

MONTE CARLO STUDY ON THE CRITICAL ADSORPTION POINT OF BOND-FLUCTUATED POLYMER CHAINS TETHERED ON ADSORBING SURFACES*

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Abstract The behavior of three-dimensional bond fluctuation model chains tethered on an adsorbing flat surface was simulated by the Monte Carlo method. The dependence of the number of surface contacts M on the interaction strength ε and the chain length N was investigated by a finite-size scaling law $M = N^\phi[a_0 + a_1 N^{1/\nu} \kappa + O((N^{1/\nu} \kappa)^2)]$ for ε near the critical adsorption point ε_c , i.e., $\kappa \equiv (\varepsilon - \varepsilon_c)/\varepsilon_c$ closes to 0. The critical adsorption point was estimated to be $\varepsilon_c = 0.93$, and the exponents $\phi = 0.49$ and $1/\nu = 0.57$.

Keywords: Critical adsorption; Polymer chain; Bond fluctuation model; Scaling; Monte Carlo.

INTRODUCTION

The adsorption of polymers on surfaces is relevant to many technological applications and biological processes. Therefore, it has attracted extensive studies experimentally and theoretically and continued to receive intense interest. It is well known that a single chain adsorbed on an attractive surface exhibits a phase transition from a desorbed state to an adsorbed state when the adsorption strength ε of the surface increases beyond a critical value ε_c ^[1–6]. The critical adsorption strength is named as the critical adsorption point (CAP). Scaling laws for a variety of quantities below, above and at the CAP were developed by Eisenriegler, Kremer and Binder (EKB)^[2]. For example, when a chain of length N goes from a desorbed state to an adsorbed state, the energy of the chain E , which is in proportional to the number of surface contacts M via $E = -M\varepsilon$, changes from $E/N \sim \text{constant}$ to $E/N \sim N^{-1}$. And at the critical adsorption point, E is expected to scale with $E \sim N^\phi$, where ϕ is the crossover exponent.

Numerical studies, including exact enumeration^[7], the scanning method^[4, 5], and the multiple Markov chain method^[8] have been performed to determine the location of the CAP and the crossover exponent ϕ for self-avoiding walk (SAW) chains. The values reported are however not completely in agreement with each other and are still under debate^[9]. The disagreement can be traced to different methods used for determining the CAP and the crossover exponent.

Meirovitch and Livne studied the CAP for SAWs in simple cubic lattice with Monte Carlo simulations using the scanning method^[4]. They relied on the asymptotic behavior of the energy close to ε_c . They divided a chain into three consecutive sub-chains ($N = 20\text{--}60$, $60\text{--}170$, $170\text{--}350$), calculated ϕ_j in $E \sim N^{\phi_j}$ for each sub-chain j separately. They obtained $\varepsilon_c = 0.291 \pm 0.001$, where the values of ϕ_j was same, $\phi = 0.530 \pm 0.007$, for three different sub-chains.

Recently Descas *et al.* explored the values of ε_c and ϕ using four different methods^[9]. The polymer chain model they used is a three-dimensional (3D) bond fluctuation model (BFM) which is also a SAW model chain on simple cubic (SC) lattice. They found two sets ($\varepsilon_c = 1.01$, $\phi = 0.59$) and ($\varepsilon_c = 0.98$, $\phi = 0.50$) are good

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candidates. Especially, in their double logarithmic plot of M/N versus N , they didn't observe the bending of curves for $0.98 < \varepsilon_c < 1.05$, which indicating all the values in this range are possible candidates for CAP. The results showed the crossover exponent ϕ was very sensitive to the precise location of the CAP ε_c , which implied that simultaneous determination of ε_c and ϕ may not give the true location of CAP.

In this paper, the phase transition of 3D BFM polymer chain is investigated using the finite-size scaling method. The number of surface contacts M depends on the chain length N and interaction energy strength ε by a finite-size scaling relation: $M = N^\phi f(N^{1/\nu}(\varepsilon - \varepsilon_c)/\varepsilon_c)$. The finite-size scaling relation can describe the behavior of at and near CAP and also describe the asymptotic behavior $\varepsilon \ll \varepsilon_c$ and $\varepsilon \gg \varepsilon_c$. We estimated the value of, ε_c , ϕ and ν from the scaling relation.

SIMULATION METHODS

Our simulation system is embedded in the SC lattice. A polymer chain of length N is comprised of N self-avoiding identical monomers. In the BFM^[9, 10], each monomer of the polymer is represented by a cubic unit with eight nodes, all lying on the vertexes of the SC lattice. There are 108 possible 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 by all other vectors which follow from them through SC point-group operations. The simulated box is a cuboid with size L_x , L_y and L_z in x , y , and z directions, respectively. Periodic boundary conditions are considered in x and y directions, while in z direction there is an infinite impenetrable surface locating at $z = 1$. Polymer chain lengths studied are in the range of $N = 20$ to 300. In the simulation, we use a large simulation box with size $L_x = L_y = L_z = 600$ for all chain lengths. The size of box is much larger than the chain length N , so that the size effect on the simulation results is negligible.

Since we want to study the influence of the wall, we let the first monomer of the chain be tethered at the center of the $z = 1$ layer, as it has been considered also in previous works^[9, 11, 12]. The dynamics is realized by local moves only. In a local move, a randomly chosen monomer attempts randomly a step to a nearest neighbor position along one of the main axes. The move is rejected if one of the nodes comes to lie on an occupied vertex, if the new bond vectors do not all belong to the set of the 108 allowed ones, or if the new position crosses hard walls. Any polymer monomers that are located on the $z = 1$ layer are considered to be adsorbed to the surface. For the adsorbed monomers, an attractive polymer-surface interaction, $-\varepsilon$, is applied. We adopt the standard Metropolis algorithm in the process of chain configuration relaxing, which implies that a monomer located on $z = 1$ layer jumps to $z = 2$ layer in a probability

$$p = \exp(-\varepsilon / k_B T) \quad (1)$$

k_B is the Boltzmann constant, and T is the temperature. $k_B T = 1$ in this work.

To avoid the correlation between two configurations, we measure chain's statistical properties at regular interval time $\tau = 2N^{2.2}$ MCS, which is in the same scale as the relaxation time at CAP for BFM chain^[9]. The time unit, MCS, is one Monte Carlo step during which $N-1$ trial moves are attempted because the first monomer is tethered on the layer $z = 1$. We use 2000 independent runs, and each run costs for 500 τ . The results are thus averaged over one million independent configuration samples.

RESULTS AND DISCUSSION

For continue phase transitions, like paramagnetic to ferromagnetic transition in Ising mode^[13], Z2 like phase transition in XY and Coulomb gas model systems^[14, 15], order parameter is dependent on the system size and temperature. Square magnetization M^2 is often referred as order parameter for Ising model. Near the critical temperature, it can be expressed to second order of small variable $(T - T_c)L^{1/\nu}$

$$M^2(T, L) = L^{-2\beta/\nu} (a_0 + a_1(T - T_c)L^{1/\nu} + O((T - T_c)^2 L^{2/\nu})) \quad (2)$$

where L is the system size and β and ν are two exponents^[15].

For the adsorption of polymer, the number of monomers in contract with surface M plays the role of an order parameter^[9]. As the natural size of the polymer chain is the chain length N , we replace the system size L in Eq. (2) by the chain length N and replace temperature by the interaction^[16]. Thus we get

$$M = N^\phi f(N^{1/\nu} \kappa) \quad (3)$$

with $\kappa \equiv (\varepsilon - \varepsilon_c)/\varepsilon_c$, here the term N is adopted from EKB^[2]. Near the CAP ($\kappa = 0$), we obtain

$$M = N^\phi (a_0 + a_1 N^{1/\nu} \kappa + O(N^{2/\nu} \kappa^2)) \quad (4)$$

by expanding $f(N^{1/\nu} \kappa)$ to second term since $N^{1/\nu} \kappa$ is small.

From the scaling form (4), we can see that, at the critical adsorption point ε_c , the order parameter M has the best power law behavior:

$$M = a_0 N^\phi \quad (5)$$

While the order parameters M at interaction below ε_c and above ε_c , different behaviors present since the second term $a_1 N^{1/\nu} (\varepsilon - \varepsilon_c)/\varepsilon_c$ in the scaling form (4) changes sign when the interaction ε varies from $\varepsilon > \varepsilon_c$ to $\varepsilon < \varepsilon_c$.

We plot the dependence of the number of surface contacts M on the chain length N in lg-lg scale at different interactions ε , $\varepsilon = 0.88, 0.90, 0.92, 0.94, 0.96, 0.98$, in Fig. 1. The different behaviors for the interaction ε changes from $\varepsilon > \varepsilon_c$ to $\varepsilon < \varepsilon_c$ are clearly seen in Fig. 1: concave upwards curves at large ε ($\varepsilon = 0.96, 0.98$) and convex curves at small ε ($\varepsilon = 0.88, 0.90$).

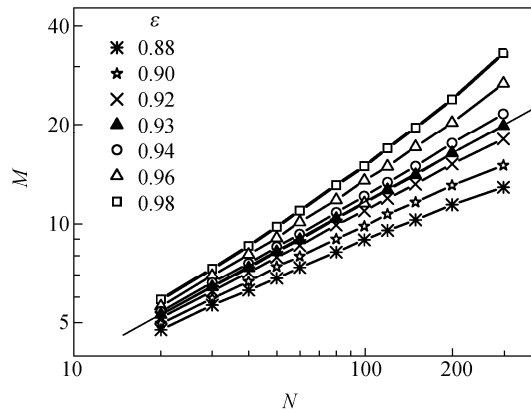


Fig. 1 lg-lg plot of the number of surface contacts M versus chain length N . Concave upwards curves are found at large $\varepsilon = 0.96$ and 0.98 and convex curves at small $\varepsilon = 0.88$ and 0.90 ; The solid line at $\varepsilon = 0.93$ is the best fit for linear fitting.

Therefore, the CAP ε_c locates in the interaction region $(0.92, 0.94)$. We then simulated the dependence of M on N at interaction $\varepsilon = 0.93$. The results for $\varepsilon = 0.93$ is also presented in Fig. 1. We find that at $\varepsilon = 0.93$ the simulation data have the best linear fit, *i.e.* the standard division from the linear fit is minimum at $\varepsilon = 0.93$. Taken into account the statistical error, we estimated that the CAP $\varepsilon_c = 0.93 \pm 0.01$. The slope of the lg-lg curve at $\varepsilon = 0.93$ gives $\phi = 0.49 \pm 0.01$. The value of ϕ is in agreement with results obtained by other papers where $\phi = 0.5$ was derived^[8, 17, 18].

To obtain the parameters $1/\nu$ in Eq. (4), we plot the $MN^{-\phi}$ versus κ as κ close to 0 in Fig. 2(a) with the parameters $\varepsilon_c = 0.93$ and $\phi = 0.49$. Near the CAP, these curves can be approximately expressed by a second order polynomial $MN^{-\phi} = c_0 + c_1 \kappa + c_2 \kappa^2$. Based on Eq. (4), the value c_1 should be proportional to $N^{1/\nu}$. From the lg-lg plot of c_1 versus N shown in Fig. 2(b), we obtain $1/\nu = 0.57$.

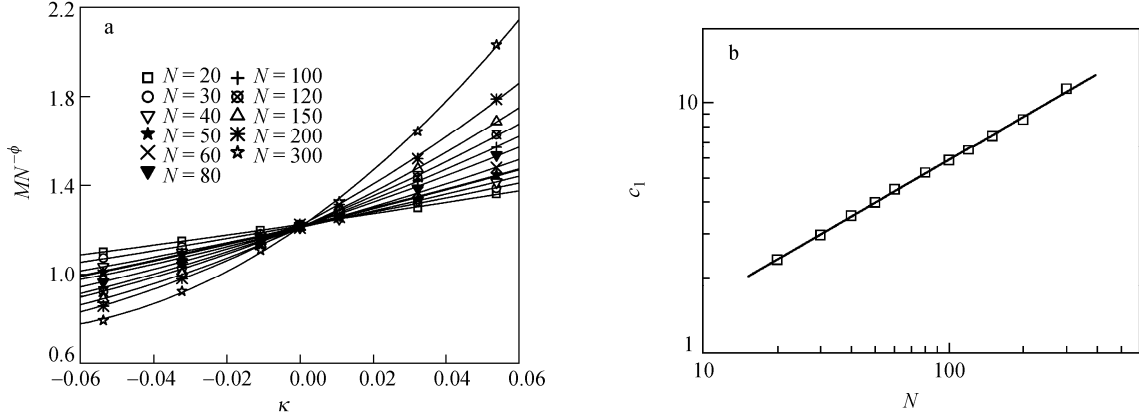


Fig. 2 Plot of $MN^{-\phi}$ versus κ (a) and lg-lg plot of c_1 versus N (b)

Figure 3 presents the dependence of $MN^{-\phi}$ on $N^{1/\nu}(\varepsilon - \varepsilon_c)/\varepsilon_c$ for chain length N from 20 to 300 near ε_c . All data collapse very well, indicating that the finite-size scaling relation Eq. (4) is very good to describe the behavior of adsorbed chains near the critical adsorption point ε_c .

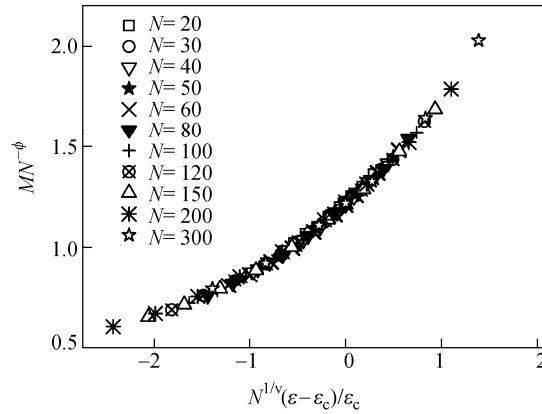


Fig. 3 $MN^{-\phi}$ as a function of $N^{1/\nu}(\varepsilon - \varepsilon_c)/\varepsilon_c$ at ε close to ε_c
Parameters used are: $\varepsilon_c = 0.93$, $\phi = 0.49$ and $1/\nu = 0.57$.

Giving $\varepsilon_c = 0.93$, $\phi = 0.49$ and $1/\nu = 0.57$, we investigate the behavior at ε far from ε_c , i.e. $\varepsilon \gg \varepsilon_c$ and $\varepsilon \ll \varepsilon_c$. The asymptotic relation is estimated in Fig. 4. The simulation data can be expressed approximately by $y \approx x^{0.84}$ for $\varepsilon \gg \varepsilon_c$ and $y \approx x^{-0.87}$ for $\varepsilon \ll \varepsilon_c$. Then we obtain $M \propto N^{0.97}$ for $\varepsilon \gg \varepsilon_c$ and $M \propto N^0$ for $\varepsilon \ll \varepsilon_c$. It is interesting to find that both limits are in good agreement with the scaling analysis of EKB where $M \propto N^1$ for $\varepsilon \gg \varepsilon_c$ and $M \propto N^0$ for $\varepsilon \ll \varepsilon_c$ were expected^[2].

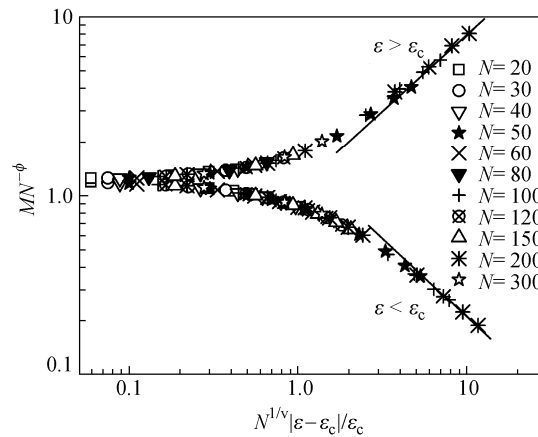


Fig. 4 lg-lg plot of the scaling function $MN^{-\phi}$ versus $N^{1/\nu}|\varepsilon - \varepsilon_c|/\varepsilon_c$ for $\varepsilon > \varepsilon_c$ and $\varepsilon < \varepsilon_c$

CONCLUSIONS

In the present work, we reported an alternative way to determine the critical adsorption point. The finite-size scaling analysis method was applied to describe the behavior of single tethered SAW chains at adsorbing surfaces. By using the scaling $M = N^\phi(a_0 + a_1N^{1/\nu}(\varepsilon - \varepsilon_c)/\varepsilon_c + O(N^{2/\nu}(\varepsilon - \varepsilon_c)^2/\varepsilon_c^2))$ for the number of surface contacts M when interaction ε is close to the CAP ε_c , we estimated the critical adsorption point $\varepsilon_c = 0.93$, the exponent $\phi = 0.49$ and $1/\nu = 0.57$. We also obtained $M \propto N^{0.97}$ for $\varepsilon \gg \varepsilon_c$ and $M \propto N^0$ for $\varepsilon \ll \varepsilon_c$, that are in agreement with scaling analysis of EKB^[2].

The chain model adopted in the present work is a SAW chain, which is a good model to represent chains in good solvents. The finite-size scaling analysis method may also be suitable to describe the critical behavior of chains in theta solvent. It is known that behaviors of a chain in theta solutions are similar to random walk (RW) or nonreversible random walk (NRRW) chains. The value of CAP is 0.182 for RW chains and 0.223 for NRRW chains in cubic lattice^[19]. But for chains in poor solvent, one should also take into account the long-range monomer-monomer attraction besides the self-avoiding interaction and monomer-surface interaction. Thus the critical behaviors of chains in poor solvent will be dependent on the property of solvents. So, whether the finite-size scaling analysis method can be applied to describe the critical behavior of chains in poor solvents deserves further studies.

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