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Critical adsorption of a flexible polymer confined between two parallel interacting surfaces

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Critical adsorption of a lattice self-avoiding bond fluctuation polymer chain confined between two parallel impenetrable surfaces is studied using the Monte Carlo method. The dependence of the mean contact number $\langle M \rangle$ on the temperature T and on the chain length N is simulated for a polymer-surface interaction $E = -1$. A critical adsorption of the polymer is found at $T_c = 1.65$ for large surface separation distance $D > N^{\nu} b$, whereas no critical adsorption is observed for small distance $D < N^{\nu} b$, where $\nu \approx 0.58$ is the Flory exponent and b is the mean bond length. The critical adsorption point $T_c = 1.65$ is the same as that of a grafted polymer. Normal diffusion is observed for the confined polymer; however, the diffusion rate is dependent on the temperature and surface separation distance.

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I. INTRODUCTION

The properties of polymers near surfaces are significantly different from those in bulk solution. A detailed understanding of the static and dynamic properties of polymers near surfaces or interfaces is important for many chemical and biological processes, such as size-exclusion chromatography, polymer adhesion, colloidal stabilization, development of composite materials, coating and lubrication [1], DNA segregation in bacteria [2], and DNA packaging in viruses [3]. This field has attracted a large number of studies for a long time. Recently, with the development of nanotechnology, parallel-plate slit micochannels [4–7] and slitlike nanochannels [8,9] were developed to study the statistical and dynamics properties of DNA in the single-molecule level.

A grafted polymer chain with one end tethered to an attractive surface has been widely studied in theory [10–13], computer simulation [13–22], and experiment [23,24]. Theoretically, the polymer is often represented by a self-avoiding walk (SAW) on the simple cubic lattice. Every walk contacting the surface is assigned an attraction energy E (or a scaled energy $\varepsilon = E/k_B T$ with k_B the Boltzmann constant and T the temperature). The polymer chain can be adsorbed or desorbed depending on the scaled energy ε. For an infinitely long polymer, a transition from a desorbed state to an adsorbed state occurs at the critical adsorption point (CAP) ε_c (or T_c). At CAP, the number of segments M contacting the surface is in a power-law relation with the chain length N as $M \sim N^{\phi}$ with ϕ the crossover exponent. While for finite long polymers, the transition displays a smooth crossover fashion, which is controlled by a single scaling variable given by $(\varepsilon - \varepsilon_c)N^{\phi}$. The crossover exponent ϕ is essential for the scaling behavior of the polymer at adsorbing surfaces, but its exact value is difficult to estimate. Theoretical works often determine the set of critical parameters (ε_c, ϕ) simultaneously from the power-law relation. But a small variation in ε_c would lead to a large change in ϕ [17]. For example, it has been found that values of ε_c vary including 0.276 [16], 0.286 [14], 0.288 [18], 0.291 [19], and 0.294 [15], while the crossover exponent ϕ ranges from about 0.5 [14,16,18,22], to 0.54 [19], to about 0.59 [13,17]. In our recent work, we found that the mean square end-to-end distance $\langle R^2 \rangle$ was dependent on the temperature and $\langle R^2 \rangle$ reached its minimum at CAP, which might provide an alternate way to determine CAP [21]. Moreover, the minimum place of $\langle R^2 \rangle$ is roughly independent of the chain length; thus we can use this method to locate CAP even if we do not know exactly the chain length. So it is relatively easier than the scaling method by which chain lengths need to be known.

The conformation and dynamics of a polymer confined between two surfaces is more complicated and interesting [25,26]. Considering a polymer with a radius of gyration R_{g0} and a persistence length a in bulk solution confined between two parallel surfaces with a surface separation distance D, different regimes can be distinguished depending on the ratio between D and R_{g0}. At $D \gg R_{g0}$, the polymer is roughly free. With the decrease of D, the polymer at first undergoes an orientation changing and then a shape squeezing. At $D \sim R_{g0}$, the size of the polymer reaches a minimum. A further reduction of D is accompanied by a sharp increase in the polymer size, corresponding to a conformational transition of the polymer from a three-dimensional (3D) to a two-dimensional (2D) behavior [27,28]. Recently, the equilibrium conformation and dynamics of single-λ DNA [48.5 kilobase pairs (kbp)] molecules in slitlike nanochannels were investigated using fluorescence microscopy at small D less than 100 nm [7]. Results showed that the in-plane radius of gyration increases monotonically with decreasing D, which was in agreement with simulations. Moreover, there are two regimes called the de Gennes regime ($2a < D < 2R_{g0}$) [29] and the Odijk regime ($D \leqslant 2a$) [30] for small D. In the de Gennes regime, the polymer has a 2D conformation at large length scale, but it still has a 3D freedom at short scale, whereas in the Odijk regime, the orientation of the polymer becomes restricted even at the shortest length scales. The polymer has different static and dynamic characteristics in these two regimes [4–9].

Although there has been significant progress in understanding the properties of a polymer confined between two surfaces, it is still incomplete. In a recent theoretical work, Odijk argued that there might be several other regimes between the de Gennes regime and the Odijk regime [31], and only a few works concerned the attraction of surface. For a SAW polymer confined between two attractive surfaces, the competition between the exclusive effect and the attraction effect of the surfaces would make the problem more complicated. The effects of the surface separation distance and the interaction energy on the thermodynamic properties of polymers were investigated by transfer-matrix methods [26]. They found a second-order transition at CAP for both an infinitely large system and an infinitely long polymer [26]. The attractive interaction can also significantly change the conformational structure and the dynamics of a polymer [32–34]. The polymer adopts structures containing trains, loops, bridges, and tails at high temperature, while it is fully adsorbed on one of the two surfaces at low temperature. At moderate temperature, the adsorbed polymer may detach and jump to another surface after a certain period of time.

In the present work we study the critical adsorption of a SAW polymer confined between two parallel attractive surfaces using the dynamic Monte Carlo method. The attractive interaction between polymer and surface is taken into account. A polymer monomer will contribute one contact pair and gain an energy $E = -1$ if it locates at the nearest neighbor site of either surface. We find that the scaling relation between the mean contact number $\langle M\rangle$ and the chain length N is different for small and large surface separation distances. A critical adsorption point is found at $T_c = 1.65$ (in units of E/k_B) for large D, whereas no critical adsorption can be detected for small D. The diffusion of a polymer parallel to surfaces is also studied. Normal diffusion is found at any temperature for both large and small D's.

II. MODEL AND CALCULATION METHOD

The simulation system is embedded in the simple cubic lattice. There are two parallel impenetrable flat surfaces located at $z = 0$ and $z = D$, respectively. Periodic boundary conditions (PBCs) are employed in the x and y directions. In our work, the improved bond fluctuation model (BFM) for a SAW polymer chain is adopted [35,36]. A chain with length N is comprised of N identical monomers sequentially linked with fluctuating bond lengths. Each monomer occupies one lattice site. The bond length between two successive monomers along the chain can be 1, $\sqrt{2}$, or $\sqrt{3}$ lattice unit, which is taken from a set of 26 allowed bond vectors obtained from the set {(1, 0, 0), (1, 1, 0), (1, 1, 1)} by symmetry operations of the simple cubic lattice.

A SAW chain is generated at the beginning of the simulation using the Rosenbluth-Rosenbluth chain generation method between the two surfaces [37]. It then undergoes a long period of Brownian motion to reach an equilibrium state, resulting from random collisions between monomers and solvent molecules. In the dynamic Monte Carlo simulation, a trial move is achieved by randomly picking a monomer and attempting to move one lattice spacing in one of the six randomly selected directions: $\{(1,0,0), (0,1,0), (0,0,1), (-1,0,0), (0,-1,0), (0,0,-1)\}$. This trial move will be accepted if the following five conditions are satisfied simultaneously: (1) The excluded volume condition is obeyed, (2) the new bond vector still belongs to the allowed bond set, (3) no bond crossing occurs, (4) the new site locates at $z > 0$ and $z < D$, and (5) the Boltzmann factor $\exp(-\Delta E/k_BT)$ is greater than a random number uniformly distributed in the interval (0, 1), where ΔE is the energy shift due to the trial move. In one Monte Carlo step (MCS) all monomers in the polymer chain attempt to move once on average. In this study, we have made two kinds of simulations: (1) the polymer chain lies between two noninteracting surfaces with $E = 0$, and (2) the polymer chain lies between two interacting surfaces with $E = -1$. The first case is equivalent to the system at an infinitely high temperature, while for the second case, we investigate the dependence of the configuration properties of the polymer at different temperatures. The unit of temperature is $1/k_B$ with k_B the Boltzmann constant.

We use a large simulation box and PBCs along the x and y directions to eliminate the size effect of a finite simulation system. For a polymer with length N, the simulation box is also N in both the x and y directions. Therefore there is no size effect of the simulation box.

The polymer is first equilibrated for about $2.5N^{2.13}$ MCS [19]. Then we record polymer conformation at every $0.1N^{2.13}$ MCS in the next $100N^{2.13}$ MCS. The results are averaged over 1000 conformations in one independent simulation run. And the final results are further averaged over 1000 independent runs.

III. RESULTS AND DISCUSSION

At first, we perform a series of simulations for a polymer confined between two noninteracting parallel surfaces, i.e., $E = 0$. In order to compare the results for different chain lengths and different surface separation distances, a scaled surface separation distance defined as [27]

$$\Delta = \frac{D}{N^{v} b} \tag{1}$$

is used instead. Here $v = 0.58$ is the Flory exponent and $b = 1.42$ is the mean bond length. The mean square end-to-end distance $\langle R^2\rangle$ and the mean contact number $\langle M\rangle$ are calculated. The dependence of $\langle R^2\rangle$ and $\langle M\rangle$ on Δ is presented in Fig. 1 for $N = 50$, 100, and 200. Different behaviors are found

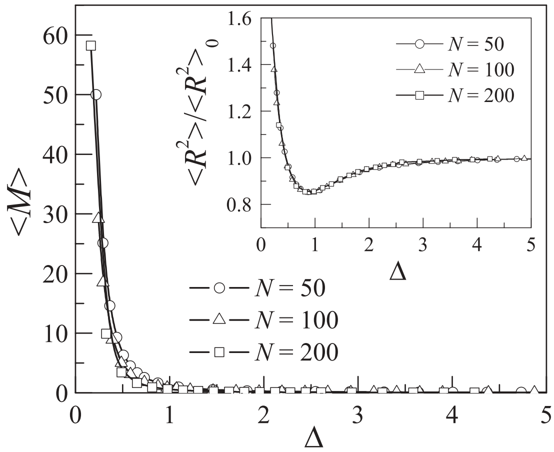

FIG. 1. Mean contact number $\langle M\rangle$ vs the scaled distance Δ for a confined polymer with chain length $N = 50$, 100, and 200. The inset shows $\langle R^2\rangle/\langle R^2\rangle_0$ vs Δ for the three chain lengths. $\langle R^2\rangle$ is the mean square end-to-end distance of a polymer confined between two surfaces while $\langle R^2\rangle_0$ is that in dilute solution. Polymer-surface interaction is set as $E = 0$.

TABLE I. The scaled surface distance $\Delta = \frac{D}{N^{\nu}b}$ for different polymer lengths at $D = 10$ and 100.

	$N = 50$	$N = 100$	$N = 200$	$N = 400$
$D = 10$	0.728	0.487	0.326	0.218
$D = 100$	7.28	4.87	3.26	2.18

for $\langle R^2\rangle$ and $\langle M\rangle$. $\langle R^2\rangle$ is roughly a constant at large Δ, indicating that the influence of the surfaces is negligible at large Δ. It decreases slowly with the decrease of Δ and reaches minimum at about $\Delta = 1$. Afterwards it increases quickly below $\Delta = 1$. The results are in agreement with previous simulation results [38]. On the other hand, the value of $\langle M\rangle$ increases monotonically with the decrease of Δ. $\langle M\rangle$ is about 0 at $\Delta > 1$ and it increases significantly with the decrease in Δ at $\Delta < 1$. The results indicate a large number of monomers are in contact with surfaces at $\Delta < 1$ although there is no attraction between the polymer and the surfaces. Two impenetrable surfaces suppress many conformational degrees of freedom in the vertical direction of the surfaces if the scaled distance Δ is small. The scaled distances for different polymer lengths are listed in Table I for distance $D = 10$ and $D = 100$. We find $\Delta < 1$ at $D = 10$ and $\Delta > 1$ at $D = 100$ for these chain lengths. So, in the following text, we only choose $D = 10$ and 100, corresponding to the strong confinement and weak confinement, respectively.

Then we simulate the conformational properties of polymer confined between two attractive surfaces with polymer-surface interaction $E = -1$. Starting from an initial randomly generated configuration, we slowly decrease the system temperature from a high temperature $T = 8$ to a low temperature $T = 0.1$. We relax the polymer for a time duration $2.5N^{2.13}$ MCS to reach an equilibrium state [19] and use the next $100N^{2.13}$ MCS for statistics at each temperature. The mean contact number $\langle M\rangle$ for different polymer lengths at different temperatures are calculated. For the adsorption of a polymer on a flat surface, the number $\langle M\rangle$ plays the role of an order parameter, and it can be expressed as a finite-size scaling against chain length N and temperature T [19],

$$\langle M\rangle = N^{\phi}(a_0 + a_1(T - T_c)N^{1/\delta} + O\{[(T - T_c)N^{1/\delta}]^2\}), \qquad (2)$$

where the term N^{ϕ} is adopted from Eisenriegler *et al.* [13]. Here, another scaling exponent δ is introduced. If we have $\phi = 1/\delta$, then Eq. (2) is the same as that using one exponent [13], where $\langle M\rangle = N^{\phi} f[(T - T_c)N^{\phi}]$ with $\phi = 0.59$ for end-grafted SAW polymer chains [13,17]. In fact, our previous calculations find that $\delta = 1.78$ is close to $1/\phi$ ($\phi = 0.54$) [19], but the relation $\phi = 1/\delta$ does not always satisfy for an end-grafted BFM polymer model where $\phi = 0.52$ and $\delta = 1.63$ were estimated [39]. Therefore one could use two exponents to describe the critical adsorption of the polymer.

$\langle M\rangle$ behaves differently at temperatures T below and above T_c, since the second term $(T - T_c)N^{1/\delta}$ in the scaling form [Eq. (2)] changes its sign when the temperature T rises from $T < T_c$ to $T > T_c$. At $T = T_c$ the order parameter $\langle M\rangle$ has the best power-law behavior,

$$\langle M\rangle = a_0 N^{\phi}. \qquad (3)$$

The dependence of $\langle M\rangle$ on N is plotted in Fig. 2(a) for the small distance $D = 10$ and in Fig. 2(b) for the large distance $D = 100$. Different scaling behaviors are found for the two cases. For $D = 10$, power-law relations are observed at any temperature with the same exponent $\phi = 1$. That means there is no critical adsorption for this case, whereas for $D = 100$, a different behavior is clearly seen in Fig. 2(b) as concave curves at low T ($T = 1.5$ and 1.6) and convex curves at high T ($T = 1.7$ and 1.8) are observed. Therefore, there must be a critical adsorption point T_c located in the temperature region (1.6, 1.7), at which the dependence of $\langle M\rangle$ on N can be expressed by the power-law relation given by Eq. (3). Values of $\langle M\rangle$ at other temperatures in the interval (1.6, 1.7) are obtained by quadratic interpolation from the simulation data. The best power-law fitting is found at $T_c = 1.65$. It is interesting to find that $T_c = 1.65$ is equal to the CAP of an end-grafted polymer [39]. Our simulation results show that the critical adsorption of a weakly confined polymer at $\Delta > 1$ takes place at the same temperature as that of an end-grafted polymer.

At $T_c = 1.65$, we get the crossover exponent $\phi = 1$, the same as that for small distance $D = 10$. However, it is larger than that of an end-grafted chain where $\phi = 0.52$ was estimated [39]. The increase in ϕ is due to the confinement of two surfaces. The contact number $\langle M\rangle$ decreases with the increase in D. At $T_c = 1.65$, we find that $\langle M\rangle$ decreases in a power-law relation with D as shown in Fig. 3(a) for different

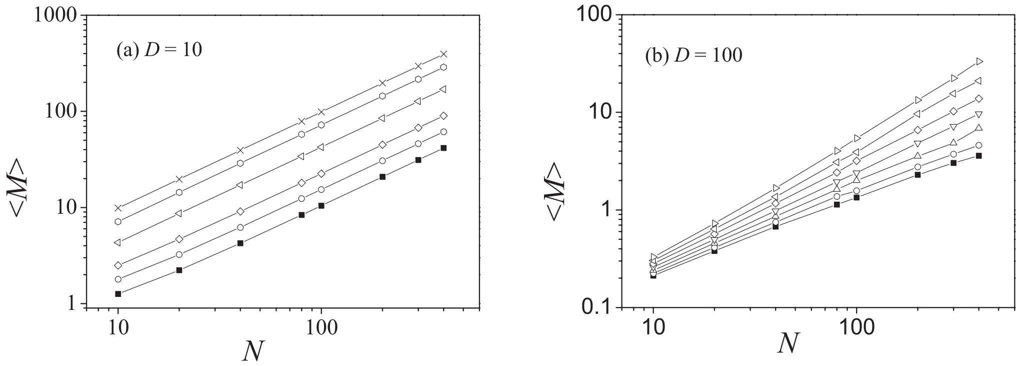

FIG. 2. Log-log plot of the mean contact number $\langle M\rangle$ vs chain length N (a) for surface distance $D = 10$ at temperature $T = 0.2$, 0.6, 1.0, 1.5, 2.0, and 3.0 (from top to bottom) and (b) for $D = 100$ at $T = 1.5$, 1.55, 1.6, 1.65, 1.7, 1.75, and 1.8 (from top to bottom).

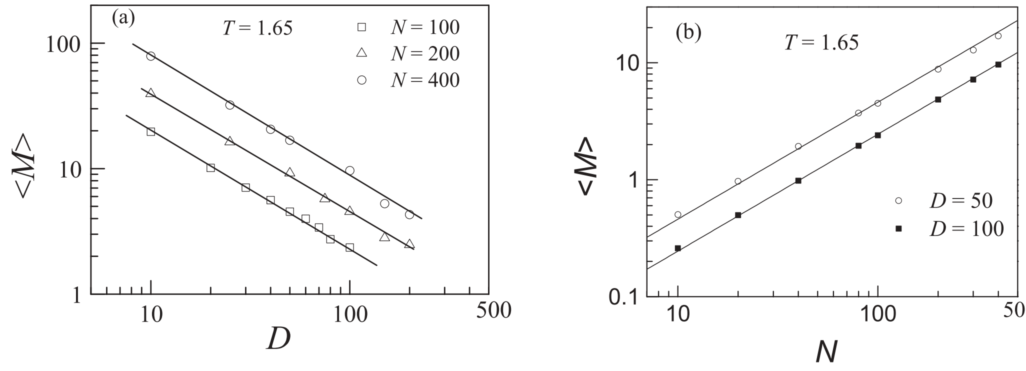

FIG. 3. (a) Log-log plot of the mean contact number $\langle M \rangle$ vs surface distance D for polymer with length $N = 100$, 200, and 400 at temperature $T = 1.65$. (b) Log-log plot of $\langle M \rangle$ vs chain length N for surface separation distance $D = 50$ and $D = 100$ at $T = 1.65$.

chain lengths $N = 100$, 200, and 400. Here the smallest scaled surface separation distance $\Delta = \frac{D}{N^\nu b}$ is about 1 for the surface separation distance $D = 20$, so the weak confinement condition is still satisfied. Similarly, a longer chain more easily contacts the surfaces at the same D, i.e., $\langle M \rangle$ increases with the decrease of D. At $T = 1.65$, we find $\phi \sim 1$ for another surface distance $D = 50$ as shown in Fig. 3(b). Again the smallest scaled surface distance Δ is 1.09 for the longest chain $N = 400$. Our results indicate that the value ϕ seems universal for the adsorption of a polymer between two surfaces.

From the known values of T_c and ϕ, we then determine the critical exponent δ for the large distance case. Eq. (2) can be rewritten as

$$\langle M \rangle N^{-\phi} = a_0 + a_1 (T - T_c) N^{1/\delta} + O[(T - T_c)^2 N^{2/\delta}]. \quad (4)$$

To determine the value of the exponent δ, we have calculated the product $\langle M \rangle N^{-\phi}$ near T_c for different chain lengths at $D = 100$ and performed a least squares fit of the product $\langle M \rangle N^{-\phi}$ to the second-order expansion of $(T - T_c) N^{1/\delta}$. Since T_c and ϕ are already known, the critical exponent δ can be determined as the only free parameter. We find that $\delta = 2$ gives the best fitting with the least deviation, as shown in Fig. 4(a) where the simulated data near T_c are presented. The value $\delta = 2$ for the confined polymer is different from the exponent $\delta = 1.63$ [39] for the end-grafted polymer of the same polymer model. It also different from $\delta = 1.78$ [19] of the end-grafted SAW polymer with fixed bond length ($b = 1$) on the simple cubic lattice. In the present case, we find $\delta = 2/\phi$ instead of $\delta = 1/\phi$. Though the chain length dependent term $\phi = 1$ is different from that of the end-grafted polymers on a single surface, for example, $\phi = 0.59$ [13,17], 0.54 [19], and 0.52 [39], the temperature dependent term $(T - T_c) N^{0.5}$ is somewhat close to that of the grafted polymers [13,17,19]. The exponent 0.5 indicates that the transition of the critical adsorption is of second order, which is roughly the same as that of grafted polymers.

Figure 4(b) presents a log-log plot of $\langle M \rangle N^{-\phi}$ vs $|(T - T_c) N^{1/\delta}|$ for the confined polymer with a large temperature range from 0.1 to 3. All data at $T > T_c$ collapse and give a slope of -1 for the asymptotic behavior at high temperatures. Then we have $\langle M \rangle \sim N^{0.5}$ at $T \gg T_c$, which is different from $\langle M \rangle \sim N^0$ for end-grafted polymers [13]. The relation $\langle M \rangle \sim N^{0.5}$ at high temperature results from the confinement of the two surfaces. Data do not collapse, however, at $T < T_c$. We find that data shift to large $|(T - T_c) N^{1/\delta}|$ for large N; thus the asymptotic behavior is $\langle M \rangle N^{-\phi} =$ constant, or, $\langle M \rangle \sim N$ at low temperatures. This is the same as that of end-grafted polymers, indicating that all monomers are adsorbed on surfaces at low temperatures.

We have calculated the difference of contact numbers $\delta M = |M_0 - M_D|$, here M_0 and M_D represent the contact number at surface $z = 0$ and at surface $z = D$, respectively. To study the adsorption asymmetry of a polymer at upper and lower

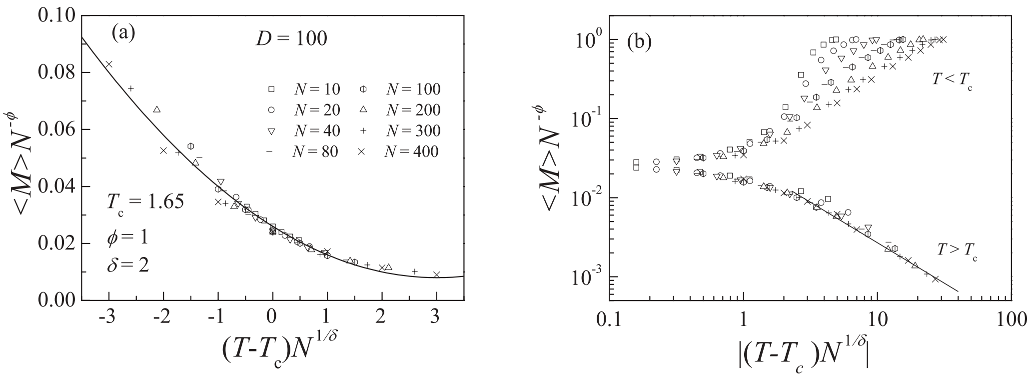

FIG. 4. The value $\langle M \rangle N^{-\phi}$ vs $(T - T_c) N^{1/\delta}$ for different chain lengths at different temperatures. (a) Linear plot with a small range of T from 1.5 to 1.8. The solid line in (a) is a second-order polynomial fitting of the simulation data. (b) Log-log plot with a large range of T from 0.1 to 3. Symbols used in (b) are the same as that in (a). The solid in (b) has a slope of -1. Parameters used are $T_c = 1.65$, $\phi = 1$, and $\delta = 2$.

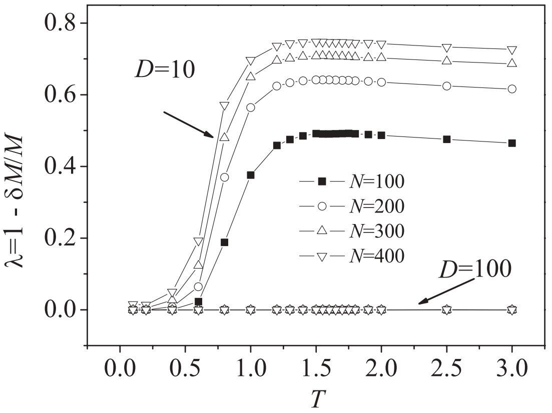

FIG. 5. The adsorption asymmetry of a polymer at upper and lower surfaces λ vs temperature T for surface separation distance $D = 10$ and 100.

surfaces, we define λ as

$$\lambda = 1 - \frac{\delta M}{M} = 1 - \frac{|M_0 - M_D|}{M}, \tag{5}$$

where $M = M_0 + M_{\mathrm{D}}$. The value λ is in the range (0, 1). Here $\lambda = 0$ means that polymer is only adsorbed on one surface, i.e., no monomers are adsorbed simultaneously on two surfaces. Whereas $\lambda = 1$ means that the polymer is adsorbed simultaneously on two surfaces with a symmetrical manner, i.e., $M_0 = M_D$. An intermediate value $0 < \lambda < 1$ means that different numbers of monomers are adsorbed on the upper and lower surfaces, i.e., $M_0 \neq M_D$. Figure 5 shows the dependence of λ on T for both small $D = 10$ and large $D = 100$, where N ranges from 100 to 400. The value of λ remains 0 at any temperature for $D = 100$, whereas it remains a high value at high temperature and decreases to zero at very low temperature for $D = 10$.

For the large surface distance $D = 100$ ($\Delta > 1$), we have $\lambda = 0$ at any temperature. In this case, the polymer is not long enough to touch two surfaces simultaneously at high or low temperature. The polymer prefers to keep away from the two surfaces at high temperature since desorption is entropically favored, and it can only be adsorbed onto one surface at low temperature, whereas for the small surface distance $D = 10$ ($\Delta < 1$), monomers dynamically contact the two surfaces at high temperature simply because of the strong confinement. However, the nonzero value of λ indicates that the dynamic contacting is instantaneously asymmetric, whereas at low temperature, $\lambda = 0$ indicates that the polymer chain is always adsorbed onto one surface instantaneously even at $D = 10$. For the case $D = 10$, the change of λ from a nonzero value to zero indicates a transition from two-surface adsorption to one-surface adsorption. This is "a symmetry-breaking transition," where a long chain collapses upon either surface, but not partly on both surfaces [40]. We would understand the simulation result from the viewpoint of the free energy $F = U - TS$. Adsorbed onto both surfaces, the polymer has larger entropy, but it has lower energy if adsorbed onto a single (upper or lower) surface. Therefore a polymer should be adsorbed onto a single surface at low enough temperature. This is somewhat similar to the known Oswald ripening process.

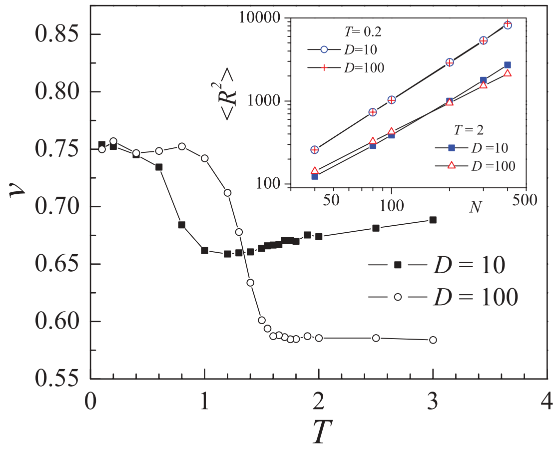

FIG. 6. (Color online) The scaling exponent v vs the temperature T for a polymer confined between two parallel interacting surfaces for two surface separation distances $D = 10$ and 100. The inset shows the mean square end-to-end distance $\langle R^2 \rangle$ as a function of chain length N at temperatures $T = 0.2$ and 2.

The conformational properties of a polymer between two parallel interacting surfaces are also studied. We find that the dependence of the mean square end-to-end distance $\langle R^2 \rangle$ on the chain length can also be expressed by the power-law relation

$$\langle R^2 \rangle \propto N^{2v}, \tag{6}$$

as shown in the inset of Fig. 6 for $D = 10$ and 100 at a high temperature $T = 2$ and at a low temperature $T = 0.2$. The scaling exponent v is found to be dependent on the temperature T as shown in Fig. 6 for both $D = 10$ and $D = 100$. At high temperature ($T > T_c$), we have $v = 0.58$ for $D = 100$, which is the same as that of a 3D SAW chain in bulk dilute solution, indicating that the confinement of the surfaces is weak and the polymer shows 3D behavior. But for $D = 10$, a large value of v is found at high temperature ($T > T_c$), indicating that the effect of the surface is strong. As the confinement is strong at $D = 10$, the polymer chain is strongly squeezed along the normal direction and stretched along the parallel direction [27,28]; thus the polymer shows a behavior between 2D and 3D with an exponent $0.6 < v < 0.75$. Nevertheless, we get $v \approx 0.75$ for both distances $D = 10$ and 100 at low temperature $T \ll T_c$, which is the same as that of a 2D SAW chain, indicating that the polymer is strongly adsorbed onto one surface. There is a transition for the exponent v with the decrease of temperature, with a critical point near T_c for $D = 100$. However, the transition of $D = 10$ is far below T_c, possibly because the polymer forms a bridge structure more easily when D is small, i.e., it contacts both surfaces at the same time. Strong confinement is a disadvantage for the polymer chain forming a 2D conformation [32].

At last, we have studied the diffusion characteristics of the confined polymer. The mean square displacement of the center of mass of the polymer,

$$\langle \Delta R^2 \rangle = \langle [\boldsymbol{R}_{\mathrm{c.m.}}(t) - \boldsymbol{R}_{\mathrm{c.m.}}(0)]^2 \rangle, \tag{7}$$

is calculated at different times. Here $\boldsymbol{R}_{\mathrm{c.m.}}(t)$ and $\boldsymbol{R}_{\mathrm{c.m.}}(0)$ are the position vectors of the center of mass at time t and at initial time $t = 0$, respectively. As the diffusion of the polymer

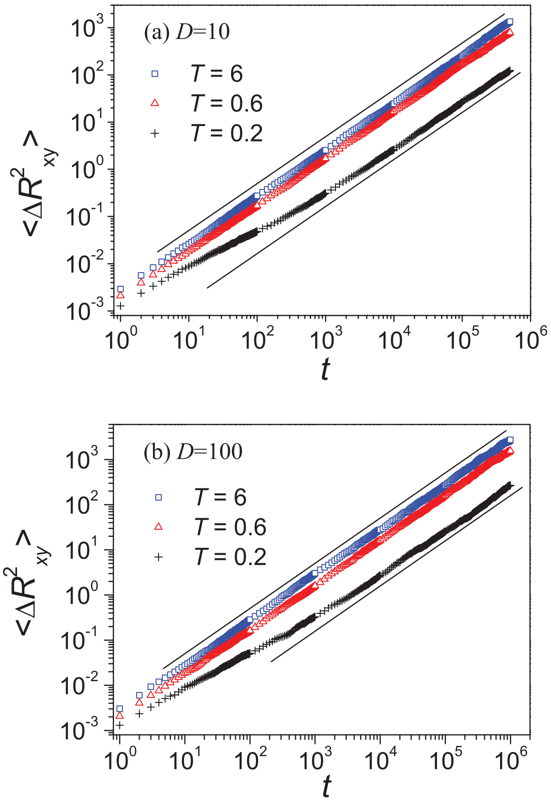

FIG. 7. (Color online) The mean square displacement of a polymer parallel to a surface, $\langle \Delta R^2_{xy}\rangle$, for chain length $N = 200$ at different temperatures $T = 0.2$, 0.6, and 6. (a) Surface separation distance $D = 10$, and (b) $D = 100$. Solid lines have a slope of 1, indicating normal diffusion of polymer.

is confined in the vertical direction, we only calculate the component parallel to the surface $\langle \Delta R^2_{xy}\rangle$. Figure 7 presents the evolution of $\langle \Delta R^2_{xy}\rangle$ of the polymer with length $N = 200$ at different temperatures for surface separation distances $D = 10$ and $D = 100$, respectively. We can see that the diffusion behaviors are the same for both small and large distances. Normal diffusion $\langle \Delta R^2_{xy}\rangle \propto t$ is observed at high temperature $T = 6$ as well as at relatively low temperature $T = 0.6$. It indicates that the polymer diffuses roughly freely even below $T_c = 1.65$ for $D = 100$. Only at very low temperature, for example, at $T = 0.2$, abnormal diffusion is found at short time scale for both cases. However, the polymer always diffuses normally at long time scale. As $T = 0.2$ is far below T_c, we thus conclude that normal diffusion will always exist at long time scale.

Though the polymer shows a critical adsorption at low temperature, our simulation results on the diffusion show that it does not necessarily mean that the polymer is motionless below T_c. On the contrary, the polymer chain still undergoes adsorption and desorption frequently at low temperature [34], so it can diffuse with a certain rate. However, it becomes much more difficult for desorption with the decrease in the temperature, leading to the slowing in the diffusion as shown in Fig. 7. We observe normal diffusion after $\langle \Delta R^2_{xy}\rangle = 1$ though the diffusion is very slow.

IV. CONCLUSION

Dynamical Monte Carlo simulations have been carried out to study the critical adsorption of a single-polymer chain confined between two parallel interacting surfaces. A three-dimensional bond fluctuation polymer model is adopted with bond length 1, $\sqrt{2}$, or $\sqrt{3}$ on the simple cubic lattice. The mean square end-to-end distance $\langle R^2\rangle$ and the mean number contacting surfaces $\langle M\rangle$ can be scaled by $\Delta = D/N^{\nu}b$. We find that a large number of monomers are in contact with surfaces at $\Delta < 1$ even if there is no attraction between polymer and surface.

For large scaled distance Δ, the mean contact number $\langle M\rangle$ is scaled by N and T by $\langle M\rangle(T,N) = N^{\phi}\{a_0 + a_1(T - T_c)N^{1/\delta} + O[(T - T_c)N^{1/\delta}]^2\}$ with $T_c = 1.65$, $\phi = 1$, and $\delta = 2$. The critical adsorption point $T_c = 1.65$ is roughly the same as that of an end-grafted chain. But for small scaled distance Δ we find $\langle M\rangle(T,N) \propto N^{\phi}$ at all temperatures. The results show that there is no critical adsorption point for $\Delta < 1$.

At last, we find that the chain exhibits normal diffusion along the direction parallel to surfaces for both $\Delta < 1$ and $\Delta > 1$ at long time scale. The polymer chain diffuses roughly freely above T_c. We find that the polymer still diffuses randomly at temperatures far below T_c.

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