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First-order transition of a homopolymer chain with Lennard-Jones potential

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The thermodynamics of a homopolymer chain with the Lennard-Jones (LJ) potential was studied by the multicanonical Monte Carlo method. The results confirm there indeed exists a liquid–solid-like first-order transition at lower temperatures for a free-joint chain, revealing that the transition is a characteristic of a homopolymer chain, independent of the algorithms and potential used in simulation. © 2000 American Institute of Physics. [S0021-9606(00)50534-0]

I. INTRODUCTION

In addition to the temperature and solubility dependent of second order coil-to-globule transition,^{1,2} both theoretical and experimental studies suggested more complex behaviors for a homopolymer in solution.³⁻⁹ Recently, Zhou *et al.*^{10,11} used the discontinuous molecular dynamics (DMD) simulation to show that there exists a first-order liquid-solid-like transition for a square-well free-joint homopolymer chain. Noguchi et al.¹² observed the similar behavior for a freely jointed square-well homopolymer chain with a bending potential by multicanonical Monte Carlo simulation. López¹³ found that the application of J-walking Monte Carlo method on a cluster of 55 LJ atoms also yielded a liquid-to-solid-like transition. However, two questions remained, namely, whether the transition is induced by the discontinuous feature of the square-well potential, and how it will change if different MC algorithms are used. We present our recent Monte Carlo simulation on a free-joint Lennard-Jones (LJ) homopolymer chain and address these two questions.

II. MODEL AND SIMULATION

The conformation of a homopolymer chain made up of nsegments is defined by *n* coordinates r_1, r_2, \ldots, r_n of beads in a three-dimensional space. In this study, the off-lattice Monte Carlo model developed by Binder et al.¹⁴ was used, in which each randomly selected bead on the chain was allowed to move around its position with a restriction of the bond fluctuation between 1.001 (l_{max}) and 0.999 (l_{min}) . The interaction potential between two successive bonded segments was treated as $U(l) = k(l-l_0)^2$, where k is a constant, set as a unit, and l_0 is the equilibrium distance between the segments, which is set as 1 Å. The interaction potential between two nonbonded segments i and j is defined as E_{ij} $= \eta [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6],$ where $r_{ij} (= |r_i - r_j|)$ is the intersegments distance, and η and σ are two adjustable parameters controlling, respectively, the energy scale and the interaction length between two segments. The system has a Hamiltonian of

$$H = \sum_{i=1}^{N-1} U(l_i) + \sum_{i=1}^{N-2} \sum_{j=i+2}^{N} E_{ij}.$$

In this study, we simply set $\eta = 1$ and $\sigma = 1$.

In the Metropolis algorithm, the evolution of conformation of a polymer chain is allowed with a probability $\exp(-\Delta E/k_BT)$, where ΔE is positive, reflecting an attractive energy between two segments. At low temperatures, the probability is so small that it is difficult, if not impossible, to sample sufficient configurations for an accurate statistical calculation.¹⁰ To overcome this difficulty, we used the multicanonical Monte Carlo algorithms,^{15,16} in which all energies have an equal weight in the multicanonical ensemble, so the energy is forced into a one-dimentional random walk, so the system can overcome any energy barrier.

In multicanonical algorithms, the $P_B \propto \exp(\alpha(E))$ $+\beta(E)E$) is used, unlike exp $(-\beta E)$ which is used in the Metropolis algorithm, where E is the configuration energy. The values of $\alpha(E)$ and $\beta(E)$ are determined as follows. Perform a canonical Monte Carlo simulation with N energy bins at sufficiently high temperature, e.g., β_0^{-1} $=k_BT_0=1000$, to approximate $P_B(\beta_0, E)$ with a histogram $P_B(\beta_0, E_i)$ $(i=1,2,\ldots,N)$, and determine the histogram made of E_{max} at which the histogram reaches its maximum. The simulation is limited in the energy range $E \leq E_{\text{max}}$, outside of which $\beta(E) = 0$ and $\alpha(E) = 0$. Therefore, $\beta(E_i)E_i$ $-\alpha(E_i) = \ln(P(\beta_0, E_i)) + \text{const} = y_i$. The parameters $\beta(E_i)$ and $\alpha(E_i)$ are obtained from a straight-line connection between two adjacent points (E_i, y_i) and (E_{i+1}, y_{i+1}) . The Metropolis criterion of the transition probability $w(E \rightarrow E')$ is defined as

$$W(E \to E') = 1 \quad \text{if } \Delta \equiv B(E') - B(E) \le 0,$$

$$W(E \to E') = e^{-\Delta} \quad \text{if } \Delta \equiv B(E') - B(E) > 0.$$

where $B(E) = [\beta_0 + \beta(E)]E + \alpha(E)$. In this way, the probability distribution is flatter and the low energy region is explored as the iteration number increases. The iteration stops when the obtained probability distribution is reasonably flat in a chosen energy range. It is expected that near the ground state, such a flat distribution would abruptly go to zero like a step function, a criterion for an optimal choice of $\beta(E)$ and $\alpha(E)$. With a pair of optimal $\beta(E)$ and $\alpha(E)$, we

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FIG. 1. Reduced temperature (K_BT) dependence of heat capacity (C_v) , and potential energy (E), and average squared radius of gyration $(\langle R_g^2 \rangle)$ of a Lennard-Jones homopolymer chain with different lengths.

can make a long production run. On the basis of this run, not only the global-energy minimum, but also the canonical distribution at any temperature as long as $\beta \ge \beta_0$ can be determined by a reweighting technique as follows:

$$P_B(\beta, E) = \frac{e^{B(E) - \beta E} P_{\rm mu}(E)}{\sum_E e^{B(E) - \beta E} P_{\rm mu}(E)},$$

where the $P_{mu}(E)$ is the probability distribution in the multicanonical ensemble.

III. RESULTS AND DISCUSSION

Figure 1(a) shows that the 6mer has a similar thermodynamics behavior as the square-well 6mer obtained by Zhou et al.^{9,10} in a DMD simulation. The two heat-capacity peaks clearly indicated the existence of two equilibrium transitions. The simulation of a longer 30mer chain shows that the lower temperature peak is much sharper [Fig. 1(b)], while the higher temperature peak overlaps with the lower temperature peak and becomes a shoulder. For a 30mer homopolymer chain, the decrease of reduced temperature K_BT from 2.0 to 0.5 led to the drastic decrease of the system energy E from -52.75 to -100.41, and the radius of gyration $\langle R_g^2 \rangle$ from =6.01 to 2.03, indicating the chain collapse. Therefore, the high-temperature peak corresponds to the coil-to-globule transition. Further decrease of the temperature led to a discontinuous energy change at $K_BT = 0.32$, revealing a firstorder transition, but has less of an effect on $\langle R_g \rangle$. The sudden change of energy is more clearly reflected by the lowtemperature heat-capacity peak. Figure 2 confirms the existence of this first-order transition in terms of bimode potential energy distribution f(E) at transition temperature of $K_BT=0.32$. It shows that two stable state coexist at transition temperature. Following Zhou *et al.*,^{9,10} we can attribute the lower energy peak to solid and the higher energy peak to liquid, i.e., a homopolymer chain at the transition temperature is either liquid-like or solid-like, or in other words, the solid and liquid states coexist in a dynamical equilibrium. The unimode distribution of f(E) at $k_BT=0.2$ and 0.4 indicates that when below and above the transition temperature, the polymer chain is in its solid and liquid states.

Figure 3 is the typical snapshot of the 30mer Lennard-Jones homopolymer chain frozen. Similar to the result of



FIG. 2. Potential energy distribution f(E) for 30mer homopolymer chain at different temperature.



FIG. 3. A typical snapshot of the 30mer after being frozen. The potential energy of the polymer chain at this conformation is -118.37.

Zhou *et al.*,¹⁰ the solid three-dimensional structure shows the mixes of the hexagonal and cubic lattice. The only different is there are some irregular parts contained in the solid structure of a Lennard-Jones chain.

Further, this first-order transition of an isolated homopolymer chain at lower temperatures can be attributed to the existence of a molten globule state between two wellknown coil and uniform globule states, which was observed in simulation and real experiments.^{7–9} One of the features of the molten globule state is that its center has a higher density than its periphery. The collapse of a coil into a molten globule results in a significant volume change, while the transition from a molten globule to a uniform globule involves little volume change.

In summary, on the basis of our simulation, we are able to conclude that the transitions between the coil and the molten globule and between molten globule and uniform globule resemble that between gas and liquid and between liquid and solid.

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- ¹P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- ²P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).
- ³I. M. Lifshiz, A. Y. Grosberg, and A. R. Khokhlov, Rev. Mod. Phys. **50**, 683 (1978).
- ⁴R. Finsy, M. Janssens, and A. Bellemans, J. Phys. A 8, L106 (1975).
- ⁵E. I. Tiktopulo, V. N. Uversky, V. B. Lushchik, S. I. Klenin, V. E. Bychkova, and O. B. Ptitsyn, Macromolecules **28**, 7519 (1995).
- ⁶B. Chu, Q. Ying, and A. Y. Grosberg, Macromolecules 28, 180 (1995).
- ⁷C. Wu and S. Zhou, Macromolecules **28**, 8381 (1995).
- ⁸C. Wu and S. Zhou, Phys. Rev. Lett. 77, 3053 (1996).
- ⁹H. Liang, J. Chem. Phys. **110**, 10212 (1999).
- Y. Zhou, C. K. Hill, and M. Karplus, Phys. Rev. Lett. **77**, 2822 (1996).
 Y. Zhou, M. Karplus, J. M. Wichert, and C. K. Hall, J. Chem. Phys. **107**, 10691 (1997).
- ¹²H. Noguchi and K. Yoshikawa, J. Chem. Phys. **109**, 5070 (1998).
- ¹³G. E. López, J. Chem. Phys. **104**, 6650 (1996).
- ¹⁴I. Gerroff, A. Milchev, K. Binder, and W. Paul, J. Chem. Phys. 98, 6526 (1993).
- ¹⁵U. H. E. Hansmann and Y. Okamoto, J. Comput. Chem. 14, 1333 (1993).
- ¹⁶Y. Okamoto and U. H. E. Hansmann, J. Phys. Chem. **99**, 11276 (1995).