Effect of surface undulation on polymer adsorption

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We study the adsorption of a long, flexible polymer (ideal or self-avoiding chain) interacting with a rough surface via a finite-range attraction. Within the Edwards equation approach, we develop a variational method to find the segmental distribution and the free energy of an adsorbed chain. As adsorption becomes strong, the segments tend to be localized within the valleys rather than above the hills of the undulating surface, resulting in a decrease of adsorption thickness. Consequently, the surface undulation enhances adsorption in the case of a strongly adsorbed chain whereas the undulation suppresses it for a weakly adsorbed one, since the enhanced entropic repulsion is dominant over the attraction from the surface. Considering the surface with undulation characterized by a Gaussian correlation as an example, we find an optimal correlation length at which the adsorption becomes the strongest and a critical correlation length below which desorption is induced.

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I. INTRODUCTION

Polymer adsorption on surface is a subject of scientific interest that has extensive practical applications. For example, it is important in surface adhesion, surface protection, wetting, stabilization of colloids such as inks, coatings and paints, and in numerous biological applications. Since surfaces are usually rough, there have been numerous theoretical [1–13], simulational [14–16], and experimental [17,18] studies on the effect of surface roughness on polymer adsorption. Most theoretical studies, dominantly done for the model of contact interaction between polymer segments and surface, have shown that the higher degree of roughness of surface induces the stronger adsorption of polymer. The surfaces, such as sinusoidally undulating ones [1–3], completely random ones characterized by fractal dimension [4–6], a "randomized" de Genne's boundary condition [8], other corrugated surfaces [7,14], and stochastic distributions of binding sites [9], have been considered in the work. Recently, this trend of enhancement of adsorption is also observed in an experiment on nanoscale patterned glass surfaces designed by thermal evaporation of gold [18].

There are two types of arguments for the enhancement of adsorption. One is that the randomness gives rise to an area increase of the attracting surface [1,4,6]. This effect is pronounced when the polymer conformational entropy is neglected as in the case of a Brownian particle floating on a binding surface. Another argument is that a polymer prefers to be confined on a concave surface rather than on a flat surface due to the less entropic cost [4,9]. For a *relatively short chain* this argument seems to be reasonable, as is supported by a Monte Carlo simulation of the polymers adsorbing to a surface with undulation periodicity (wavelength) comparable to the polymer radius of gyration [15]. In this case, the polymer conforms itself to be within a valley of the undulating surface due to increase of both entropy and attraction. Related with the enhancement of adsorption, the previous studies also have shown that the polymer layer thickness decreases on a rough surface than on a flat surface [4,8]. All these effects of enhanced adsorption are reasonable in the case of short chain strong adsorption. For weak adsorption of a long chain, however, more care needs to be taken in properly evaluating the effect of entropy. Depending upon surface shapes, the polymer enjoys more entropy outside [12] or inside [13] of the curved surface where there is more space for polymer fluctuation than in the case of flat surface. For weak adsorption, the undulation-enhanced entropy reduction can compete with the attraction and can also affect the adsorption-desorption transition, which has been seldom investigated. Here we study these aspects of flexible polymer adsorption in the case where chain length is much longer than characteristic length of the surface randomness. Also we confine ourselves to the case where polymer segments and surface interact with a *finite-range* attraction and a hard-wall repulsion. This model of finite-range interaction, compared with the contact attraction model mostly used, can be relevant to a variety of technological and biological situations.

For the cases mentioned above, the authors including one of us found that the membrane undulation enhances the Helfrich-like entropic repulsion between the polymer and membrane, and enhances desorption (suppresses adsorption) [11]. It was shown that for small undulation, the adsorption-desorption transition temperature is lowered below that for the flat surface by a factor proportional to the surface area increase. The key physics is that a long flexible polymer chain sees a greater steric barrier near a surface with undulation. Although this aspect of entropic reduction is physically reasonable, surface-polymer interaction induced by the undulation has not been considered in the work. Another limitation of the work lies in its basic ansatz on chain conformation on the surface, which states that the segments conform affinely on the undulating surface [10,11].

In this paper we extend the previous work [11] to explore and understand, in a systematic manner, the contrasting ef-

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fects of surface undulation, viz., the enhancement of adsorption of a strongly adsorbed polymer and of desorption of a weakly adsorbed one. First, we incorporate the undulation-induced effect on surface-polymer interaction and analyze the results in detail. The interaction is modeled by a pairwise additive continuous potential between a polymer segment and a surface element supplemented by the boundary condition (BC) to describe the polymer impenetrability to the surface. Consideration of this hard-wall BC is important for implementing the Helfrich-like interaction [11] which is not incorporated by the delta-function-like contact potential or the de Gennes' boundary condition adopted by many investigators [1–10]. Second, we modify the ansatz above mentioned in a way to incorporate the optimal distribution of the segments by minimizing free energy of the chain. For the cases where both the attraction range and the correlation length are longer than amplitude of surface undulation, we derive analytical expressions, giving numerical results. We not only explain the avowed undulation-induced mechanism of adsorption, but also discover other novel effects, of which the most notable is that the desorption is induced when the characteristic (correlation) length of surface randomness is below a critical value.

This paper is organized as follows. We present, in Sec. II, a general formulation of a long flexible polymer interacting with an undulating surface. Here we adopt the Edwards propagator approach of an ideal chain and the ground-state dominance approximation. To tackle the Edwards equation for the undulating surface, we develop a variational method using the modified ansatz mentioned above. In Sec. III, we consider an interaction model given by a Yukawa potential and a surface model described by Gaussian height correlation function. Using these potential and surface models, several physical quantities are examined by numerical plots, and analytical results for limiting behaviors. We analyze the polymer layer thickness, and the concentration ratio of the segments within a valley to that above a hill of the undulating surface. By investigating the free energy per segment, we explain the affect of undulation on the adsorption-desorption transition. Finally, we analyze the above quantities with the excluded volume effect (EVE) between polymer segments incorporated in a mean field approximation.

II. POLYMER INTERACTING WITH AN UNDULATING SURFACE: GENERAL FORMULATION

A long, flexible polymer of N segments interacting with a surface is described by the Edwards equation [22,23],

$$-\frac{\partial}{\partial N}G_N(\vec{r},\vec{r}_0) = \mathcal{L}G_N(\vec{r},\vec{r}_0). \tag{1}$$

Here $G_N(\vec{r},\vec{r}_0)$ is the Green's function descriptive of the probability density for finding the last segment at the position at $\vec{r}$ given the initial segment at $\vec{r}_0$ (Fig. 1). $\mathcal{L}$, which will be called the Edwards operator, is

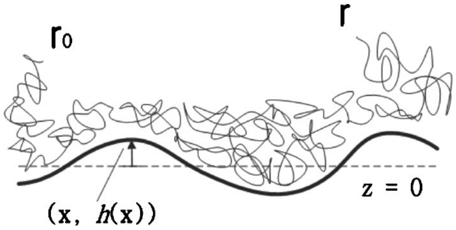

FIG. 1. A long flexible polymer chain is adsorbed on an undulating surface. $\vec{r}_0$ and $\vec{r}$ are the positions of initial and final segments, and $[\vec{x},h(\vec{x})]$ is a position on the undulating surface.

$$\mathcal{L} = -\frac{l^2}{6}\nabla^2 + \beta U(\vec{r}), \tag{2}$$

where the first term represents the entropic contribution of the conformational free energy and the second yields the internal energy due to the interaction. l is the segmental(Kuhn) length and $\beta = T^{-1}$ with $k_B = 1$. $U(\vec{r})$, the effective potential energy of polymer(per segment located at $\vec{r}$), is assumed to vary slowly over the segmental length l [19]. This includes the interaction with the surface and the other intersegment interaction that is not incorporated in chain connectivity. Here we first neglect the excluded volume interaction between segments in our formulation, and then estimate its effect within a simple approximation.

The adsorbed polymer is long enough to uniformly cover over a surface of projected area $A = L^2$, where L is much longer than the characteristic length of surface roughness. We first consider the case of a completely flat surface, described by a two-dimensional coordinate $\vec{x} = (x,y)$. With the potential reduced as $U_0(z)$, where z is the vertical distance to the surface, the Green's function is given as

$$G_N^0(\vec{r},\vec{r}_0) = \frac{1}{A}\sum_k e^{-Nf_k}\phi_k(z)\phi_k(z_0). \tag{3}$$

Here $\phi_k(z)$ is the normalized eigenfunction of the one-dimensional (1D) Schrödinger-like equation

$$\mathcal{L}_0\phi_k(z) = f_k^0\phi_k(z), \tag{4}$$

where $\mathcal{L}_0 = -(l^2/6)(\partial^2/\partial z^2) + \beta U_0(z)$. If discrete, bound(adsorbed) states exist, the summation in Eq. (3) is dominated by the ground state with the eigenfunction $\phi_m(z)$ and eigenvalue f_m^0; for the long chain ($N \gg 1$) polymer we consider

$$G_N^0(\vec{r},\vec{r}_0) \approx \frac{1}{A}e^{-Nf_m^0}\phi_m(z)\phi_m(z_0). \tag{5}$$

Complication arises when the surface is not flat but random. Let us consider the randomness represented by position-dependent undulation $h(\vec{x})$ relative to a flat surface given by $\vec{x} = (x,y)$ (Fig. 1). Since thermal fluctuation of the surface, even if any, is much slower than that of the polymer, we make an approximation of the Born–Oppenheimer type that the polymer conforms as if the surface has fixed undulation. In the ground-state dominance approximation

$$G_N(\vec{r},\vec{r}_0) \approx e^{-Nf_m}\psi_m(\vec{r})\psi_m(\vec{r}_0) \tag{6}$$

the f_m and ψ_m represent the adsorbed (ground) state eigenvalue (negative) and eigenfunction perturbed by the presence of the undulation $h(\vec{x})$:

$$\mathcal{L}\{h(\vec{x})\}\psi_m(\vec{r}) = f_m\psi_m(\vec{r}). \tag{7}$$

In the ground state dominance approximation, the segment distribution of the adsorbed chain is given by $N\psi_m^2$ while the chain end distribution is proportional to ψ_m [19]. The free energy change divided by k_BT per segment upon adsorption, called dimensionless free energy, is given by f_m as can be seen from the polymer partition function obtained upon intergrating the Green's function over $\vec{r}$ and $\vec{r}_0$ [19]. In order to obtain f_m and ψ_m, the central objectives of our study, via Eq. (7), we develop a variational method as below.

The presence of the surface undulation affects neighboring polymer segments in two ways. First, the surface restricts the polymer conformation via a boundry condition (BC) on the surface, e.g., for a impenetrable, flat surface at $z=0$,

$$\phi_m(z)|_{z=0} = 0, \tag{8}$$

which we will adopt in this work. Such polymer impenetrability to the surface is conceivable even in a fluid membrane unless the steric barrier formed by the lipid bilayer assembly is disturbed. The surface undulation has the direct steric consequence of modifying the BC to

$$\psi_m(\vec{r})|_{z=h(\vec{x})} = 0. \tag{9}$$

This along with the form Eq. (5) guides us to make a variational ansatz for ψ_m

$$\psi_m(\vec{r}) = \frac{\mathcal{N}}{A^{1/2}}\phi_m(z-h(\vec{x}))[1+\alpha h(\vec{x})], \tag{10}$$

where α is what we call a "layer thickness parameter" to be determined variationally so as to minimize the free energy, and $\mathcal{N}$ is the normalization constant. The ansatz is an improved version of the earlier one [10,11] which corresponds to the case with $\alpha=0$. It was shown that even the earlier version can adequately describe a certain aspect of surface effect on polymer conformation. In particular, the steric repulsion of Helfrich type is enhanced on the polymer by the undulation of the confining surface owing to the impenetrability BC (10) we impose. The $\alpha \neq 0$ correction on our variational ansatz can incorporate some departure from this strict condition that the chain conforms affinely to the surface. As we will find, the optimal α that minimizes the free energy is usually negative for any adsorbed cases, indicating that the segments are localized preferentially within the valleys (Fig. 2) rather than above the hills of the undulating surface. A direct observable consequence of nonvanishing α is found in the ratio of segmental concentration at $\vec{r}_v=[\vec{x}_v, h(\vec{x}_v)]$ on the valley to that at $\vec{r}_h=[\vec{x}_h, h(\vec{x}_h)]$ with a same height above the hill,

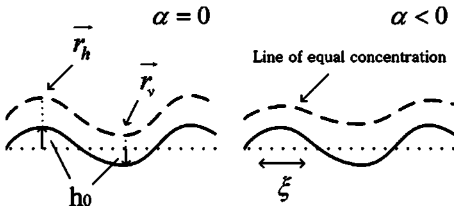

FIG. 2. The solid line is a sinusoidally oscillating surface and the dashed line is a line of equal concentration of adsorbed polymer segments. h_0 is the amplitude of the oscillation and ξ is correlation length of the surface. $\vec{r}_h$ and $\vec{r}_v$ indicate the positions that have the same height from the surface, $z'=z-h(\vec{x})$, above the hill and the valley of the undulating surface, respectively. The line of equal concentration changes by the influence of the layer thickness parameter α. When the α is negative, the concentration within the valley is higher than that above the hill at the same height, i.e., $\rho(\vec{r}_v)/\rho(\vec{r}_h) > 1$.

$$\frac{\rho_v}{\rho_h} = \frac{|\psi_m(\vec{r}_v)|^2}{|\psi_m(\vec{r}_h)|^2} = \left(\frac{1+\alpha h(\vec{x}_v)}{1+\alpha h(\vec{x}_h)}\right)^2. \tag{11}$$

For a sinusoidal surface, Fig. 2, the ratio is evidently shown to be larger than unity if $\alpha < 0$. Also a related quantity is the polymer thickness of adsorption. Considering the polymer-adsorbed surface to be effectively flat, we define the thickness as

$$D = \int_{z>h(\vec{x})} d^3\vec{r}\,\psi_m^2(\vec{r})z, \tag{12}$$

so that the change in thickness induced by undulation is given by

$$\Delta D = \int_{z>h} d^3\vec{r}(\psi_m^2(\vec{r}) - A^{-1}\phi_m^2(z))z = \frac{2\alpha\overline{h^2}}{1+\alpha^2\overline{h^2}}, \tag{13}$$

where the overbar denotes the average over the polymer covered surface, e.g., $\overline{h^2}=(1/A)\int d^2\vec{x}h^2(\vec{x})$. The change in thickness is also negative for $\alpha < 0$. Using the ansatz (10) we find the free energy f_m to be minimized is obtained by

$$\begin{aligned} f_m = \langle\psi_m|L|\psi_m\rangle &\equiv \int_A d^2\vec{x}\int_0^\infty dz'[\psi_m(\vec{x},z')\mathcal{L}(\vec{r})\psi_m(\vec{x},z')] \\ &= K_m + \beta U_m, \end{aligned} \tag{14}$$

where $z'=z-h(\vec{x})$, $K_m=\langle\psi_m|-(l^2/6)\nabla^2|\psi_m\rangle$, and $U_m=\langle\psi_m|U(\vec{r})|\psi_m\rangle$.

K_m, the "kinetic energy" for the undulating case, indicates entropy reduction incurred by confining the segments to the state ψ_m. We find that

$$K_m = \left(\frac{1+\overline{(\nabla_{\mathbf{x}}h)^2}}{1+\alpha^2\overline{h^2}}\right)K_m^0 + \alpha^2\left(\frac{\overline{h^2}K_m^0 + \frac{l^2}{6}\overline{(\nabla_{\mathbf{x}}h)^2}}{1+\alpha^2\overline{h^2}}\right), \tag{15}$$

where $K_m^0=-\int dz\,\phi_m(z)(l^2/6)(\partial^2/\partial z^2)\phi_m(z)$. In the case of $\alpha=0$, the first term on the right of Eq. (15) is the additional steric effect of undulating surface on the confined polymer, which was already obtained [10,11]. The effect of nonvanishing α in the denominators is to reduce the entropic cost of confining the chain segments within the valleys of the undulation below that obtained by assuming the affine conformation.

Another way how the undulation affects the polymer free energy is via its effect on the potential energy which can be expressed by

$$U(\vec{r}) = \int_{z=h(\vec{x})} d^2\vec{r}_s u(\vec{r}-\vec{r}_s). \tag{16}$$

Here $u(\vec{r}-\vec{r}_s)$ represents the interaction between a segment at $\vec{r}$ and the undulating surface per unit area at $\vec{r}_s = \boldsymbol{(}\vec{x}_s, h(\vec{x}_s)\boldsymbol{)}$ (Fig. 1). When the surface is flat, the equation reduces to

$$U_0(z) = \int_{z=0} d^2\vec{x}_s u(\vec{r}-\vec{x}_s). \tag{17}$$

In calculating the potential energy Eq. (16), we first note that surface element area increases due to the undulation are given by

$$\frac{d^2\vec{r}_s}{d^2\vec{x}_s} = \{1 + [\boldsymbol{\nabla}_{\mathbf{x}} h(\vec{x}_s)]^2\}^{1/2}. \tag{18}$$

Then, we have

$$U_m = \int d^3\vec{r}\,\psi_m{}^2(\vec{r}) \int d^2\vec{x}_s \boldsymbol{(}\{1 + [\boldsymbol{\nabla}_{\mathbf{x}} h(\vec{x}_s)]^2\}^{1/2} u[\vec{r} - \vec{x}_s - h(\vec{x}_s)\hat{z}]\boldsymbol{)}. \tag{19}$$

Upon coordinate transformation $\{\vec{x},\vec{x}_s\} \rightarrow \{\vec{x},\vec{\rho}\}$ where $\vec{\rho} = \vec{x}_s - \vec{x}$ and expansion to the second order in h and $\boldsymbol{\nabla} h$ in the bold parentheses $\boldsymbol{(\,)}$ in Eq. (19),

$$U_m = \left(1 + \frac{\frac{1}{2}\overline{(\boldsymbol{\nabla}_{\mathbf{x}} h)^2}}{1+\alpha^2\overline{h^2}}\right) U_m^0 + \frac{1}{1+\alpha^2\overline{h^2}} \int d^2\vec{\rho} \left\{ \frac{1}{2}\overline{[h(\vec{\rho}+\vec{x}) - h(x)]^2} \times \left\langle \left(\frac{\partial^2}{\partial z^2} + 2\alpha\frac{\partial}{\partial z} \right) u(\vec{\rho} + z\hat{z}) \right\rangle_m \right\}, \tag{20}$$

where $U_m^0 = \int dz \phi_m^2(z)\ U_0(z)$, and $\langle \cdots \rangle_m = \int dz \phi_m^2 \cdots$ denoting the average over the state $\phi_m(z)$. It may be noted that the second-order approximation is at its best when the following conditions are met

$$\overline{(\boldsymbol{\nabla}_{\mathbf{x}} h)^2} \approx \frac{\overline{h^2}}{\xi^2} \ll 1, \quad \frac{\overline{h^2}}{a^2} \ll 1, \tag{21}$$

where ξ and a are the characteristic lengths for the surface correlation and interaction respectively which we shall discuss later in detail.

The first term in Eq. (20) with $\alpha = 0$ reflects the enhancement of attraction energy due to the increase in surface area. In expressing the other terms we note that

$$\overline{[h(\vec{x}+\vec{\rho}) - h(\vec{x})]^2} = 2\overline{h^2}(1 - C(\vec{\rho})) \tag{22}$$

where

$$C(\vec{\rho}) \equiv \overline{h(\vec{x}+\vec{\rho})h(\vec{x})}/\overline{h^2(\vec{x})} = \overline{h(\vec{\rho})h(0)}/\overline{h^2} \tag{23}$$

is the normalized height correlation function. Then Eq. (20) is expressed as

$$U_m = \left(1 + \frac{\frac{1}{2}\overline{(\boldsymbol{\nabla}_{\mathbf{x}} h)^2}}{1+\alpha^2\overline{h^2}}\right) U_m^0 + \frac{\overline{h^2}}{1+\alpha^2\overline{h^2}} (\langle V'' \rangle_m + 2\alpha \langle V' \rangle_m), \tag{24}$$

where

$$\langle V^{(n)} \rangle_m = \int dz \phi_m^2(z) \frac{d^n}{dz^n} V(z), \tag{25}$$

and

$$V(z) \equiv \int d^2\vec{\rho}[1 - C(\vec{\rho})]u(\vec{\rho},z), \tag{26}$$

which we call a "screened surface potential."

Now the free energy per segment at equilibrium is obtained by minimizing $f_m = K_m + \beta U_m$. The optimal α that does so is found to be, to the leading order in $\overline{h^2}/a^2$,

$$\alpha_m = -\frac{6}{l^2}\frac{\overline{h^2}}{\overline{(\boldsymbol{\nabla}_{\mathbf{x}} h)^2}} \beta \langle V' \rangle_m \tag{27}$$

and then the minimized free energy per segment f_m, denoted as f hereafter, is

$$f = f_0 + f', \tag{28}$$

$$f_0 = K_m^0 + \beta U_m^0, \tag{29}$$

$$f' = \frac{1}{1+\alpha_m^2\overline{h^2}} \left\{ \left(K_m^0 + \frac{1}{2}\beta U_m^0 \right) \overline{(\boldsymbol{\nabla}_{\mathbf{x}} h)^2} + \beta\overline{h^2}\langle V'' \rangle_m - \frac{6}{l^2}\frac{(\overline{h^2})^2}{\overline{(\boldsymbol{\nabla}_{\mathbf{x}} h)^2}} \beta^2 \langle V' \rangle_m{}^2 \right\}. \tag{30}$$

Each term in f' can be given a reasonable interpretation. The first term in brace represents the reduction of the free energy due to excess area compared with the flat surface given by the nonaffinity ($\alpha \neq 0$) of the segmental distribution. The second and third terms denote the new effects due to the interplay of surface undulation and interaction we will study below. Note that for a weakly adsorbed polymer, $f_0 \approx 0$ or $K_m^0 \approx -\beta U_m^0$. Therefore, the first term (surface area term) in f' tends to yield a net positive contribution to the polymer free energy in the weakly adsorbed state, while the last two terms may counterbalence it depending upon the strength of adsorption and surface randomness. Below we investigate the quantitative details of our predictions (27) and (28), which shows a great variety as a function of the two parameters.

III. THE ANALYSIS OF ADSORBED POLYMER DISTRIBUTION AND FREE ENERGY

To illustrate the points discussed in the preceding section, let us consider a simple model of polymer-surface attraction characterized by its strength and range. A representative example of such a model is the Yukawa potential with a hard core,

$$u(\vec{r}) = \begin{cases} \dfrac{1}{2\pi a}\dfrac{u_0}{r}e^{-r/a}, & r > 0, \\ \infty, & r = 0, \end{cases} \tag{31}$$

where $u_0(<0)$ and a define the interaction (attraction) strength and range. For a flat surface we have

$$U_0(z) = \begin{cases} u_0 e^{-z/a}, & z > 0, \\ \infty, & z < 0. \end{cases} \tag{32}$$

The unperturbed ground state, over which the average $(\langle\cdots\rangle_m)$ are to be taken, is given by

$$\phi_m(z) = CJ_n(S_0 e^{-z/2a}), \tag{33}$$

as obtained from the exact solution of Eq. (4) [20]. Here C is the normalization constant and J_n is the Bessel function of the order n which has to be the largest positive value of ν that satisfies the BC $J_\nu(S_0)=0$. The eigenvalue $f=-\frac{1}{24}(l/a)^2 n^2$ is the adsorption energy per segment in units of T. As the $S_0 \equiv (24\beta|u_0|)^{1/2} a/l$ has to be larger than $j_{01} \approx 2.4048$, the first zero of $J_0(x)$, the T_c is given by

$$T_c = \frac{24|u_0|}{j_{01}^2}\frac{a^2}{l^2}. \tag{34}$$

For the undulating surface, we consider a simple model of height correlation function [21,22],

$$C(\vec{\rho}) = \exp[-(\rho/\xi)^2], \tag{35}$$

where ξ is the correlation length of surface randomness. The screened surface potential $V(z)$, defined by Eq. (26), now takes the form

$$V(z) = U_0(z)\left\{1 - \frac{\sqrt{\pi}}{2}\frac{\xi}{a}e^{(\xi/2a + z/\xi)^2}\,\mathrm{erfc}\left(\frac{\xi}{2a} + \frac{z}{\xi}\right)\right\}. \tag{36}$$

The correlation function Eq. (35), which is the inverse Fourier transform of $|h(\vec{q})|^2/\overline{h^2}$, also determines

$$\frac{\overline{(\nabla_{\mathbf{x}} h)^2}}{\overline{h^2}} = \frac{\sum_{\vec{q}} q^2 |h(\vec{q})|^2}{\sum_{\vec{q}} |h(\vec{q})|^2} = \frac{\int d^2\vec{q}\, q^2 |h(\vec{q})|^2}{\int d^2\vec{q}\, |h(\vec{q})|^2} = 4\xi^{-2}. \tag{37}$$

The advantage of the Gaussian correlation (35) is that it has an interesting connection to a sinusoidally oscillating surface,

$$h(\vec{x}) = h_0 \sin(\vec{k}\cdot\vec{x}). \tag{38}$$

It can be easily shown that it gives

$$C(\vec{\rho}) = \cos(k\rho) \tag{39}$$

if we take the distance ρ along the direction of the wave vector $\vec{k}$. Here the both long and short wavelength (correlation length) limits are identical to those of Gaussian correlation function. In the long wavelength limit $(\xi/a \gg 1)$ we find that

$$C(\vec{\rho}) \approx 1 - \left(\frac{\rho}{\xi}\right)^2 \text{ with } k = \frac{\sqrt{2}}{\xi}, \tag{40}$$

$$V(z) \approx 2\left(\frac{a}{\xi}\right)^2 U_0(z). \tag{41}$$

Also in the short wavelength (correlation length) limit $(\xi/a \ll 1)$, both Gaussian and sinusoidal models yield

$$V(z) \approx U_0(z). \tag{42}$$

Therefore, a sinusoidal surface, which can be easily visualized, can provide a convenient picture for the polymer adsorption on random surfaces in these two limits. Furthermore, the sinusoidal surface, which can be artificially constructed, can facilitate a comparison of our theoretical model with those of experiments and simulations. We use our surface interaction and correlation models to calculate the α and f in detail as follows.

A. The polymer distribution near surface

Equation (27) is rewritten as

$$\alpha_m = -\frac{3}{2}\frac{\xi^2}{l^2}\beta\langle V'\rangle_m, \tag{43}$$

with

$$\langle V'\rangle_m = \int dz\left(-\frac{d}{dz}\phi_m^2(z)\right)V(z), \tag{44}$$

obtained by integrating Eq. (25) by parts with $n=1$, and using the BCs $\phi_m(0)=0$ and $\phi_m(\infty)=0$. The layer thickness parameter α_m, Eq. (43), is in general negative in an adsorbed state, since $V(z)$ is similar to $U_0(z)$ in z dependence [see Eqs. (41) and (42)] and mostly negative for the region where $\phi_m^2(z)$, the concentration of segments in the absence of surface undulation, is a sharply increasing function of z. On the other hand, it is proportional to the effective surface force on a segment, as can be seen in Eq. (25), and thus the α_m tends to be vanish approaching the desorption transition. We will analyze the layer thickness parameter, α_m, as a function of two parameters, adsorption strength $\beta|u_0|$ and correlation length ξ. As the quantities related with α_m, we will analyze the polymer adsorption thickness and the ratio of segment concentration within valleys to that above hills of the undulating surface.

Figure 3 is the plot (solid line) of layer thickness parameter, α_m, as a function of the adsorption strength, $\beta|u_0|$, for the case of $l=1$ nm, $a=5$ nm, $\xi=15$ nm, and $(\overline{h^2})^{1/2} \equiv h_{\mathrm{rms}} = 1$ nm. The choice of these parameters here and hereafter are tentative, as we merely want to see the trends of the phenomena predicted. It shows that α_m is negative with the magnitude increasing monotonically as temperature decreases below T_c. This means that as the adsorption becomes stronger the segments tend to be more concentrated within

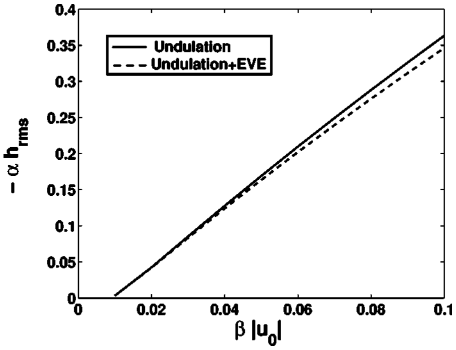

FIG. 3. Polymer layer thickness parameter α_m as a function of adsorption strength, $\beta|u_0|$. The dashed line is the result obtained by including the excluded volume effect (EVE) to be discussed in Sec. IV. Here $l=1$ nm, $a=5$ nm, $\xi=15$ nm, $h_{\text{rms}}=1$ nm, $v=l^3/300$, and $c=1/(8l^2)$.

the valleys than above the hills, because the effect of attraction for segments is dominant over the entropic cost for confinement. This is consistent with an earlier study based on scaling theory where strong adsorption induces a flexible surface to bend toward the polymer while weak adsorption drive the surface to bend away from the polymer [23]. More quantitatively, this behavior is measured by the ratio of concentration at a height within the valley to that at the same height above the hill ρ_v/ρ_h (Fig. 2). For a sinusoidal surface Eq. (38), Eq. (11) yields

$$\frac{\rho_v}{\rho_h}=\left(\frac{1-\alpha_m h_0}{1+\alpha_m h_0}\right)^2, \tag{45}$$

where h_0 is the amplitude of oscillation related with h_{rms} via $h_{\text{rms}}=h_0/\sqrt{2}$. When $\beta|u_0|=0.1$, the case corresponding to strong adsorption, the ratio is $\rho_v/\rho_h\approx 10$ [Fig. 4(a)]. Surface undulation induces the layer thickness D of adsorbed polymer to be thinner than the case of flat surface. The change in the thickness, Eq. (13), induced by the undulation is given by

$$\Delta D=\frac{2\alpha_m {h_{\text{rms}}}^2}{1+{\alpha_m}^2 {h_{\text{rms}}}^2}. \tag{46}$$

In Fig. 5 when $\beta|u_0|$ is 0.1, layer thickness(solid line) decreases to the order of the attraction range. In this case of strong adsorption, layer thickness decreases due to the undulation below that of the flat surface (dotted, dashed, and dot +dashed lines in Fig. 5). The figure shows that the higher undulation induces the thinner layer thickness, indicating the enhanced adsorption by undulation. Figure 4(b) shows thickness change (solid line) is as large as $|\Delta D|\approx 0.65\ h_{\text{rms}}$.

Figures 6(a) and 6(b), the plots of α_m (solid line) vs the surface correlation length ξ, show that α_m approaches to certain plateau values as ξ increases. We have considered both the weak [$\beta|u_0|=0.01$, Fig. 6(a)] and the strong adsorption case [$\beta|u_0|=0.1$, Fig. 6(b)] with fixed values of $l=1$ nm, $a=5$ nm, and $h_{\text{rms}}=1$ nm. The plateau value for $\xi/a\gg 1$ is given from Eq. (27) and (41) as

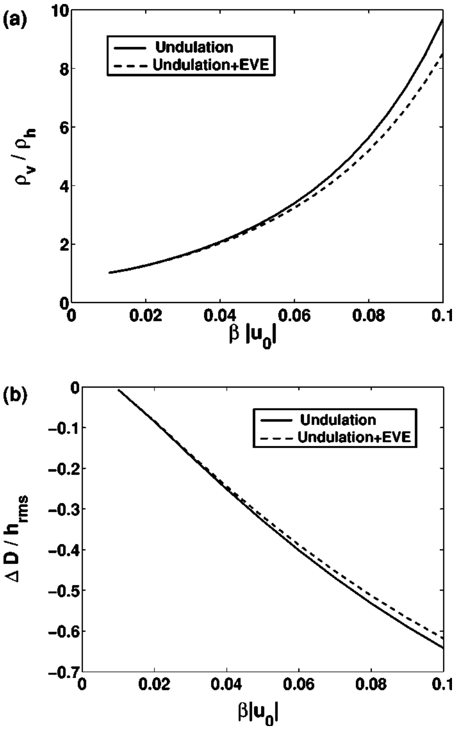

FIG. 4. (a) The ratio of polymer segment concentration at a height within a valley to that at the same height above a hill, and (b) changes of polymer layer thickness, as a function of adsorption strength, $\beta|u_0|$. The dashed line is the result of EVE. The parameter values used are the same as in Fig. 3.

$$\alpha_m \sim -\frac{a}{l^2}\beta|u_0|. \tag{47}$$

As correlation length of the surface increases, entropy loss of a polymer, due to the confinement within valleys, decreases. Thus, in the region of large ξ/a the polymer can be more concentrated within wider valleys owing to the dominant effect of the attraction. This trend appears to be enhanced for the strong adsorption [Fig. 6(b)]. In this case, $\alpha_m h_{\text{rms}}\approx -0.5$, the concentration ratio is $\rho_v/\rho_h\approx 30$ [Fig. 7(a)], and the adsorption thickness change is $\Delta D\approx -0.8h_{\text{rms}}$ [Fig. 7(b)].

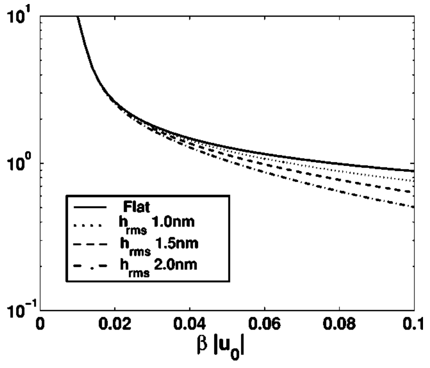

FIG. 5. The linear-log plot of polymer layer thickness as a function of adsorption strength, $\beta|u_0|$, for flat surface and several values of $h_{\text{rms}}\equiv(\overline{h^2})^{1/2}$. Here $l=1$ nm, $a=5$ nm, and $\xi=15$ nm.

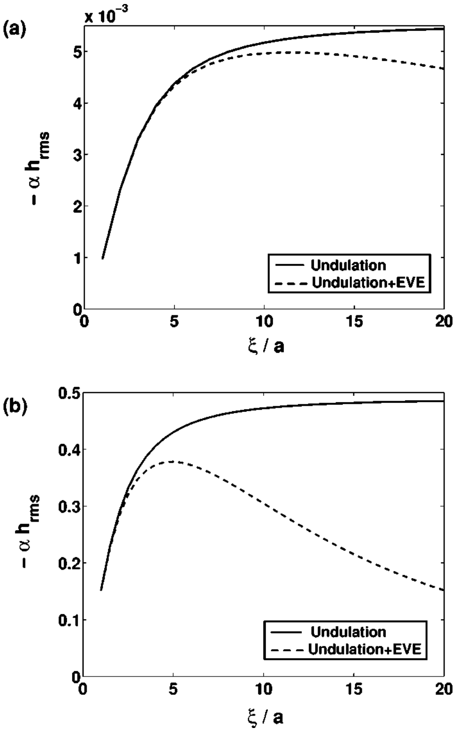

FIG. 6. Polymer layer thickness parameter, α_m, as a function of correlation length, ξ, for (a) weak adsorption ($\beta|u_0|=0.01$) and (b) strong adsorption ($\beta|u_0|=0.1$). Here $l=1$ nm, $a=5$ nm, $h_{\mathrm{rms}}=1$ nm, $v=l^3/300$, and $c=1/(8l^2)$.

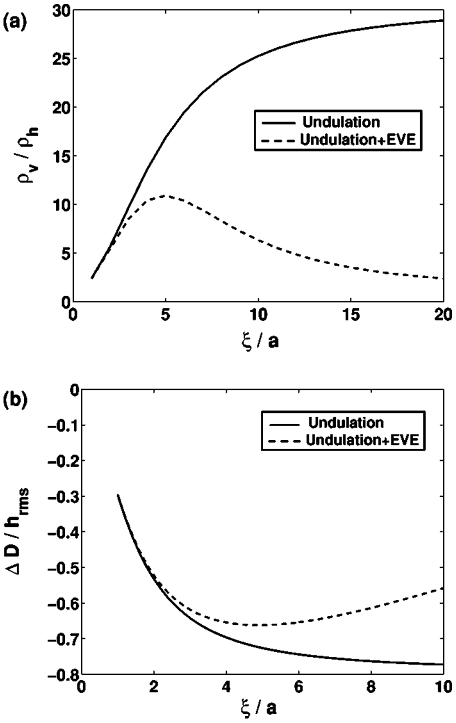

FIG. 7. (a) The ratio of polymer segment concentration at a height within the valley to that at the same height above the hill and (b) changes of polymer layer thickness, as a function of correlation length, ξ, for a strongly adsorbed polymer ($\beta|u_0|=0.1$). The dashed line is the result of EVE. The parameter values used are the same as in Fig. 6.

Such large values of ρ_v/ρ_h and α_m, although can be reduced greatly by the excluded volume effect [dashed lines in Fig. 7(a) and Fig. 6(b)] treated later, could be artifacts of our ansatz that may fail in the limit of large ξ. It should be borne in mind that at the outset we are limiting ourselves to value the ξ which is smaller than the polymer covered distance L. As far as the free energy, which is considered in the next section, is concerned, however, this restriction does not matter, since it approaches to that of flat surface in this limit as it should.

On the other hand, when ξ/a gets much smaller than unity, we have

$$\alpha_m \sim -\frac{\xi^2}{l^2 a}\beta|u_0|, \tag{48}$$

suggesting that α_m tends to be much smaller than the case of large correlation length. This implies that the polymer tends to escape from the narrow valleys driven by higher entropy above the hills rather than to accumulate within the valleys due to the surface attraction.

B. Free energy per segment *f*

The change of dimensionless free energy of adsorption induced by undulation, Eq. (30), is rewritten as

$$f' = \frac{\overline{h^2}}{1+\alpha_m^2\overline{h^2}}\left\{\frac{4}{\xi^2}\left(K_m^0+\frac{1}{2}\beta U_m^0\right)+\beta\langle V''\rangle_m-\frac{3}{2}\frac{\xi^2}{l^2}\beta^2\langle V'\rangle_m{}^2\right\} \tag{49}$$

with $\langle V'\rangle_m$ given by Eq. (44), and

$$\langle V''\rangle_m = \int dz\left(-\frac{d}{dz}\phi_m^2(z)\right)\frac{d}{dz}V(z). \tag{50}$$

The second term in the brace tends to be negative because in our model potential, Eq. (32), $(d/dz)V(z)$ has large positive value for the region of z less than a, where $\phi_m^2(z)$ is a sharply increasing function of z. The last term, representative of intrinsic $\alpha\neq 0$ effect, i.e., preferential localization of segments in the valleys, is always negative, playing a significant role in reducing the free energy for strongly adsorbed polymers.

Let us first study the effect of the undulation on the nature of desorption transition. The transition temperature T_c^0 for flat surface is obtained from the condition $f_0=0$, i.e., $T_c^0=-U_m^0/K_m^0$. Similarly, $f=0$ [Eq. (28)] determines the critical temperature T_c and the desorbed state as well for undulating surface. However, an analytic calculation of T_c is not easy because of the complexity involved in the temperature dependence in the polymer wave function. Instead, numerical plots of free energy can be obtained in order to visualize the changes of critical temperature in several conditions. Figure 8 is the plot of total free energy f for a weakly adsorbed polymer as a function of $\beta|u_0|$ in the case of $l=1$ nm, $a=5$ nm, $\xi=10$ nm, and $h_{\mathrm{rms}}=1$ nm. It shows that the free energy per segment decreases monotonically as temperature decreases in the two cases of flat (dotted line) and undulating surface (solid line). The value of $\beta|u_0|$ where $f=0$ is found to be higher ($\beta_c|u_0|\approx 0.0101$), compared with the case of the

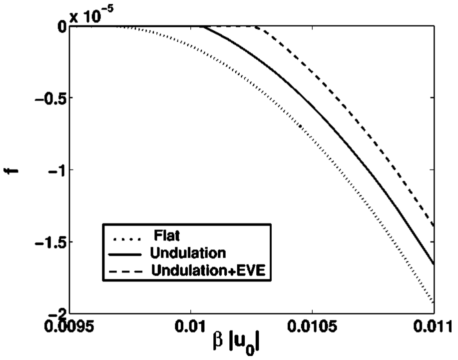

FIG. 8. Dimensionless free energy per segment f for a weakly adsorbed polymer as a function of adsorption strength, $\beta|u_0|$. The value of $\beta|u_0|$ that meets with $f=0$ indicates the critical temperature of adsorption transition. Here $l=1$ nm, $a=5$ nm, $\xi=10$ nm, $h_{\rm rms}=1$ nm, $v=l^3/300$, and $c=1/(8l^2)$.

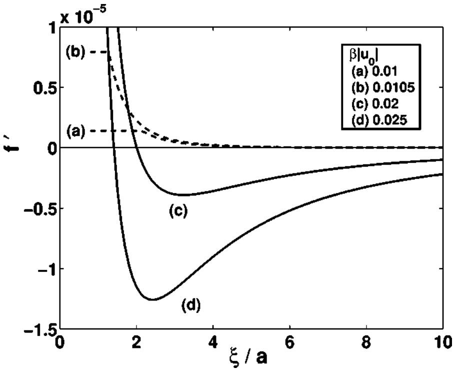

FIG. 10. Dimensionless free energy changes per segment, $f'=f-f_0$, as a function of correlation length, ξ, for weak adsorption and stronger one. Cusps exist where adsorption-desorption transitions occur. The plateaus indicate the desorption state. Here $l=1$ nm, $a=5$ nm, and $h_{\rm rms}=1$ nm.

flat surface ($\beta_c|u_0|\approx 0.0096$), meaning that critical temperature of the adsorption on the undulating surface is lowered. This is because in weak adsorption the entropic effect of enhanced steric repulsion induced by the undulation [11] is larger than the effect of attraction, i.e., f', dominated by the first term in Eq. (49), is positive as shown below.

Consider that the polymer is adsorbed on a flat surface, and then ask what will happen if the surface undulations of various correlation lengths are turned on. Figure 9 is the plot of the free energy change per segment induced by undulation, f', as a function of $\beta|u_0|$ for several values of $\xi=10$, 15, and 20 nm with $l=1$ nm, $a=5$ nm, and $h_{\rm rms}=1$ nm. It shows that the free energy change increases to a maximum in the weak adsorption region, but it drops precipitously as the adsorption strength increases. In the case of $\xi=10$ nm, the value of f' is positive for $\beta|u_0|<0.02$ and negative for $\beta|u_0|$ above. The large decrease of the free energy to negativity mainly comes from the increased attraction reflected in the larger value of $|\alpha_m|$, which makes the segments concentrate within the attracting valleys. As ξ increases to $\xi=15$ and 20 nm, the f' is lowered owing to the suppressed steric repulsion by less confinement. For $\beta|u_0|$ smaller than the critical value $\beta_c|u_0|$, the polymer desorbs with $f=0$. Then, the free energy change due to undulation is given by $f'=-f_0$ [Eq. (28)], which is positive since f_0, the free energy of polymer adsorption on flat surface, is considered to be negative. This means that the polymer can desorb on an undulating surface, although it adsorbs on a flat one. The single desorption line $f=0$ or $f'=-f_0$, independent of the surface correlation, meets adsorption lines ($f<0$) at the cusps, which indicates the adsorption-desorption transition point. From the cusps, we find that the transition temperature is higher for the longer correlation.

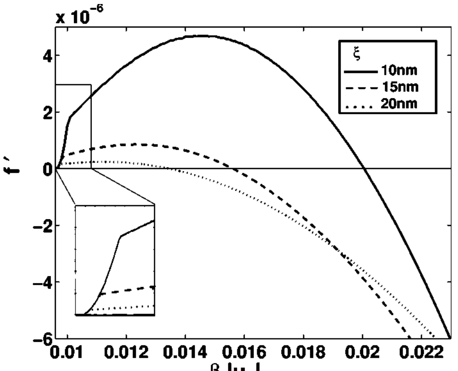

FIG. 9. Dimensionless free energy changes per segment, $f'=f-f_0$, as a function of $\beta|u_0|$ for three values of ξ. Three adsorption curves meet a single desorption curve at cusps where adsorption-desorption transition occurs (inlet). The parameter values used are the same as in Fig. 10.

Figure 10 reveals that free energy change, f', dramatically depends upon the surface correlation length. Dashed lines in the figure show the free energy change for a weakly adsorbed polymer chain ($\beta|u_0|=0.01, 0.0105$). As correlation length ξ decreases, free energy change increases until ξ reaches a critical value ξ_c, a cusp of free energy corresponding to the adsorption-desorption transition point. For the values of ξ smaller than ξ_c, f' approaches $-f_0$, positive value independent of ξ, and thus the adsorbed chain on flat surface ($f_0<0$) becomes desorbed ($f=0$) due to the steric repulsion enhanced by confining the chain within the narrower valleys. The solid lines in the figure show the free energy change for stronger adsorption ($\beta|u_0|=0.02, 0.025$). As ξ/a decreases far below unity, the adsorbed chain on an undulating surface have a free energy change (which is sharply increasing) and tends to be desorbed as in the case of weak adsorption. For $\xi/a\ll 1$, substitution Eq. (42) and Eq. (48) into Eq. (49) yields

$$f' \approx \frac{4\overline{h^2}}{\xi^2}\left(K_m^0 + \frac{1}{2}\beta U_m^0\right) \tag{51}$$

which should be equal to $-f_0$ for the desorption transition. From this and $T_c^0=-U_m^0/K_m^0$, one obtains

$$\xi_c = \sqrt{2}h_{\rm rms}\left(\frac{2T_c - T_c^0}{T_c^0 - T_c}\right)^{1/2}. \tag{52}$$

As ξ/a increases, the free energy change tends to be small on the undulating surface. For $\xi/a\gg 1$, Eq. (41) and Eq. (47) yield

$$f' \approx \frac{4\overline{h^2}/\xi^2}{1+\alpha_m^2\overline{h^2}}\left(f_0 - \frac{3}{2}\frac{a^2}{l^2}\beta^2 U_m^{0\,2}\right). \tag{53}$$

In this region free energy change f' approaches zero like $-\overline{h^2}/\xi^2$. As Eq. (53) suggests, the strong adsorption (free energy reduction) is enhanced by the surface undulation. As its correlation length increases to infinity (with $\overline{h^2}$ finite), f' tends to vanish. This is expected since in this limit the surface becomes flat ($f=f_0$). It is shown that in between two limits there exists an optimal value of ξ_m for which free energy is minimum, i.e., adsorption becomes the strongest. Using the data for solid lines the optimal correlation lengths are about 2–3 times of the attraction range a.

IV. EXCLUDED VOLUME EFFECT

Until now we have neglected the self-avoiding interaction (excluded volume effect) which can appreciably influence polymer distribution at highly concentrated regions. As a consequence, we obtained quite unrealistically high values for ratio of segments within valleys to that above hills for low temperature and large correlation length of surface undulation. In order to assess the additional trends the excluded volume effect (EVE) gives, we develop a simple approximation within our formalism of Sec. II.

The Edwards operator, Eq. (2), is modified to

$$\mathcal{L} = -\frac{l^2}{6}\nabla^2 + \beta U(\vec{r}) + \frac{1}{2}\upsilon\rho(\vec{r}), \tag{54}$$

where $\upsilon > 0$ is the excluded volume parameter, and the chain volume segmental density is

$$\rho(\vec{r}(n)) = \int_0^N dn'\,\delta(\vec{r}(n)-\vec{r}(n')). \tag{55}$$

For this, we use the mean field approximation [19],

$$\rho(\vec{r}) = N\psi_m^2(\vec{r}). \tag{56}$$

For simplicity, we assume that the reference state ϕ_m, the polymer wave function in the absence of undulation, is not affected by the presence of EVE. Basically EVE is treated as the first order perturbation, whose magnitude is modulated by the parameters, υ and c. Then using our ansatz (10), free energy per segment, Eq. (14), becomes

$$f = K_m + \beta U_m + E_m, \tag{57}$$

with

$$E_m = \frac{1}{2}\upsilon N\int d^3\vec{r}\,\psi_m^4(\vec{r}) = \frac{1}{2}\upsilon c\epsilon\left(\frac{1+5\alpha^2\overline{h^2}}{1+\alpha^2\overline{h^2}}\right), \tag{58}$$

where $c \equiv N/A$, surface segmental density, and $\epsilon \equiv \int dz\,\phi_m^4$. Then the α_m that minimizes free energy per segment, Eq. (27), is modified to

$$\alpha_m' = \frac{-\beta\dfrac{\overline{h^2}}{\overline{(\nabla_{\mathbf{x}}h)^2}}\langle V'\rangle_m}{\dfrac{l^2}{6} + 2\upsilon c\epsilon\dfrac{\overline{h^2}}{\overline{(\nabla_{\mathbf{x}}h)^2}}}, \tag{59}$$

where the magnitude is smaller than the earlier result of Eq. (27). The minimum free energy per segment f, with $\overline{h^2} = \frac{1}{4}\xi^2\overline{(\nabla_{\mathbf{x}}h)^2}$ for a Gaussian surface, is

$$f = f_0 + f',$$

$$f_0 = K_m^0 + \beta U_m^0,$$

$$f' = \frac{1}{1+\alpha_m'^2\overline{h^2}}\left[\left\{K_m^0 + \frac{1}{2}\beta U_m^0\right\}\overline{(\nabla_{\mathbf{x}}h)^2} + \beta\overline{h^2}\langle V''\rangle_m + 2\alpha_m'\beta\overline{h^2}\langle V'\rangle_m + \frac{\upsilon c\epsilon}{2} + \alpha_m'^2\left\{\frac{l^2}{6}\overline{(\nabla_{\mathbf{x}}h)^2} + \frac{5}{2}\upsilon c\epsilon\overline{h^2}\right\}\right]. \tag{60}$$

EVE is depicted by the dashed lines in most of the figures discussed previously. Using parameters $\upsilon = l^3/300$, $c = 1/(8l^2)$ as tentative examples, Figs. 3 and 4(a), respectively, show that the absolute value of $|\alpha_m'|$ and ρ_h'/ρ_υ' decrease as EVE becomes stronger. Figure 4(b) shows that the undulation-induced decrease in layer thickness is also less due to EVE. These trends are readily understandable because the EVE prevents polymer segments from being highly concentrated within a limited space. In Figs. 6(a) and 6(b), the magnitude of $|\alpha_m'|$ is lower than $|\alpha_m|$ for all values of ξ/a. The strongly adsorbed polymer is much more affected by the EVE than the weakly adsorbed one due to the enhanced EVE on more concentrated segments within a valley as shown in Fig. 7(a).

The $|\alpha_m'|$ and ρ_h'/ρ_υ' show interesting turnover behaviors as function of ξ showing a maximum at a certain value, say $\xi \approx 5a$ for the strongly adsorbed case. When ξ/a is small $|\alpha_m'|$ tends to be vanishing, since the high entropy cost for confining segments within narrow ($\xi/a \ll 1$) valleys drives them to escape towards the hills. When ξ/a is large, the surface looks very much like flat one which $|\alpha_m'|$ is also shown to be vanishingly small. The change of the layer thickness, Fig. 7(b), also shows a similar effects of excluded volume, that is, the thickness change decreases less.

Figure 8 is a plot of free energy per segment f_{EVE} as a function of adsorption strength $\beta|u_0|$, where the free energy f_{EVE} is higher than the f. Consequently the value of $\beta|u_0|$ where $f_{\mathrm{EVE}}=0$ is also found to be higher, which means that the critical temperature is lowered compared with that without EVE. This trend of increased free energy is due to the effect of more enhanced steric repulsion induced by the EVE. Nevertheless, EVE yields no appreciable changes qualitatively in physics explained before in Figs. 9 and 10. All of these excluded volume effects show reasonable trends of the quantities under study despite the simple approaches that we have used: the mean field approximation combined with the first order perturbation.

V. SUMMARY AND DISCUSSION

In this paper, we have investigated the effect of surface randomness on polymer adsorption. We consider that the surface is nearly flat with small-scale undulations whose correlation function is given as Gaussian. For the polymer conformation and free energy, we used the Edwards equation, considering that the polymer-surface attraction can be long-ranged, supplemented with the hard-wall repulsion.

First, by developing a variational scheme, we found that the polymer segments tend to be increasingly localized within valleys of the undulating surface as the adsorption strength ($\beta|u_0|$) or the correlation length (ξ/a) increases. For strong adsorption, this is due to enhanced effect of attraction dominant over the steric repulsion within the valleys, which increases as the surface correlation length increases. This enhanced attraction is owing to the larger space for the polymer fluctuation within the influence of the attractive field in the valley, more than to the increased surface area of contact which often has been attributed to enhancement of adsorption. As a consequence, the thickness of the adsorbed polymer layer becomes smaller than that in the case of a flat surface, and also as $\beta|u_0|$ and ξ/a increase, the free energy decreases due to the undulation, leading to enhanced surface adsorption. We have dealt with a long chain interacting with the surface *via* finite-to-long range attraction, and thus the qualitative agreement of these trends with the models using the contact interaction may not be sufficiently explained.

Second, it was shown that the undulation suppresses the polymer adsorption transition, lowering the transition temperature below that for a surface without undulation. This is a direct consequence of the fact that for weak adsorption the additional free energy arising from the undulation, dominated by the entropic reduction, is positive. This steric effect is due to Helfrich-like repulsion between the polymer and surface which is induced by the hard-wall BC on the Edwards equation as found earlier [11]. Care should be exercised, however, in extrapolating our result to the case of contact attraction, which does not incorporate the Helfrich-like repulsion.

Next, we found how the correlation length of the surface significantly affects the segment distribution, free energy, and adsorption-desorption transition of the polymer as well. The enhancement of desorption transition induced by the undulation can be negligible in the region of long correlation length, but it becomes strong in the region of short correlation length. Thus, for a polymer adsorbed on a flat surface the desorption transition occurs if the surface becomes random with the correlation length below a critical value, ξ_c, as shown by dashed lines in Fig. 10. Also, we found the optimal correlation length, ξ_m, at which the free energy of the adsorbed chain is at a minimum, as shown by solid lines in Fig. 10. This implies that if a surface is flexible enough, it can spontaneously develop an instability with respect to oscillation with the wavelength of the order of this length. This aspect is in accord with a recent work [24].

Finally, in Sec. IV we incorporated the excluded volume effect into our analytical results of an ideal chain, which resulted in more realistic chain behaviors. The tendency of segments to be localized within valleys is constrained, resulting in a higher free energy cost for the chain adsorption.

Our approximation is at its best validity for smooth undulation ($|h| \ll \xi$), long range interaction ($|h| \ll a$), and for small variation of polymer distribution as required by the Edwards equation. Moreover, we treated EVE as a perturbation, which may not be so in some cases. In spite of these limitations, our study gives reasonable explanations about the essential behaviors of long chain adsorption on an undulating surface. To the best of our knowledge, most work have been done for the contact (polymer-surface) attraction, not the finite-range interaction we consider here. Our analytical theory, demonstrated numerically here only for several cases of parameters, can be easily extended to a variety of situations and can be readily assessed by experiment and simulation studies.

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