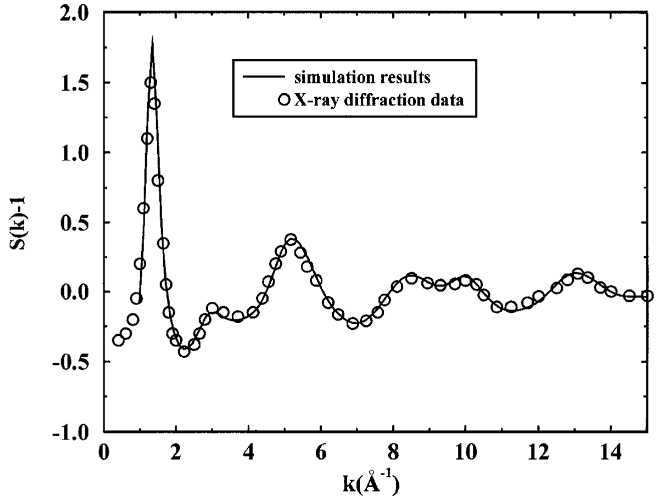

FIG. 6. Simulated and experimental x-ray diffraction patterns of linear polyethylene at $P = 1$ atm. The simulation data are at $T = 450$ K whereas the experimental values at $T = 430$ K.

moves or to MD, whose performance drops dramatically for systems above C_{100} [11]. Also shown in Fig. 4 is the corresponding curve obtained from an MD simulation run in the microcanonical (NVE) ensemble using the same potentials and incorporating a Fixman potential to ensure that the configuration-space probability density sampled is identical to that of the MC. It is observed that MD is almost 2 orders of magnitude less effective.

Figure 5 displays the variation of the specific volume of linear PE melts with molecular length (solid squares), at $T = 450$ K and $P = 1$ atm, and how it compares with experimental data [15] (open circles) at the conditions of the simulation. For all linear PE melt systems studied, with the new united-atom molecular model adopted in the present Letter, the density is predicted within less than 1% of the value measured experimentally [15]. This is a significant improvement over previous models which, in their majority, overestimated the density of linear PE melts by about 4%.

Additional results concerning the mean-square end-to-end distance and the mean radius of gyration of the chains in the well-equilibrated melt [11] demonstrate that the new model provides excellent predictions also for the conformational characteristics of the PE melts. The predicted characteristic ratio in the limit of infinite chain is $C_\infty = 8.0$, which compares very well with the commonly accepted experimental value of 7.8 in the melt state [16].

The ability of the DB and IDR moves and of the new molecular model adopted in this Letter to predict reliably the structure of the PE melts is further investigated by calculating the static structure factor $S(k)$, which is the Fourier transform of the total pair correlation function, and which can be measured experimentally by x-ray diffraction. $S(k)$ was seen to be very similar for all systems studied in the present work. In Fig. 6 only the $S(k)$ curve for the C_{1000} system is reported (solid line). Also plotted in the same figure (open circles) are experimental points from x-ray diffraction measurements at $P = 1$ atm and $T = 430$ K reported by Honnell *et al.* [17]. The agreement between the two curves is excellent, even for the first peak in $S(k)$, which reflects mainly intermolecular correlations.

In summary, the new MC moves presented in this Letter solve the problem of the fast equilibration of atomistic model systems of a precisely defined molecular architecture. They open up the way towards the modeling of LCB polymers for which no efficient sampling method exists so far, of long-chain cyclic molecules, and of infinite-chain length polymers. In addition, the new united-atom molecular model introduced gives accurate predictions of the volumetric and conformational properties of linear long PE melts, thus offering significant improvement over previous models.

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