

Simulation of a Flexible Polymer Tethered to a Flat Adsorbing Surface

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ABSTRACT: A lattice self-avoiding polymer chain with one end attached to an adsorbing flat surface is simulated using Monte Carlo method. The chain model has $z = 26$ bond vectors with bond length being 1, $\sqrt{2}$, and $\sqrt{3}$ on the simple cubic lattice. The dependence of the number of surface contacts M on temperature T in the unit E/k_B with E the interacting energy and k_B the Boltzmann constant and chain length N is investigated by a finite-size scaling law $M = N^\phi(a_0 + a_1(T - T_c)N^{1/\delta} + O((T - T_c)^2N^{2/\delta}))$ near the critical adsorption point T_c . It was estimated that $T_c = 1.625$ and the exponents $\phi = 0.52$ and $\delta = 1.63$. It was

observed that both mean square end-to-end distance $\langle R^2 \rangle$ and mean square radius of gyration $\langle R_g^2 \rangle$ reach minimum at T_c . And we discover that the asphericity parameter $\langle A \rangle$ is independent of chain length at T_c . A simple relationship is discovered between T_c and bond vector number n_b for lattice chain models, and which can be extended to nonlattice chain models by introducing an attraction range fraction f . © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 282–287, 2012

Key words: critical adsorption; polymer; Monte Carlo simulation

INTRODUCTION

Understanding the properties of polymers near a surface or interface is important in polymer and biology sciences. The polymer chain can be adsorbed or desorbed, depending on the interaction between polymer and surface. The phenomenon is relevant to many technological applications, such as polymer compatibilizers, colloid stabilization, and polymeric surfactants.^{1–3} Uncovering the relationship between the adsorption of polymers and the interactions with surfaces is of great interest in biological process. A proper turning of the interactions may improve biocompatibility. For example, the inclusion of tethered polymers on the surface of liposomes results in their increased longevity in the blood stream.⁴ Tethered polymers can be used for the specific targeting of liposomes to cells by chemically inserting a specific binding reagent to the free ends of the tethered polymer.⁴ In many biological systems, ligands are attached to a surface through flexible tethered

chains.^{5,6} The conformation of the attached tether chains will affect the binding of ligand to receptor and thus influences the whole biological process.⁷

The growing interest in polymers interacting with substrates requires a thorough understanding of static and dynamics properties of tethered chain. The properties of tethered chain have attracted a large number of theoretical and experimental researches.^{8–12} A mathematical model often used for studying the adsorption is the self-avoiding walk (SAW) chain of length N in a three-dimensional (3D) simple cubic (SC) lattice interacting with a flat surface and restricted to lie on one side of the surface.^{13–17} Every walk contacting with the surface is assigned an attractive energy $-E$. The chain exhibits a phase transition from a desorbed state at $T > T_c$ to an adsorbed state at $T < T_c$ when the adsorption strength increases beyond a critical value. T_c (or the scaled energy $\varepsilon_c = E/k_B T_c$ with k_B the Boltzmann constant) is named as the critical adsorption point (CAP).

In the view of free energy, the CAP can be understood as the condition where the limiting free energy of an adsorbed chain becomes equal to that of bulk chain.^{10,15,18} Therefore, the CAP can also be determined from the free energy difference between an adsorbed chain and a free chain. The CAP can also be determined from the configurational properties. It was pointed out that the ratio between

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perpendicular and parallel component of mean square end-to-end distance $\langle R^2 \rangle$, $\langle R^2 \rangle_z / \langle R^2 \rangle_{xy}$, becomes independent of chain length at CAP.^{11,19} A widely used method is scaling law proposed by Eisenriegler, Kremer, and Binder (EKB).¹³ The energy of the chain U , which is proportional to the number of surface contacts M via $U = -ME$, changes from $U \sim N$ at low temperature to $U \sim N^0$ at high temperature. At CAP, U is expected to scale as $U \sim N^\phi$ with a crossover exponent ϕ . Therefore, T_c and the crossover exponent ϕ can be estimated by searching the scaling behavior. It was also proposed that a finite-size scaling relation $M = N^\phi(a_0 + a_1(T - T_c)N^{1/\delta} + O((T - T_c)^2N^{2/\delta}))$ with two exponents ϕ and δ exists near CAP.¹⁹

The simplest model is the SAW chain with bond vector number $n_b = 6$ obtained from symmetry operations on the vector set $\{(1,0,0)\}$ on SC lattice.^{10-12,17,18} There are many studies on this model. For example, Meirovitch and Livne obtained $\varepsilon_c = 0.291 \pm 0.001$ and $\phi = 0.530 \pm 0.007$ using Monte Carlo simulations by the criterion that chain energy $U \sim N^\phi$ at CAP.¹⁷ By applying finite-size scaling relation, $\varepsilon_c = 0.291 \pm 0.002$, $\phi = 0.54 \pm 0.01$, and $\delta = 1.78$ were estimated.²⁰

Descas et al. explored the values of ε_c and ϕ using four different methods for a 3D bond fluctuation model (BFM) on SC lattice.¹¹ Each monomer in BFM is represented by a cubic unit with eight lattice sites. There are $n_b = 108$ possible bond vectors for bonds connecting two sequential segments along the chain. They correspond to a basis set given by the vectors $\{(2,0,0), (2,1,0), (2,1,1), (2,2,1), (3,0,0), (3,1,0)\}$ and all symmetry on SC lattice.²¹ They found that the two sets ($\varepsilon_c = 1.01$, $\phi = 0.59$) and ($\varepsilon_c = 0.98$, $\phi = 0.50$) are good candidates. While based on the finite-size scaling relation, it was estimated that $\varepsilon_c = 0.93$, $\phi = 0.49$, and $\delta = 1.75$.²²

In this work, we study the critical adsorption for another bond fluctuation polymer chain on 3D SC lattice with $n_b = 26$ bond vectors obtained from symmetry operations on the vector set $\{(1,0,0), (1,1,0), (1,1,1)\}$. The bond length can be 1, $\sqrt{2}$, and $\sqrt{3}$ on the lattice and number of bond vectors is 6, 12, and 8, respectively. The values of T_c , ϕ and δ are estimated from the finite-size scaling relation. T_c is consistent with that estimated from $\langle R^2 \rangle_z / \langle R^2 \rangle_{xy}$. We find that both the mean square end-to-end distance $\langle R^2 \rangle$ and the mean square radius of gyration $\langle R_g^2 \rangle$ reach minimum at T_c . We have studied the relationship between CAP $\varepsilon_c (= E/k_B T_c)$ and bond vector number n_b , and we find a relation $\varepsilon_c \propto \ln n_b$. By introducing an interaction range fraction $f = \sigma / \langle b \rangle$ (σ is the interaction range and $\langle b \rangle$ is the mean bond length), we can extend our result to nonlattice chain models and we find that ε_c decreases linearly with f .

MODEL AND CALCULATION METHOD

The chain model adopted in this work is a SAW chain embedded in a 3D SC lattice with one end grafted to a flat surface. The flat surface is assumed infinitely large and impenetrable to polymer chain and locates at $z = 0$. Here the direction z is perpendicular to the flat surface. Monomeric units are restricted to lie in the upper half space ($z > 0$). The SAW polymer chain is comprised of N identical monomers consecutively linked with fluctuating bond length from 1, $\sqrt{2}$, and $\sqrt{3}$ lattice unit. Each monomer occupies one site of the lattice. The first monomer of the chain is fixed at position (0,0,1) and is considered to be adsorbed to the impenetrable surface. Here (0,0,0) is the center of flat surface. The bond between successive monomers along a chain can be taken from the set $\{(1,0,0), (1,1,0), (1,1,1)\}$ by symmetry operations of the SC lattice. Every monomer contacting with the surface, i.e., locating at layer $z = 1$, is assigned an interaction energy $-E$. Since there is an impenetrable flat surface at $z = 0$, periodic boundary conditions (PBC) are only employed in the x and y directions. With PBC one side of the simulation loops back to the opposite side, mimicking a bulk phase. For a polymer with length N , the maximum length in one direction is N . To avoid the finite size effect of finite simulation box, we use $L_x = L_y = N$ and $L_z = 2N$. Here L_x , L_y , and L_z are the simulation box size in x , y , and z directions, respectively.

At the beginning of simulation, a tethered SAW chain is grown using the chain growing method with the first monomer fixed at (0,0,1). After creating a whole chain, we let it undergo a series of Brownian motion resulting from random collisions between chain monomers and solvent molecules. In the dynamic model, a monomer is chosen randomly and attempted to move one lattice spacing in one of the six randomly selected directions: $\pm x$, $\pm y$, $\pm z$. This trial move will be accepted if the following five conditions are satisfied: (1) self-avoidance is obeyed, (2) the new site locates at $z > 0$, (3) the new bond vector still belong to the allowed bond set, (4) two bonds do not intersect, and (5) the Boltzmann factor $\exp(-\Delta E/k_B T)$ is greater than a random number uniformly distributed in the interval (0,1), where ΔE is the energy shift due to the change of monomer sites. In one Monte Carlo step (MCS) all monomers in the chain attempt to move once. The Boltzmann constant k_B is set unity in the simulation. In the simulation, the unit of temperature is set as E/k_B .

Annealing method is adopted to simulate the temperature dependence of polymer properties. Starting at a high temperature $T = 5$, we slowly decrease T with step ΔT . The step is chosen as small as 0.05 near T_c , whereas a slightly big value is chosen away

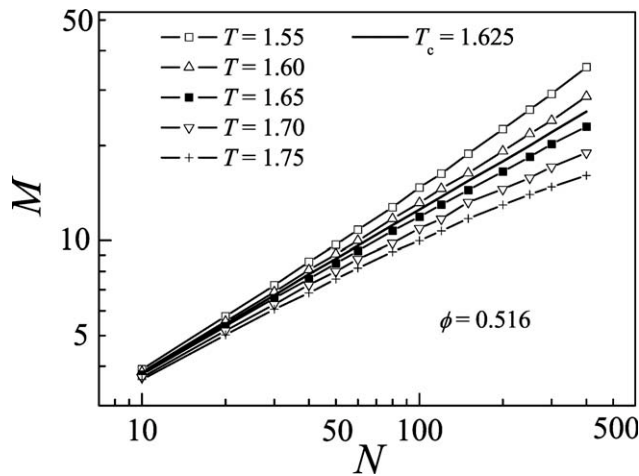


Figure 1 Log-log plot of the number of surface contacts M versus chain length N at temperature $T = 1.55, 1.6, 1.65, 1.7, 1.75$. The solid line at the critical point $T_c = 1.625$ is the linear fit of data from chain length $N = 10$ –400.

from T_c . The chain changed its configuration with time. At each T , the chain is relaxed for a time duration $\Delta t = 2.5N^{2.13}$ which was proved long enough for the simulation of a grafted chain.²³ In the present calculation, 100,000 independent runs with different starting configurations and random number series are performed. All quantities are thus averaged over these 100,000 runs.

RESULTS AND DISCUSSION

The number of surface contacts M is calculated at different temperatures. For the adsorption of polymer, the number M plays the role of an order parameter. It can be expressed as a finite-size scaling against chain length N and temperature T ,

$$M(T, N) = N^\phi (a_0 + a_1(T - T_c)N^{1/\delta} + O((T - T_c)^2 N^{2/\delta})) \quad (1)$$

where the term N^ϕ is adopted from EKB. It is clear that the values of M at temperatures below and above T_c have different behaviors since the second term $(T - T_c)N^{1/\delta}$ in the scaling form [Eq. (1)] changes sign when the temperature T change from $T < T_c$ to $T > T_c$. At $T = T_c$ the order parameter M has the best power law behavior,

$$M = a_0 N^\phi. \quad (2)$$

We plot the dependence of M on N in log-log scales at temperature $T = 1.55, 1.6, 1.65, 1.7, 1.75$ in Figure 1. The different behaviors for the temperature T changes from $T < T_c$ to $T > T_c$ are clearly seen in Figure 1: concave curves at low T ($T = 1.55, 1.6$) and convex curves at high T ($T = 1.7, 1.75$).

Therefore, the CAP T_c locates in the temperature region (1.6, 1.7). Values M 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 achieved at $T_c = 1.625$ as shown in Figure 1. At $T_c = 1.625$, we get the exponent $\phi = 0.52$.

To extract the critical exponent δ , we perform a least square fit of the value $MN^{-\phi}$ to the second order expansion of $(T - T_c)N^{1/\delta}$ as

$$MN^{-\phi} = a_0 + a_1(T - T_c)N^{1/\delta} + O((T - T_c)^2 N^{2/\delta}). \quad (3)$$

Figure 2 presents the results for T near T_c and for chain length N from 10 to 400. The range of T is from 1.55 to 1.75. Since T_c and ϕ are already known, the critical exponent δ can be estimated as the only free parameter. From the least square fitting of $MN^{-\phi}$ against $(T - T_c)N^{1/\delta}$ with a set of values δ , we find $\delta = 1.63$ gives the best fitting with the least deviation.

To characterize the average size of the polymer chain we use mean square end-to-end distance $\langle R^2 \rangle$. $\langle R^2 \rangle$ at different temperature T as well as their components parallel to the surface $\langle R^2 \rangle_{xy}$ and that normal to the surface $\langle R^2 \rangle_z$ are calculated. The dependence of ratio $\langle R^2 \rangle_z / \langle R^2 \rangle_{xy}$ on the temperature is presented in Figure 3 for chain lengths $N = 50, 100, 200, 400$. It was pointed out that the ratio should be a constant independence of N at the CAP.^{11,19} These curves do intersect at a cross point around $T = 1.62$ in the inset of Figure 3. This value is in agreement with the CAP $T_c = 1.625$ obtained from the finite-size scaling of M . We have also calculated the mean square radius of gyration $\langle R_g^2 \rangle$ and its two components parallel to the surface $\langle R_g^2 \rangle_{xy}$ and normal

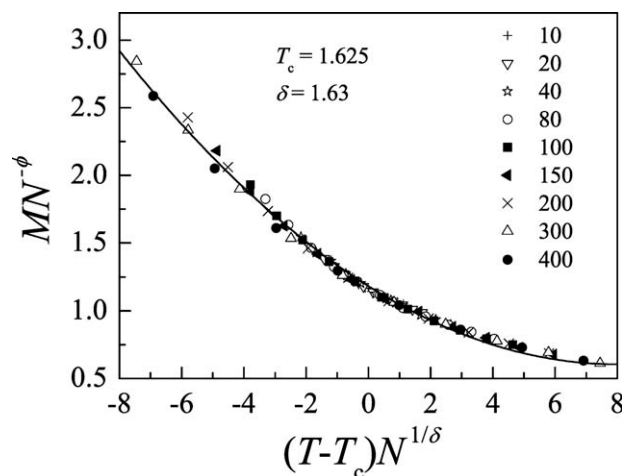


Figure 2 $MN^{-\phi}$ versus $(T - T_c)N^{1/\delta}$ for different chain lengths. The different symbols represent simulation results with the chain length N from 10 to 400. The solid line is second order polynomial fitting of the simulation data. Parameters used are $T_c = 1.625$, $\phi = 0.52$, and $\delta = 1.63$.

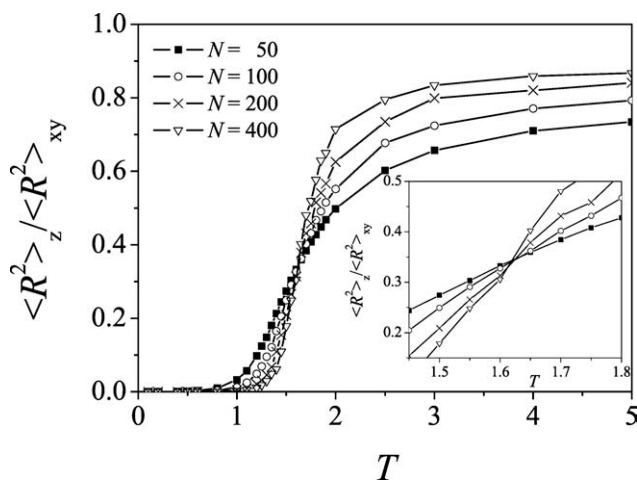


Figure 3 Plot of the ratio $\langle R^2 \rangle_z / \langle R^2 \rangle_{xy}$ versus the temperature T for different chain lengths $N = 50, 100, 200,$ and 400 . The inset shows the cross point near $T_c = 1.625$.

to the surface $\langle R_g^2 \rangle_z$. The dependence of ratio $\langle R_g^2 \rangle_z / \langle R_g^2 \rangle_{xy}$ on the temperature is similar to that of $\langle R^2 \rangle_z / \langle R^2 \rangle_{xy}$, which also indicates that the CAP is close to $T_c = 1.625$.

The dependence of $\langle R^2 \rangle / N$ on the temperature T is plotted in Figure 4 for a variety of chain lengths. We find that each curve has a minimum below, but near the T_c and the minimum comes close to T_c for large chain, similar to that of chain model with coordination number $z = 6$ on SC lattice.²⁴ Below T_c , $\langle R^2 \rangle$ grows rapidly with the decrease of temperature T , while above T_c , $\langle R^2 \rangle$ increases slowly with T . And the minimum of $\langle R^2 \rangle$ becomes more obvious with the increase of chain length N . An interesting finding is that the minimum of $\langle R^2 \rangle$ locates at CAP. The result indicates that one can locate T_c from $\langle R^2 \rangle$. $\langle R^2 \rangle$ can be measured from the angular distribution of the scattered light.²⁵ One advantage of this method is that one need not to know the chain length, so it can be performed easily in experiment. We find that the dependence of $\langle R_g^2 \rangle$ on temperature in a similar way as $\langle R^2 \rangle$ and $\langle R_g^2 \rangle$ also reaches minimum around T_c .

We have also calculated the mean asphericity parameter $\langle A \rangle$ which is defined as

$$\langle A \rangle = \left\langle \frac{\sum_{i>j}^3 (L_i^2 - L_j^2)^2 / 2 \left(\sum_{i=1}^3 L_i^2 \right)^2} \right\rangle \quad (4)$$

in three-dimension space. Here, L_1^2 , L_2^2 , and L_3^2 ($L_1^2 \leq L_2^2 \leq L_3^2$) are the eigenvalues of the radius of gyration tensor²⁶

$$S = \frac{1}{n} \sum_{i=1}^n s_i s_i^T = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{xy} & S_{yy} & S_{yz} \\ S_{xz} & S_{yz} & S_{zz} \end{pmatrix}, \quad (5)$$

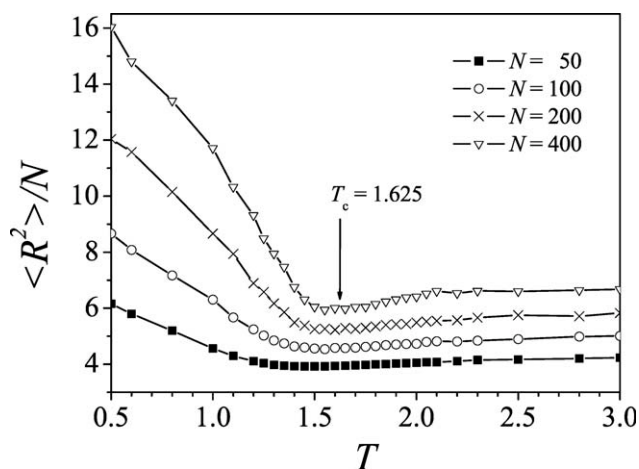


Figure 4 Mean square end-to-end distance $\langle R^2 \rangle$ versus temperature T for chain length $N = 50, 100, 200,$ and 400 .

where $s_i = \text{col}(x_i, y_i, z_i)$ is the position of monomer i in a frame of reference with its origin at the center of mass. This parameter ranges from zero for spherically symmetric chain conformations, to 0.5 for circular ones, and to one for rod-shaped ones. For a linear SAW chain, $\langle A \rangle$ is about 0.44 for long chain.²⁷ Figure 5 shows the dependence of $\langle A \rangle$ on temperature T for various chain lengths. The asphericity parameter $\langle A \rangle$ shows a steep increase around T_c when we anneal the system. The curves intersect at a cross point in the range of temperature (1.6–1.65), which includes the CAP value $T_c = 1.625$. Therefore, we find $\langle A \rangle$ is also independent of chain length N at CAP, similar to the behavior of $\langle R^2 \rangle_z / \langle R^2 \rangle_{xy}$ as well as $\langle R_g^2 \rangle_z / \langle R_g^2 \rangle_{xy}$.

The CAP and exponents of different polymer chain models on the 3D SC lattice are listed in Table I. They are all obtained from the finite-size scaling of Eq. (1). We find that ε_c increases with the

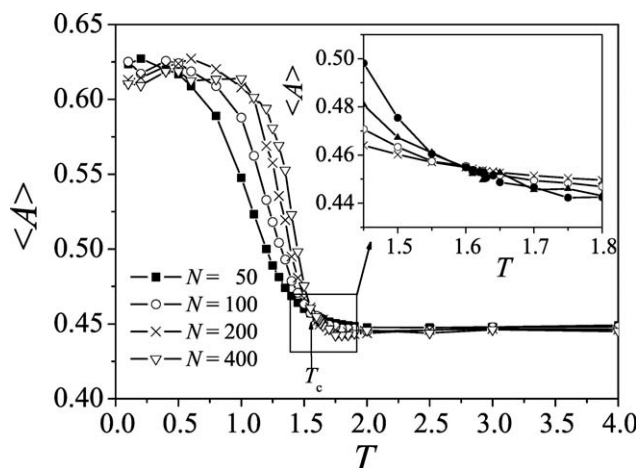


Figure 5 Plot of the asphericity parameter $\langle A \rangle$ versus temperature T for chain length $N = 50, 100, 200,$ and 400 . The inset shows the variation of $\langle A \rangle$ near T_c .

number of allowed bond vectors n_b . The relation between ε_c and n_b can be expressed as

$$\varepsilon_c \propto \ln n_b \quad (6)$$

as shown in Figure 6(a). Assuming the monomer-surface interaction is a constant, then we find that the critical adsorption temperature T_c decreases as n_b increases since $\varepsilon_c = E/k_B T_c$. Therefore, we can predict T_c from the bond vector number. However, the critical exponents ϕ and δ are roughly independent of the bond vector number n_b .

From the view of free energy, at the CAP the free energy, $F = U - TS$ of an adsorbed chain becomes equal to that of bulk chain. Adsorbing chain to surface will decrease both the entropy S and the energy U . For chain model on SC lattice, the decrease in energy U is in proportional to the contact number M , i.e., $\Delta U = -ME$. However, the decrease of entropy is proportional to M and $k_B \ln n_b$, since it loses almost $n_b/2$ configurations if one monomer contacts to surface. Therefore, we have $T\Delta S \propto Mk_B T \ln n_b$. At CAP, the two terms should be equal and we have $\varepsilon_c \propto \ln n_b$.

For lattice model, n_b can be well defined. Viewed from geometry, the probability of surface contact for each walk of polymer decreases with the increase of n_b . Considering a nonlattice polymer model, we should use a general value which can describe the probability of surface contact. For a monomer near the surface as shown in Figure 6(b), the surface contact probability can be roughly characterized by a dimensionless ratio between attraction range σ and mean bond length $\langle b \rangle$ of polymer. σ is the thickness of attractive layer. The attraction range fraction $f = \sigma/\langle b \rangle$ is then suitable for a nonlattice polymer model. We have $\sigma = 1$ in all the three models we mentioned, while the mean bond length $\langle b \rangle$ varies from 1 for $n_b = 6$ to 1.46 for $n_b = 26$, and to 2.89 for $n_b = 108$. The dependence of ε_c on f is presented in Figure 6b. We find ε_c decreases linearly with the interaction range fraction f in the range we studied. If the concept f is suitable for nonlattice flexible polymer models where both σ and $\langle b \rangle$ can vary with model, we expect the result can also describe the adsorption behavior of nonlattice flexible polymer models.

TABLE I

The Critical Adsorption Point ε_c and Exponents for Polymer Models of Different Bond Vector Number n_b or Interaction Range Fraction f on the Simple Cubic Lattice

n_b	f	ε_c	ϕ	δ
6^{20}	1	0.29	0.54	1.78
26	0.685	0.62	0.52	1.63
108^{22}	0.372	0.93	0.49	1.75

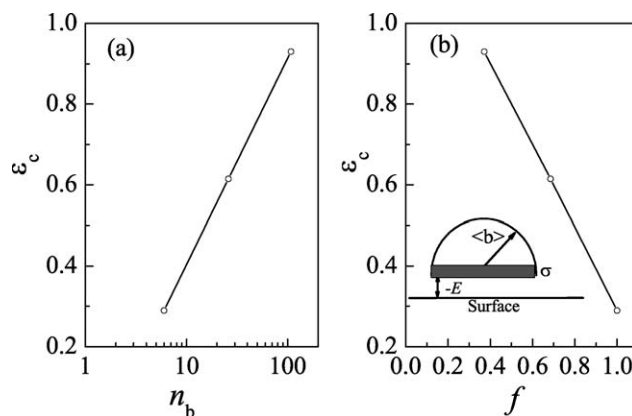


Figure 6 Plot of the critical adsorption point ε_c versus coordination number n_b (a) and attraction range fraction f (b) for different polymer models on the simple cubic lattice. The inset shows a monomer near the surface has an attractive layer σ while it can visit half sphere with radius $\langle b \rangle$.

CONCLUSIONS

Dynamic Monte Carlo simulations are carried out for a bond fluctuation polymer chain model on simple cubic lattice with one end grafted to a flat interacting surface. Conformational properties of the tethered chain are dependent on the temperature. The finite-size scaling law determines the CAP $T_c = 1.625$, and exponents $\phi = 0.52$ and $\delta = 1.63$. The ratio $\langle R^2 \rangle_z / \langle R^2 \rangle_{xy}$ is constant at the CAP. Our results provide alternative ways to determine the CAP. We find the asphericity parameter $\langle A \rangle$ is also independent of chain length at T_c . Interestingly, we find that the mean square end-to-end distance $\langle R^2 \rangle$ reaches minimum at T_c . Thus T_c can be easily determined from experiment without knowing the chain length exactly. Comparing the adsorption behaviors of different lattice chain models on the simple cubic lattice with bond vector number $n_b = 6, 26$, and 108 , we find a simple relation $E/k_B T_c \propto \ln n_b$, but ϕ and δ are roughly independent of n_b . To extend our results to nonlattice polymer models, we introduce the attraction range fraction f and we find ε_c decreases with the increase in f .

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