Effects of surface roughness on adsorbed polymers

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(Received 26 September 1990; accepted 30 November 1990)

Polymer chains adsorbed on rough impenetrable surfaces have been investigated analytically and by simulations. The cases of physical and chemical roughness of surfaces are identified and their distinctive effects on the adsorption characteristics are studied. For the chemically rough surface the adsorption temperature is depressed by an amount proportional to the concentration of the impurities. A polymer adsorbed on a physically rough surface can be interpreted using the analogy to a one-dimensional electron in a periodic potential. It is shown that at low temperatures the chain is “localized” in one of the wells. Between the localized regime and the unbinding transition point, there exists a “diffusive” regime, where the chain is diffusing by being shared by several potential wells. This regime is equivalent to the conduction band in the electron analogy. In contrast to the case of a flat surface, the unbinding transition of a chain from a periodically rough surface is markedly sharp due to an effective anchoring of the chain in the wells.

I. INTRODUCTION

The phenomenon of adsorption of polymer chains to surfaces is of wide occurrence and has attracted extensive experimental and theoretical investigations. While adsorption of polymers takes place in nature at all kinds of surfaces, viz., planar, spherical, cylindrical, and rough with differing extent of roughness, most of the theoretical attempts have focused on planar surfaces. Only recently, attempts were made to understand the effect of local curvature on the adsorption characteristics. In practice the surface roughness is random. The roughness can arise from physical or chemical origins. In the case of physical roughness the local curvature of the surface is a random variable (see Fig. 1). Such a surface can be modeled as consisting of “hills” and “valleys” made up of protrusions of spheres or cylinders of appropriate curvatures at different spatial locations. In the situation of chemical roughness certain regions of the surface (either planar or physically rough) have different affinity for the polymers compared to the rest of the surface (see Fig. 1). While there have not yet been controlled experiments to study the effect of surface roughness, there have been some theoretical studies focusing on the properties of the adsorbed state on periodically rough surfaces. There is also one study dealing with adsorption on a fractal surface. The basic physical origin of the criterion of adsorption of polymer chains is the competition between the gain in potential energy obtained by the monomers by binding to the attractive surface and the loss in chain entropy associated with the reduction in the number of possible chain configurations of the adsorbed chains in comparison with that of free chains.

When a surface is rough there are three principal physical effects to be taken into account. (i) The space available for a chain to assume various configurations is larger near the top of a hill when compared to the bottom of a valley so that entropy consideration alone will lead to preferential adsorption at the hills. (ii) The number of contacts per chain with the surface will be more in the valley than on the hill. Therefore, energy consideration alone will lead to preferential adsorption in the valleys. (iii) The potential interaction between the monomers and the surface is dependent on the local curvatures which in turn affects the boundary conditions used in determining the adsorption characteristics. This subtle effect can sway the competition between the above first two effects in favor of adsorption to either valleys or hills depending on the local curvature and the nature of the surface potential. In the spirit of the mean field argument with the ground state dominance approximation, it has been shown by Ball et al. that for the pairwise additive, van der Waals-type power law interactions between the surface and monomers the adsorption is preferentially in the valleys; on the other hand, adsorption will be on the hills if the dielectric mismatch between the surface material and the polymer solution is sufficiently large.

Let us now consider a rough surface with root mean square amplitude variation of order $z_0$ and characteristic horizontal length $\lambda$ for surface fluctuation. If both $z_0$ and $\lambda$ are much larger in comparison with the typical size of the polymer, then a polymer chain near such a surface can be mapped into the problem of a chain in two-dimensional random media as originally discussed by several authors. This situation is also similar to the case of chemically rough surface where the impurities are nonadsorbing. Here, the locations corresponding to the chemical impurities or the steep hills introduce an effective attraction between monomers by essentially denying the monomers to occupy such locations. This then leads to a shrinkage of the polymer chains. Furthermore, we expect the adsorption to be harder due to the presence of the impurities with the consequent suppression of the critical adsorption temperature.

If the roughness is not so wild as described above, we can fruitfully learn about the influences of surface roughness on the adsorption behavior by considering periodic fluctuations.
of the surface from a flat plane such as

\[ z = z_0 \cos\left(\frac{2\pi x}{\lambda}\right) \cos\left(\frac{2\pi y}{\lambda}\right) \quad (1) \]

where \( z \) is the local height of the surface with respect to a reference plane and \( x \) and \( y \) are the coordinate axes in the plane perpendicular to \( z \). Such an attempt was made first by Hone, Ji, and Pincus21 who modeled the rough surface as a sinusoidal cylindrical grating geometry, \( z = z_0 \cos(\frac{2\pi y}{\lambda}) \), and performed detailed calculations for the adsorption of an infinitely long Gaussian chain with the ground state dominance approximation assuming that the periodically varying rough surface is transparent allowing the chain to adsorb on both sides of the interface. The above assumptions of the model enabled Hone et al.21 to explicitly consider different regimes of \( z_0 \) and \( \lambda \) with respect to the thickness \( \delta \) of the adsorbed layer. For the cases \( \delta > z_0, \lambda \), (but \( z_0/\lambda < \infty \)), \( \lambda > z_0, \delta \), and \( z_0 > \lambda > \delta \), when the surface variations are small, \( \delta \) is only slightly smaller than the thickness \( \delta^* \) for the flat surface for the same attractive potential. On the other hand, for \( \delta > z_0 > \lambda \) and \( z_0 > \delta > \lambda \), \( \delta \) is proportional to \( \delta^* \lambda / z_0 \) and \( (\delta^* \lambda)^{1/2} \) respectively and therefore is smaller than \( \delta^* \). The effect of excluded volume between chain segments on these results were studied by Ji and Hone.30 It remains to be seen how much of these predictions get modified by the curvature dependence of the realistic potentials from the surface.

In the present work, we study the influence of both the physical and chemical roughness on the adsorption characteristics of an isolated chain using scaling arguments and Monte Carlo simulation. The scaling analysis and the mapping of the adsorption problem to an electron in a potential field is addressed in Sec. II. The models and the algorithm used in the present simulations are described in Sec. III. Results are presented and discussed in Secs. IV and V, respectively for the chemically and physically rough surfaces. The final section contains the major conclusions of this investigation.

II. ELECTRON ANALOGY AND SCALING

Among the many mathematical formulations of the adsorption of polymer chains to a surface, the simplest is the propagator method introduced by Edwards and reviewed by de Gennes32 and Wiegel.33 Representing the polymer chain as a continuous curve of random-walk statistics without any monomer–monomer excluded volume interaction, the probability distribution function \( G(\vec{r}, \vec{r}'; N) \) for the chain of contour length \( L(= N\lambda) \) where \( \lambda \) is the Kuhn length \( \lambda \) to have its ends at \( \vec{r} \) and \( \vec{r} \) is given by the Edwards path integral,

\[
G(\vec{r}, \vec{r}'; N) = \int_{\vec{r}(0)}^{\vec{r}(L)} D[\vec{R}(s)] \exp\left[-\frac{3}{2\beta} \int_0^L ds \left(\frac{d\vec{R}(s)}{ds}\right)^2 - \beta \int \frac{d^2 s}{s^2} V[\vec{R}(s)]\right].
\]

(2)

Here \( R(s) \) is the position vector of the arc length variable \( s \) (0 < \( s < L \)), \( V(r) \) is the interaction energy between a polymer segment at \( r \) and the surface, \( \beta = 1/k_B T \) with \( k_B \) denoting the Boltzmann's constant and \( T \) the absolute temperature. The integral Eq. (2) can be replaced exactly by the Schrödinger-like equation

\[
\left(\frac{\partial^2}{\partial N^2} - \frac{\partial}{\partial N} - \frac{\partial^2}{\partial \vec{r}^2} + \beta V(\vec{r})\right)G(\vec{r}, \vec{r}'; N) = 0.
\]

(3)

Using the bilinear expansion of \( G \) in terms of the eigenfunctions of the corresponding differential operator we get the "time-independent Schrödinger equation"

\[
\left[ -\frac{\partial^2}{\partial \vec{r}^2} + \beta V(\vec{r})\right] \Psi_m(\vec{r}) = E_m \Psi_m(\vec{r}).
\]

(4)

where

\[
G(\vec{r}, \vec{r}'; N) = \sum_m \Psi_m(\vec{r}) \Psi_m(\vec{r}') e^{-N E_m}.
\]

(5)

For a flat surface, the above equation for \( \Psi_m(r) \) reduces to a one-dimensional problem, \( \Psi_m(z) \), where \( z \) is the distance in the perpendicular direction from the surface at \( z = 0 \). \( \Psi_m(z) \) is determined using the de Gennes boundary condition

\[
c = \left[\frac{\partial}{\partial z}\ln\Psi\right]_{z=0}.
\]

(6)

In fact, the logarithmic derivative defines an "extrapolation length" \( \delta^* \) characterizing the evolution of \( \Psi \) which varies rapidly in the region of the attractive potential of the surface, but is constant for large \( z \), matched by

\[
\Psi(z) \sim e^{-z/\delta^*}
\]

(7)

with \( \delta^* \sim 1/c \).

It is also possible to show that when \( V(r) \) is short ranged, then \( \beta V \) can be replaced by \( \delta \delta(z) \). Thus, the problem of adsorption of a polymer chain is analogous to the binding of an electron to a potential well. The kinetic energy of the electron corresponds to the entropic term arising from the connectivity of the chain and potential energy of the well corresponds to the attractive potential experienced by the monomer from the surface.

For values of \( \beta V \) smaller than a critical value \( \beta \), \( V \), there are no bound states for Eq. (4). Now all \( E_m \) are positive and \( \Psi_m(z) \) are oscillating for all \( z \). This corresponds to the unbound state of the polymer. If \( \beta V > \beta \), \( V \), the potential has at
least one bound state with \( E_m < 0 \) corresponding to the adsorbed chain. Now, in the limit of infinitely long chains \( N \to \infty \), it is possible to assume that only the ground state dominates. In this mean field limit, the eigenfunctions and eigenvalues of the ground state and hence the statistical weight factor \( G \) can readily be determined. When \( V \) is short-ranged, the ground state \( \Psi_0 \) is proportional to \( e^{-\frac{c}{N^2} s^2} \) and the monomer concentration profile is
\[
\rho(z) = NV_0^2 \rho_0(z) - Ne^{-2c/\pi^2 z^2}
\]
Thus, \( \delta^* \) is the thickness of the adsorbed layer for the planar surface.

In fact, in the asymptotic limit of \( N \to \infty \) and \( T \to T_c \) (\( = 1/k_B T_c \)), \( c \) is the only parameter representing the short ranged surface potential. The pseudopotential \( c \) is proportional to \( (T - T_c)/T_c \). \(^{9,10,32} \) Hence, the thickness of the adsorbed layer \( \delta^* \) varies with temperature as
\[
\delta^* \sim \frac{1}{cT - T_c} \text{for the adsorption of a Gaussian chain to a planar surface. The same result can simply be obtained by the following well known scaling argument.} \(^{32} \) Assuming that the Gaussian chain is adsorbed to the planar surface with thickness \( \delta^* \) and the monomer density in the adsorbed layer is uniform, the free energy, \( \beta F \), can be written as
\[
\beta F = \frac{N}{(\delta^*)^2} - \frac{|c|N}{\delta^*},
\]
where the first term represents the entropy loss due to the confinement of \( N \) segments within a thickness of \( \delta^* \) and the second term corresponds to the gain in energy due to the contact of \( N/\delta^* \) monomers with the surface. The optimum value of \( \delta^* \) which minimizes \( F \) is given by
\[
\delta^* \sim \frac{1}{|c|}
\]
which is the same result as Eq. (9). We now proceed to discuss the effect of surface roughness.

A. Chemical roughness

Here we consider a planar adsorbing surface containing \( n \) impurities located at \( \vec{R}_i \). The impurities are taken to repel the polymer via a two-body pseudopotential \( c_i \gg c \). For this situation the surface potential appearing in Eq. (2) can explicitly be written as
\[
\beta V[\vec{R}](s) = c \left[ 1 - \sum_{i=1}^{n} \delta(\vec{R}_i(s) - \vec{R}_i) \right] \times \delta(\vec{R}_i(s)) + c_i \sum_{i=1}^{n} \delta(\vec{R}_i(s) - \vec{R}_i) \times \delta(\vec{R}_i(s)),
\]
where \( \vec{R}(s) \) is decomposed into the \( z \)-component perpendicular to the surface \( \vec{R}_z(s) \) and the \( x,y \)-component parallel to the surface \( \vec{R}_p(s) \). For the case of the quenched disorder on the surface treated here, it is straightforward to extend the replica calculation of Refs. 23 and 28 for the presence of adsorption energy \( c \). Instead of giving the details of the replica calculation we present the much simpler scaling argument with the same final results. By simply confining a Gaussian chain to a two-dimensional plane with impurities randomly distributed the chain is shrunk due to the effective attractive potential created by the repulsive interactions between the polymer segments and the quenched impurities. \(^{24-30,34} \) For two dimensions, the root mean square end-to-end distance \( R_h \) of the chain depends on the impurity density \( v \) according to \(^{23,25,28-30} \)
\[
R_h \sim \left\{ \frac{N^{1/2}}{v^{1/2}} \right\}^{1/2} + N^{3/2} v^{1/2} R_h.
\]
The scaling form of the free energy of a chain confined in a two dimensional plane with impurities, in the limit of \( vN \to \infty \), is \(^{24,29} \)
\[
F \sim \frac{N}{R_h^2} + N v \delta R_h.
\]
Combining this free energy with the adsorption free energy [see Eq. (10)] for a layer of thickness \( \delta \) we get for the total free energy
\[
F \sim \frac{N}{\delta^2} \left[ \frac{|c|N}{\delta^*} + \frac{N}{\delta^*} + \frac{N}{\delta^*} \right] + N v \delta R_h,
\]
where \( F \) is now written for only \( N/\delta \) segments which are in the parallel plane. Here \( R_h \) is the chain extension on the surface. Minimizing \( F \) with respect to both \( \delta \) and \( R_h \), the optimum values of the layer thickness and the chain extension parallel to the surface can readily be obtained. If the impurities on the surface actually stick out as poles and have spatial extensions beyond the typical size of the polymer then the minimization procedure at each layer parallel to the surface gives
\[
\delta = \frac{1}{c - v} \text{ and } R_h \sim v^{-1/2}.
\]
This is represented in Fig. 2(a). On the other hand, if the height of the impurities is less than the layer thickness \( \delta \), then a ‘mushroom-like’ configuration as portrayed in Fig. 2(b) is expected. Here the layer thickness \( \delta \) is the height of the mushroom and obeys Eq. (15a). The core of the mushroom obeys the same law as Eq. (15b), while the width of the cap of the mushroom must be the standard result of the radius of gyration of a Gaussian chain in two dimensions, \( R_g \sim N^{1/2} \).

FIG. 2. Chemical roughness: Polymer chain on an adsorbing surface with repulsive barriers.
It must be noted that the result of Eq. (15a) is independent of the height of the impurities. Since \( c \approx T_c - T \) is the adsorption energy per segment and vanishes at the adsorption critical point in the absence of impurities, we infer from Eq. (15a) that the critical temperature for adsorption is lowered by the presence of the impurities

\[
T_c(v) = T_c(v = 0) - v,
\]

where the numerical prefactor of the term linear in \( v \) is unknown. Therefore, it is harder to adsorb a Gaussian chain to a chemically impure surface than for a pure flat surface. Based on the above arguments the lowering of the critical temperature is expected to be linear in the impurity density.

### B. Physical roughness

We now consider the adsorption of a chain to a physically rough surface which is modeled with a checker-board corrugation [see Fig. 3(a)]. In view of the symmetry in the \( x \) and \( y \) directions for this model surface, we can readily anticipate the qualitative effects by considering one dimension and the consequences of the periodic potential wells. Considering the \( x \)-direction alone for simplicity, the eigenfunctions \( \psi_m(x) \) of Eq. (4) follows for the checker-board corrugation as

\[
\left[ -\frac{d^2}{dx^2} + BV(x) \right] \psi_m(x) = E_m \psi_m(x),
\]

where \( BV(x) \) is of the form shown in Fig. 3(b). In view of the analogy between polymer adsorption and the case of an electron near a potential it is not surprising that this is exactly the same as the well known Kronig-Penney model encountered in understanding the electronic properties of a metal. It is readily found from standard textbooks that such a model would support a conduction band where the electron is delocalized among all potential wells. Therefore, we expect (compare Sec. 5) a regime of “conduction band” in the analogous problem of polymer adsorption where the chain is shared by several potential wells and is delocalized. For sufficiently low temperatures there are bound states where the polymer is captured inside one of the potential wells and is localized. For higher temperatures, there is a band of states corresponding to the above mentioned conduction band regime where the chain is shared by several potential wells and is delocalized. Finally, for sufficiently high temperatures, the chain is desorbed. Therefore, we should expect to see the presence of a distinct regime where the chain is bound by several wells when the surface is periodically rough. This must be contrasted with the planar surface where such a regime does not arise.

### III. MODELS AND SIMULATION TECHNIQUE

In the present investigation, we study the adsorption characteristics and the unbinding of a polymer chain from a rough surface as the temperature is increased. We have used the Monte Carlo simulation method.

Consider a cubic lattice of unit spacing. For the case of chemical roughness, the side of this cube at \( z = 0 \) is taken as the impenetrable planar surface with linear dimensions \( L_x = L \) and \( L_y = L \). Each lattice site of the square lattice of this surface is occupied by a chemical impurity with probability \( u(0 < u < 1) \) according to the site percolation model. The occupied sites constitute the impurities which repel the polymer segments infinitely and the unoccupied sites attract the polymer with an adsorption energy \( \epsilon \) per segment for each site. The polymer chain is modeled as a self-intersecting chain of \( N \) beads and is placed on the cubic lattice. The initial configuration of the chain is generated by a random growth process where the first monomer is placed on an adsorbing site of the surface. Subsequent chain configurations are created using the well known kink–jump technique and using periodic boundary conditions in \( x \) and \( y \) directions. For a given configuration the number of beads \( n \) in contact with the surface is found so that the contact energy of the configuration is \( \epsilon n \). New configurations are accepted using the standard Metropolis rules summarized below.

The case of physical roughness is modeled as an impenetrable surface with a “checker-board” corrugation as depicted in Fig. 3a. To each site \((i,j)\) on a square lattice we assign a discrete local height \( u(i,j) \) according to patterns as depicted in Fig. 3a, as an example, where the numbers represent \( u(i,j) \). The width of the potential well is denoted by \( \lambda-\beta \) and the periodicity by \( \lambda \) as depicted in Fig. 3b. The polymer chain consisting of \( N \) beads is embedded on a cubic lattice. Multiple overlap of the chain with itself is allowed (“ideal” polymer). The initial configuration of the chain is generated by a random growth process where the first monomer is placed at a minimum of the surface. (Simulations starting with chains where one end is placed on a maximum of the surface do not differ from the former case with regard to results.) Subsequent configurational sampling has been performed using well known kink–jump and reptation techniques. A bead of the chain is defined to have a contact if one of the six neighboring sites is occupied by the surface.
Appropriate statistical weights are assigned to the configurations by Metropolis rules: attempts are accepted if (1) the moved segment does not touch or penetrate the surface, and if (2) \( \exp\left[ \epsilon(n_{\text{new}} - n_{\text{old}})/T \right] > \eta \), where \( 1 > \eta > 0 \) is a random number, \( T \) is the temperature, and \( \epsilon(n) \) is the contact energy of a given chain configuration. Obviously, the maximum number of contacts for a bead in the present model is three.

Since in the present model, there is always a nonzero probability for the chain to unbind from the surface at all nonzero temperatures, which is larger the higher the temperature and the smaller the chain length is, we have suppressed this effect by imposing the condition that at least one of the beads of the chain must be attached to the ("sticky") surface. It is commonly supposed that this technique should not alter the critical properties of a Gaussian chain below the critical ("unbinding") temperature.

**IV. CHEMICALLY ROUGH SURFACES**

Using the Monte Carlo method described in the preceding section, the fraction of beads of the chain \( E/N \) at the adsorbing surface is monitored as a function of temperature for different values of \( N \) and \( v \). We have studied Gaussian chains with \( N < 900 \) and for values of \( v = 0, 0.1, 0.2, \) and 0.3. The case of \( v = 0 \) is the situation of the pure adsorbing surface. For values larger than the percolation threshold, \( v > v_c = 0.41 \), there are only islands of adsorbing sites. In the present study we have not considered the regime of \( v \) close to \( v_c \), where the spatial correlation of the impurities play a significant role.

The typical behavior of the temperature dependence of \( E/N \) for chains of different \( N \) is given in Fig. 4(a) for \( v = 0.3 \). The behavior for other values of \( v \) is qualitatively similar. For a given value of \( N \), the adsorption energy per bead, \( E/N \), decreases monotonically as the temperature is increased and suddenly in a narrow temperature range around a certain temperature \( T_\alpha(N) \) the chain becomes unbound to the surface. The value of \( T_\alpha(N) \) depends on the chain length. The true critical adsorption temperature ought to be obtained by extrapolating the values of \( T_\alpha \) for infinitely long chains. Since an average over sufficiently large number of realizations of the randomness on the surface is necessitated in the current problem, extrapolation to \( N \to \infty \) demands considerable computer time. Since our effort in the present study is to extract the salient qualitative features arising from the surface roughness, we deal with chains of only finite lengths. We find \( T_\alpha(N) \) for a chemically impure planar surface to be suppressed when the impurity density is increased. This result is presented in Fig. 4(b) where \( T_\alpha(N) \) is plotted against \( v \) for various \( N \). We find that the suppression of the adsorption temperature \( T_\alpha \) is linearly proportional to \( v \) as predicted by the scaling argument presented in Sec. II.

**V. PHYSICALLY ROUGH SURFACES**

In the case of the physically rough surface, the adsorption must be expected to be strongly modified, because at sufficiently low temperature the polymer chain is bound in one of the potential wells. The question of how the chain unbinds from a rough surface is considered in the next subsections.

For simplicity, we consider the extreme case of a rough surface with square wells distributed according to a checkerboard (Fig. 3a). The adsorption energy indicates, according to Fig. 3a, essentially three different regimes which are characterized by three different slopes.

**A. Localized and diffusive regimes**

The first regime ("localized regime", compare Fig. 5b), where the adsorption energy starts from \( E/N = 2.5 \) at \( T = 0 \) (this value is due to the corners and edges at the bottom of a well with contact numbers three and two, respectively), and ends at the onset of a "diffusive regime" with a weaker slope. The decrease of \( E/N \) is due to the increasing desorption of chain segments from the corners and edges of the well.

Of course, one might suspect that this picture is an artifact of having various contact numbers reflecting the rather artificial nature of modeling a rough surface. This is true only from a superficial point of view. It can be shown that this picture is only quantitatively altered if, for example, the energetic preference of the corners is suppressed by attributing only one-third for the contact energy. This is represented by the broken line in Fig. 5b. Therefore, it should be...
FIG. 5. (a) Adsorption energy per monomer, $E/N$, versus temperature for various chain lengths $N$. (b) Adsorption energy $E/N$ versus temperature. The dotted line corresponds to the "uncorking" transition at $T_i$ from a single well. The line at $\lambda = \infty$ corresponds to the classical unbinding transition from a flat surface.

emphasized that the presence of various local contact numbers inside the well, as there are one, two, and three, as compared to the outer flat surface with contact number one, is a consequence of modeling "discrete" local curvatures of a "discrete" model for rough surfaces and is a necessary prerequisite in order to study curvature effects on the adsorption of a polymer chain.

The transition between the "localized regime" and the "diffusive regime", as indicated in Fig. 5b, is not sharp, but rather similar to a continuous crossover. It is justified by the diffusion coefficient $D$, which is depicted in Fig. 6a. In the "localized regime", $0 < T < 4$, the chain is essentially immobile and the chain is localized in a particular well. The diffusion coefficient is practically zero, which means that within a typical Monte Carlo time of $10^6$ the chain remains in one of the wells. At higher temperatures, in the "diffusive regime", the chain will try to explore all space accessible due to the consequent entropy gain, but is thereby subjected to the attractive potentials arising from the neighboring wells. This leads to a diffusion of the chain guided essentially by the distribution of the wells. The diffusion coefficient $D$ depends strongly on the temperature and on the chain length. Close to the transition temperature, where the chain tends to unbind from the surface and which we have estimated according to Fig. 5a to be $T_c = 5.1 \pm 0.05$, the Monte Carlo data seem to be in agreement with an exponential law,

$$D \sim \exp(\tau N^{1/2})$$

(18)

where $\tau = (T_c - T)/T_c$ (Fig. 6b).

The distinction between a "localized" and a "diffusive" regime is also supported by the observation of how the polymer chain escapes from a single, isolated well of the same width and depth. At low temperatures, in the localized regime, the chain does not "see" the neighboring environment and hence exhibits the same behavior for $E/N$ as in the present model for a rough surface. By raising the temperature, the chain tries to explore the environment by increasing its entropy at the cost of adsorption energy. At high enough temperatures, but still below the classical unbinding temperature $T_a = 5.48$ from a flat surface, the chain must move freely on the surface, but with much lower adsorption energy (as shown in Fig. 5a and 5b for $\lambda = \infty$) as compared to the rough surface. The transition between the localized state and the classical adsorbed state is very sharp within a temperature interval $\Delta T < 0.1$, as depicted in Fig. 5b by the dotted line, and resembles a kind of "uncorking" of the chain from its well. This "uncorking" transition, at $T_i \approx 4.0$ for large $N$, may be used as a definition for the crossover temperature between "localized" and "diffusive" regimes in the present model for a rough surface. It should be noted, that we expect $T_i$ to be dependent on the curvature, the width, and the depth of the well.
In the diffusive regime, the energy exhibits a weaker dependence on the temperature (Fig. 5a and 5b), because the chain is shared by several wells. The extension of the chain is characterized by the square of the parallel component of the end-to-end distance $R_f^2/\lambda$, which is depicted as a function of the temperature distance $T_c - T$ in Fig. 7a. One observes at low temperatures, in the localized regime, $R_f^2$ to be independent of $N$, whereas for $T_c - T < 1$ in the diffusive regime, a crossover to Gaussian statistics, according to $R_f^2/N = f(\tau N^{1/2})$ is observed (Fig. 7b). Since the $R_f^2/\lambda^2 > 1$ in the diffusive regime, the chain must be extended over various wells.

The distribution of the polymer among various wells is characterized by the density profile $n(z)$ of the polymer chain perpendicular to the surface, which is depicted in Fig. 8. For temperatures in the diffusive regime, say $T = 4.8$ and 5.0 in Fig. 5, the corresponding density profiles exhibit two maxima, one at $z < u$ and a second one at $z > u$. This indicates that the chain is clearly separated in one dense part inside the wells and a second part of lower density on the “flat” surface. From this observation, one must conclude that the fraction of the chain inside the wells serve as transient anchors for the chain during its diffusion on the rough surface. The minimum of $n(z)$ at $z \approx u$ indicates a depletion of the chain close to the “flat” surface at $z = u$.

B. Transition regimes

At $T_c = 5.1 \pm 0.05$, the adsorption energy exhibits a sharp transition from about $E/N = 1.3$ to 0.2 (for $N = 600$) within a narrow temperature interval of $\Delta T = 0.1$. This transition is still below the classical unbinding temperature of $T_o = 5.48$ for a flat surface. This would imply that infinitely long chains are still “classically” adsorbed between $T_c$ and $T_o$, like on a flat surface. On the other hand, one should expect $T_o$ to be decreased to $T_o' < T_o$ due to the dilution of adsorption sites on the “flat” surface (compare also Sec. IV). If in addition $T_c > T_o'$ an immediate unbinding at $T_c$ is implied. The resolution of the issue of the various relations between $T_c$, $T_o$, and $T_o'$ is not attempted in the present work. Nevertheless, the pronounced sharpness of the transition at $T_c$ for the rough surface must be noted in contrast to the transition at $T_o'$ for a flat surface.

One might consider the question of whether the markedly sharp “uncorking” transition from a single well at $T_c$, as discussed in Sec. A and indicated by the dotted line in Fig. 5b, is related to the transition at $T_c$, and in particular, whether a “cooperative uncorking”, i.e., a simultaneous detachment from many wells at $T_c$, could provide an adequate description of the transition. In fact, the density profile of the polymer chain indicates (compare in Fig. 8, $n(z)$ at $T = 5.0$) that even close to $T_c$ the majority of chain segments is still effectively anchored in the wells indicating a discontinuous release from the wells at $T_c$, which is in contrast to the classical continuous unbinding from a flat surface. Of course, the sharpness of the transition is related to the extreme “curvature” of the square well, and we expect the sharpness to be less pronounced for potentials of the type given by Eq. (1).

In order to better clarify the type of transition, we have examined the fluctuation of the adsorption energy near the transition point. The specific heat

$$ C/N = \left( \frac{E}{NT^2} \right)^2 - \left( \frac{E}{NT^2} \right)^2 $$

exhibits a maximum around the “unbinding” transition temperature $T_c = 5.1$ for large $N$ (Fig. 9). Since the specific heat
1. PI

FIG. 9. Specific heat per monomer, $C/N$, vs temperature for same parameters as in Fig. 5(a).

is a continuous function of $T$, one might be inclined to consider this as an indication of a continuous phase transition. In fact, one can show that in the vicinity of the transition point, the Monte Carlo data of the specific heat seem to be in agreement with a finite size scaling form $C \sim N^{\alpha} f(\tau N^\phi)$ with $f(x) \sim x^{-\alpha}$ for $x \gg 1$ and $\tau = (T_c - T)/T_c \ll 1$, hence asymptotically $C \sim \tau^{-\alpha}$ with $\phi = 1/2$ and $\alpha = 2$. Although this implies that desorptions from a physical rough surface is a continuous transition, the present data are not conclusive.

So far, we have reported and discussed results for a particular realization of a periodically rough surface, $u = 20$, $\lambda = 6$, and $\beta = 3$. Of course, it is of interest to investigate, at least qualitatively, the effects on the phase transitions by changing these parameters. We have restricted our attention to the behavior of $E/N$ by changing $\beta$, $u$, and $\lambda$. This is presented in Figs. 10a, 10b, and 10c.

In Fig. 10a, the effect of changing the depth $u$ of the well is shown. One observes that with increasing $u$ the diffusive regime is also increasing, which is due to the increasing ability of the chain to be shared by several wells, but thereby maintaining a high adsorption energy while still increasing its entropy. We have not undertaken to estimate the limiting value of $T_c$ for $u \to \infty$ and $N \to \infty$ at fixed $\lambda$ and $\beta$.

In Fig. 10b, the influence of the separation of the wells is demonstrated. The width and the depth of the wells are the same as discussed above, $\lambda - \beta = 3$ and $u = 20$, respectively. The pattern of the distribution of the wells are still of a checkerboard type, except that the wells are separated now by $\beta = 6$. The results for $E/N$ as depicted in Fig. 10b are very similar to those for $\beta = 3$ as presented in Fig. 5a, except that the sharpness of the transition for a shorter chain is weaker due to the intervention of larger "terraces" between the wells.

In Fig. 10c, the effect of the width $\lambda - \beta$ of the potential on the adsorption energy $E/N$ as a function of the temperature is demonstrated. Clearly, $E/N$ is more depressed for $\lambda = 12$ than for $\lambda = 6$, and the "discontinuity" of $E/N$ at $T_c$ is less pronounced the larger the width of the well is. Of course, this is due to the decreasing contact probability of a segment with the walls inside the wells if the width of the wells becomes larger.

VI. SUMMARY AND CONCLUSIONS

In summary, we have investigated the effects of the surface roughness on adsorbed ideal polymers. We have distinguished between the cases of physical and chemical roughness of surfaces and their distinctive effects on polymers in the adsorbed phase and at the unbinding transition point.

For chemically rough surfaces, where a planar surface contains a certain concentration of nonadsorbing impurities, the transition temperature is depressed by an amount proportional to the concentration of the impurities. This result
is supported by a Flory-type argument and by Monte Carlo simulations.

For physical rough surfaces, the adsorbed state of an ideal polymer is very different and more complex as compared to that in the case of a flat homogeneous surface. In the present work, the rough surfaces have been modeled by checker board corrugations. The adsorbed state of a polymer exhibits three different regimes. At low temperatures the chain is localized in one of the wells. At higher temperatures, there exist a diffusive regime, where the chain is diffusing by being shared by several wells. This regime is equivalent to the conduction band of the polymer-analog model of a one-dimensional electron in a periodic potential. The unbinding transition of a chain from the rough surface is marked sharp due to the strong transient anchoring of the chain in the wells during its diffusion on the surface. These conclusions are supported by Monte Carlo estimates of various quantities, i.e., adsorption energy, specific heat, density profile, parallel component of the radius of gyration, and diffusion coefficient.

Excluded volume effects have not been considered in the present work. Preliminary investigations have indicated that the essential aspects given above, e.g., crossover from localized to diffusive regime and discontinuous unbinding transition due to anchoring effects, are still prevailing although quantitative details are different.

Curvature effects resulting from different types of surface corrugation have not been pursued in the present study. First results on periodic “egg-tray” models, which are certainly more realistic, do not alter our basic conclusions given above. One observation for these models is, that the “discontinuity” of the unbinding transition becomes less pronounced the shallower the roughness is. In fact, this is in qualitative agreement with the corresponding observation in the present checker-board model (Fig. 10c), where the variation of the width of the wells (at constant height) reveals a similar effect.

The influence of random surface corrugations on the adsorption characteristics is of practical importance. Whether these conditions are of fundamental relevance with respect to our present understanding of the effects of surface roughness on adsorbed polymers, is still an open question. A simple extension of the present lattice model of a rough surface to its analog random version would be the “Manhattan model,” where the local height of the surface is a random variable between a lower and an upper value. First, Monte Carlo results reveal quantitative, but no qualitative differences as compared to the present periodic model. Of course, more extensive investigations are necessary.

ACKNOWLEDGMENT

M. Muthukumar gratefully thanks the support from the National Science Foundation Grant No. DMR9008192.