

Pulling alternating copolymers adsorbed on a striped surface

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We consider a partially directed walk model of a strictly alternating copolymer adsorbing on a striped surface where the energy is associated with the numbers of the two types of monomers adsorbed on the two types of surface sites. A force is applied to the last monomer and the polymer responds to this force, sometimes by desorbing. The force can be applied at various angles, with the surface component parallel or perpendicular (or at some other angle) to the stripe direction. The desorption behavior is strongly dependent on the force direction and the response gives information about the shape and direction of the polymer adsorbed on the surface, especially at low temperatures. In some cases the ground state is degenerate and this also has an important effect on the temperature dependence of the critical force needed for desorption. We give a complete solution of the problem using generating function techniques and an approximate treatment that is especially useful at low temperatures and helps in our physical understanding of the situation.

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I. INTRODUCTION

When polymers in dilute solution adsorb at an impenetrable planar surface they can be desorbed by increasing the temperature. In this situation the entropy of the desorbed polymer compensates for the energy term associated with desorption, and the location of the phase transition (i.e., the transition temperature) is determined by the energy-entropy balance. The phase transition is thought to be second order and this can be proved for some models of the adsorption process [1,2]. The polymer can be subjected to a force, e.g., using atomic force microscopy [3,4], and this force can cause desorption of an adsorbed polymer. In this case the location of the phase transition (i.e., the critical force required for desorption at a particular temperature) is primarily determined by a balance of the energy associated with adsorption and the elastic energy associated with the force, though entropy also plays a role. The phase transition is expected to be first order and, again, this can be proved for some models [5].

The polymer has conformational freedom and the model chosen must reflect this freedom. Various models of the polymer can be used, including random walks [1,2,6], directed and partially directed walks [7–9], and self-avoiding walks [10–12]. Both the polymer and the surface can be homogeneous or heterogeneous and the heterogeneity can be random [13–16] or regular [17–21]. When the inhomogeneity is random it can be annealed or quenched [15,16].

When the polymer and the surface are both inhomogeneous [13,18–21] there are connections to the biological problem of recognition [18–23]. The basic recognition question is as follows: Will a particular monomer sequence lead to more favorable adsorption on a surface with a particular pattern? Clearly, this is connected to how the polymer is arranged on the surface in the adsorbed state. It seems that pattern recognition

is likely to be more effective when the polymer and the surface both have regular heterogeneity [18–21,23] and experimental techniques exist for producing regularly patterned surfaces [24–26]. There is some experimental work on adsorption on these surfaces, for instance, on the adsorption of DNA on patterned surfaces [24,26]. Some theoretical work has been carried out on copolymer adsorption on inhomogeneous surfaces [13,17–23,27–30]. In this paper we are concerned with regular inhomogeneity and with the special case of the adsorption of a strictly alternating copolymer on a regularly striped surface [21].

When a force is applied, the case that has received the most attention is that where the force is normal to the surface [5,12,31,32]. However, pulling parallel to the surface has also been considered [33] and this *promotes* adsorption rather than causing desorption. More generally, the force can be applied at an angle to the surface [34–38]. This is particularly relevant when the surface is striped since the surface component of the force can be parallel or perpendicular (or at some other angle) to the direction of the stripes and this can have marked effects on the desorption behavior [38]. The response of the adsorbed polymer to the applied force (and to the direction in which it is applied) can give useful information about how the polymer lies on the surface. This will be especially important for the case of an alternating copolymer on a striped surface, which is a prototype for the more general case of adsorption of an inhomogeneous polymer on an inhomogeneous surface, which itself is relevant to the recognition process [16,18–20,22,23].

In Sec. II we describe a partially directed walk model (see Fig. 1) that can be solved exactly by generating function techniques. The thermodynamics can then be extracted from the asymptotics of the generating function. We give a general outline of the model and the procedure in Sec. II and postpone technical details to Sec. III. In Sec. IV we give an approximate treatment that is exact at zero temperature and gives a good approximation at low temperatures, which suggests that this type of low temperature approximation can be used with confidence in examining models that are not exactly solvable.

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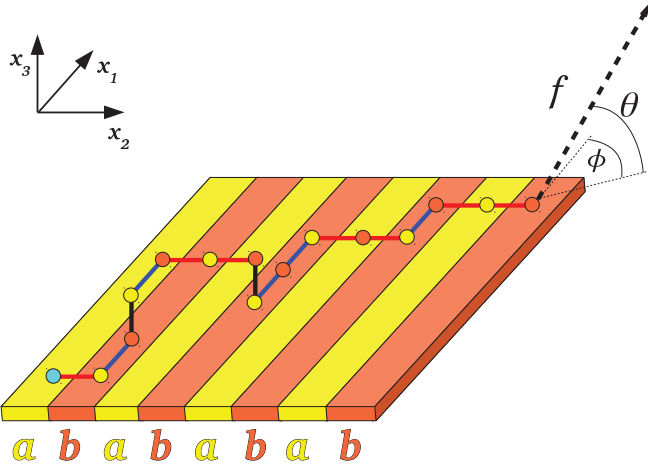


FIG. 1. (Color online) The convention used for the angles θ and ϕ . When the surface component of the force is parallel to the stripe direction, then $\phi = 0$.

This approach helps to give a physical understanding of some of the results obtained exactly in Sec. III. We close with a brief discussion of our results in Sec. V.

We show that the arrangement of the copolymer on the striped surface can be very different from that of a homopolymer on a striped surface [38], especially at low temperatures. The sequence of comonomers is interacting with the arrangement of surface sites and the copolymer is recognizing this arrangement. We also show how these differences in the adsorbed conformations are reflected in the temperature dependence of the critical force for desorption. In addition we explore the incidence of degenerate ground states and how their associated entropy affects the low temperature behavior of the critical force. The low temperature treatment developed in Sec. IV is crucial in understanding this behavior.

II. THE MODEL

In this section we describe a partially directed walk model of the adsorption of a strictly alternating copolymer on a striped surface and the response of the system to a force applied at the final vertex of the walk. The force can be applied in various directions and the results are strongly dependent on the direction of the force. The approach used will be to define generating functions for various types of walks and to use factorization techniques to write down equations relating these generating functions. The thermodynamic properties of the model will be determined by the asymptotics of the generating functions. However, we first describe the model and define appropriate thermodynamic functions.

Consider the simple cubic lattice Z^3 with vertices having integer coordinates. Attach the obvious coordinate system (x_1, x_2, x_3) . A partially directed walk is a self-avoiding walk on the simple cubic lattice that starts at the origin and has steps in the positive x_1 and x_2 directions and in both the positive and negative x_3 directions, with the final vertex at height $h \geq 0$ above the surface $x_3 = 0$. It has the restriction that every vertex of the walk has non-negative x_3 coordinate (so that the walk

lies in or on one side of the impenetrable surface), and the surface $x_3 = 0$ is the surface at which adsorption can occur.

The surface is striped with two kinds of surface site, a and b , determined by the parity of the x_2 coordinate. That is, the stripes are in the plane $x_3 = 0$ and run parallel to the x_1 axis. We are interested in the alternating copolymer case so the walk has alternating vertices of two types A and B . See Fig 1.

In principle, one could consider different energy terms, $\epsilon_{Aa}, \epsilon_{Ab}, \epsilon_{Ba}, \epsilon_{Bb}$, for the situations where an A vertex is on an a stripe, etc. We simplify the situation by setting $\epsilon_{Ab} = \epsilon_{Ba} = 0$, although the more general case could be handled by an extension of our approach. Without much loss of generality we set $\epsilon_{Aa} = -1$ and consider only $-1 \leq \epsilon_{Bb} \leq 0$. We write $\epsilon_{Bb} = \gamma \epsilon_{Aa}$ so that $0 \leq \gamma \leq 1$. This is exactly the CS model discussed in [21], though that paper considered the pure adsorption problem without an applied force. Notice that $\gamma = 1$ does *not* correspond to a homopolymer since A vertices only interact with a stripes and B vertices with b stripes.

The force is applied at the last vertex of the walk in a direction characterized by the angles θ and ϕ . ϕ is the angle that the surface component of the force makes with the (positive) stripe direction and $\pi/2 - \theta$ is the angle between the force direction and a normal to the surface. See Fig. 1 for a sketch of these angle definitions. This is the same convention as that used in [34].

The general approach used is similar to that developed in [21] but it is complicated by the fact that we need to keep track of the coordinates of the last vertex. This means that we need to track steps in the x_1 and x_2 directions when we compute the generating function of walks ending in the plane $x_3 = 0$.

Suppose that $c_n(v_{Aa}, v_{Bb}, s_1, s_2, h)$ is the number of partially directed n edge walks that start at the origin, have v_{Aa} A vertices on a stripes and v_{Bb} B vertices on b stripes, with span in the x_1 direction equal to s_1 , span in the x_2 direction equal to s_2 , and height of the last vertex above the surface equal to h . The partition function of the model is given by

$$Z_n = \sum_{v_{Aa}, v_{Bb}, s_1, s_2, h} c_n \exp[-H/kT], \quad (1)$$

where $c_n = c_n(v_{Aa}, v_{Bb}, s_1, s_2, h)$ and

$$H = v_{Aa}\epsilon_{Aa} + v_{Bb}\epsilon_{Bb} - f_1s_1 - f_2s_2 - f_3h. \quad (2)$$

f_1 , f_2 , and f_3 are the components of the force in the three coordinate directions, k is Boltzmann's constant, and T is the absolute temperature.

In Sec. III we require a variety of different generating functions for walks with various constraints but the general principles used are always the same. In the simplest case we can define a generating function $G = \sum_n Z_n z^n$ and the thermodynamics of the model can be extracted from the singularities of G . The thermodynamic limit $\lim_{n \rightarrow \infty} n^{-1} \ln Z_n \equiv \kappa$ exists and the generating function can be written as

$$G = \sum_n e^{\kappa n + o(n)} z^n. \quad (3)$$

This converges when $ze^\kappa < 1$, diverges when $ze^\kappa > 1$, and so is singular when $z = e^{-\kappa}$. Therefore, if z_c is the dominant singularity of G , then $\kappa = -\ln z_c$.

III. GENERATING FUNCTIONS AND THERMODYNAMIC PROPERTIES

In this section we give the technical details of the computation of the generating function and the extraction of thermodynamic results from the singularities of the generating function.

A. Alternating copolymers adsorbing on a striped surface

This section is devoted to the calculation of the generating function of partially directed walks that end in the plane $x_3 = 0$ (which we call *loops*), keeping track of both Aa and Bb visits and of the numbers of steps in the x_1 and x_2 directions.

First, consider walks that start and end in the plane $x_3 = 0$ with no energy terms. Let $l_n(s_1, s_2)$ be the number of loops with n steps, with spans s_1 and s_2 in the x_1 and x_2 directions. If y_1 and y_2 are conjugate to the spans of the walk in the x_1 and x_2 directions and z is conjugate to the total number of steps, the generating function $Q(y_1, y_2, z)$ is given by

$$Q(y_1, y_2, z) = \sum_{s_1, s_2, n} l_n(s_1, s_2) y_1^{s_1} y_2^{s_2} z^n \quad (4)$$

and satisfies the equation

$$Q = 1 + (y_1 + y_2)zQ + z^2(Q - 1) + z^3(y_1 + y_2)(Q - 1)Q.$$

The walk can be a single vertex, contributing 1, or its first step can be in the $x_3 = 0$ surface and then be continued as any loop, or its first step can be out of the surface. In this case the walk can return to the surface for the first time on its last step, contributing $z^2(Q - 1)$, or after returning to the surface for the first time, it can take a step in the surface and then be continued as a loop. Each of the horizontal steps can be taken in either the x_1 or the x_2 direction. The factorization scheme is sketched in Fig. 2. The generating function Q has a square

root singularity at

$$z = z_1 = \frac{-1 - y_{12} + \sqrt{y_{12}^2 + 6y_{12} + 1}}{2y_{12}}, \quad (5)$$

where $y_{12} = y_1 + y_2$. When $y_1 = y_2 = 1$ this reduces to $z_1 = (\sqrt{17} - 3)/4$ [5]. The singularity z_1 dominates in the *free phase* where the walk is neither adsorbed nor ballistic.

We shall need separate generating functions for walks with a total number of steps that are even (E) or odd (O) and that have an even (e) or odd (o) number of steps in the x_2 direction. We write Q^{Ee} , etc., for these generating functions. Write $Q^E(y_1, y_2, z) = [Q(y_1, y_2, z) + (Q(y_1, y_2, -z))/2]$ and $Q^O(y_1, y_2, z) = [Q(y_1, y_2, z) - (Q(y_1, y_2, -z))/2]$ for the generating functions of walks having an even or odd total number of steps. Then

$$Q^{Ee}(y_1, y_2, z) = \frac{Q^E(y_1, y_2, z) + Q^E(y_1, -y_2, z)}{2},$$

$$Q^{Eo}(y_1, y_2, z) = Q^E(y_1, y_2, z) - Q^{Ee}(y_1, y_2, z),$$

$$Q^{Oe}(y_1, y_2, z) = \frac{Q^O(y_1, y_2, z) + Q^O(y_1, -y_2, z)}{2},$$

and

$$Q^{Oo}(y_1, y_2, z) = Q^O(y_1, y_2, z) - Q^{Oe}(y_1, y_2, z).$$

Define $P^{Aa}(a, b, y_1, y_2, z)$ to be the generating function of walks that start with an A vertex on an a stripe, where a is conjugate to A visits to a stripes, b is conjugate to B visits to b stripes, y_1 is conjugate to steps in the x_1 direction, y_2 is conjugate to steps in the x_2 direction, and z is conjugate to the total number of steps. As usual, the first vertex does not contribute to the energy. In a similar way, define P^{Ab} , P^{Ba} , and P^{Bb} for the generating functions of walks starting with an A vertex on a b stripe, etc. [These generating functions are defined in an analogous way to the definition of Q in (4) but keeping track of additional variables.] Using factorization arguments similar to those appearing in Fig. 2 one can show that these generating functions satisfy the set of simultaneous equations

$$P^{Aa} = 1 + by_2zP^{Bb} + y_1zP^{Ba} + az^2(Q^{Ee} - 1)(1 + by_2zP^{Bb} + y_1zP^{Ba}) + bz^2Q^{Oo}(1 + ay_2zP^{Aa} + y_1zP^{Ab}) + z^2Q^{Eo}(1 + y_2zP^{Ba} + by_1zP^{Bb}) + z^2Q^{Oe}(1 + y_2zP^{Ab} + ay_1zP^{Aa}), \quad (6)$$

$$P^{Ab} = 1 + y_2zP^{Ba} + by_1zP^{Bb} + z^2(Q^{Ee} - 1)(1 + y_2zP^{Ba} + by_1zP^{Bb}) + z^2Q^{Oo}(1 + y_2zP^{Ab} + ay_1zP^{Aa}) + az^2Q^{Eo}(1 + by_2zP^{Bb} + y_1zP^{Ba}) + bz^2Q^{Oe}(1 + ay_2zP^{Aa} + y_1zP^{Ab}), \quad (7)$$

$$P^{Ba} = 1 + y_2zP^{Ab} + ay_1zP^{Aa} + z^2(Q^{Ee} - 1)(1 + y_2zP^{Ab} + ay_1zP^{Aa}) + z^2Q^{Oo}(1 + y_2zP^{Ba} + by_1zP^{Bb}) + bz^2Q^{Eo}(1 + ay_2zP^{Aa} + y_1zP^{Ab}) + az^2Q^{Oe}(1 + by_2zP^{Bb} + y_1zP^{Ba}), \quad (8)$$

$$P^{Bb} = 1 + ay_2zP^{Aa} + y_1zP^{Ab} + bz^2(Q^{Ee} - 1)(1 + ay_2zP^{Aa} + y_1zP^{Ab}) + az^2Q^{Oo}(1 + by_2zP^{Bb} + y_1zP^{Ba}) + z^2Q^{Eo}(1 + y_2zP^{Ab} + by_1zP^{Aa}) + z^2Q^{Oe}(1 + y_2zP^{Ba} + by_1zP^{Bb}). \quad (9)$$

These four generating functions each have the same two physically relevant singularities, a square root singularity at $z = z_1(y_1, y_2)$, given by (5), and a pole at

$z = z_2(a, b, y_1, y_2)$. When $y_1 = y_2 = 1$ these singularities agree with those found for the CS model in [21]. The singularity z_2 dominates in the *adsorbed phase* where the (infinite)

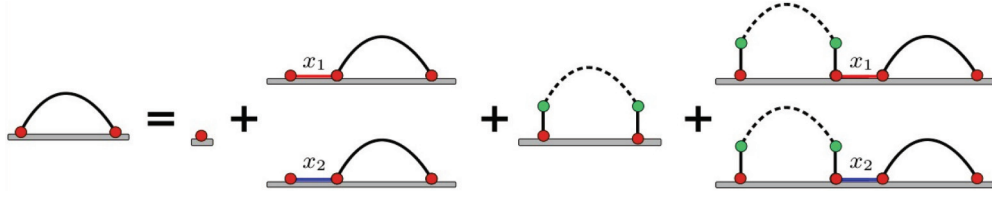


FIG. 2. (Color online) A general factorization argument for loops interacting with a surface.

walk has a nonzero fraction of its vertices in the adsorbing line.

B. Alternating copolymers subject to a force

In this section, to investigate the effect of an applied force, we relax the condition that the walk ends in the plane $x_3 = 0$. The walk can

- (1) have its last vertex in the $x_3 = 0$ surface,
- (2) have vertices in the surface but not end in the surface, in which case there is a last time that the walk is in the surface, or
- (3) leave the surface on its first step and never return.

Suppose that the first vertex is an A vertex on an a stripe. Let $T^{Aa}(a, b, y_1, y_2, y_3, z)$ be the generating function of such walks where the variable y_3 is conjugate to the x_3 coordinate of the last vertex of the walk. We can turn off the interaction with the surface by setting $a = b = 1$ and we write $T^{Aa}(1, 1, y_1, y_2, y_3, z) = T^0(y_1, y_2, y_3, z)$. Then $T^{Aa}(a, b, y_1, y_2, y_3, z)$ is given by

$$\begin{aligned} T^{Aa} = & P^{Aa} + [(y_1 z + b y_2 z) P^{Aa, Aa} \\ & + (b y_1 z + y_2 z) P^{Aa, Ab} + (a y_1 z + y_2 z) P^{Aa, Ba} \\ & + (y_1 z + a y_2 z) P^{Aa, Bb} + 1] y_3 z T^0, \end{aligned} \quad (10)$$

where $P^{Aa, Aa}$ is the generating function of loops that start with an A vertex on an a stripe and end with an A vertex on an a stripe, and $P^{Aa, Ab}$, etc., are defined analogously. These generating functions can be computed directly from P^{Aa} . For instance,

$$\begin{aligned} P^{Aa, Aa}(a, b, y_1, y_2, z) \\ = & \frac{1}{4} [P^{Aa}(a, b, y_1, y_2, z) + P^{Aa}(a, b, y_1, y_2, -z) \\ & + P^{Aa}(a, b, y_1, -y_2, z) + P^{Aa}(a, b, y_1, -y_2, -z)]. \end{aligned}$$

By setting $a = b = 1$ in (10) we can calculate T^0 and then substitute this back into (10) to obtain T^{Aa} . T^{Aa} has three physically relevant singularities, $z = z_1$ [see (5)], and two poles, $z = z_2(a, b, y_1, y_2)$ and $z = z_3(y_1, y_2, y_3)$. The singularities are independent of whether the first vertex is A or B and whether the walk starts on an a or b stripe. z_1 dominates in the free phase, z_2 dominates in the adsorbed phase, and z_3 dominates in the phase where the walk is *ballistic*, i.e., where the distance of the last vertex from the surface scales with the first power of the number of vertices in the walk. The phase boundary for the adsorption-desorption transition with a force (i.e., the critical force needed for desorption as a function of temperature) is given by the solutions of the equation $z_2(a, b, y_1, y_2) = z_3(y_1, y_2, y_3)$.

Converting to the appropriate physical variables, we make the substitutions

$$y_i = \exp(f_i/kT), \quad i = 1, 2, 3 \quad (11)$$

and

$$a = \exp(1/kT) \quad b = \exp(\gamma/kT), \quad (12)$$

where k is Boltzmann's constant, $f_1 = f \cos \theta \cos \phi$, $f_2 = f \cos \theta \sin \phi$, $f_3 = f \sin \theta$, and f is the force applied in the direction (θ, ϕ) .

When $\theta = \pi/2$ the walk is being pulled normal to the surface and there is no ϕ dependence. In Fig. 3 we show the critical force as a function of temperature for $\gamma = 1$ (top curve), $1/2$ (middle curve), and zero (bottom curve). When $\gamma = 0$ the limiting slope at $T = 0$ is positive, indicating that there is entropy in the ground state. See Sec. IV for further discussion. For $\gamma = 1/2$ and 1 the curves are monotone decreasing with zero limiting slope.

It is interesting to compare these results with those for homopolymer adsorption on a striped surface (see [38], Fig. 6). When $\theta = \pi/2$ the critical force at $T = 0$ is independent of γ for the homopolymer case but depends on γ for the alternating copolymer case. Compare Fig. 6 in [38] and Fig. 3 in this paper. Hence, the ground state depends on γ for the copolymer but

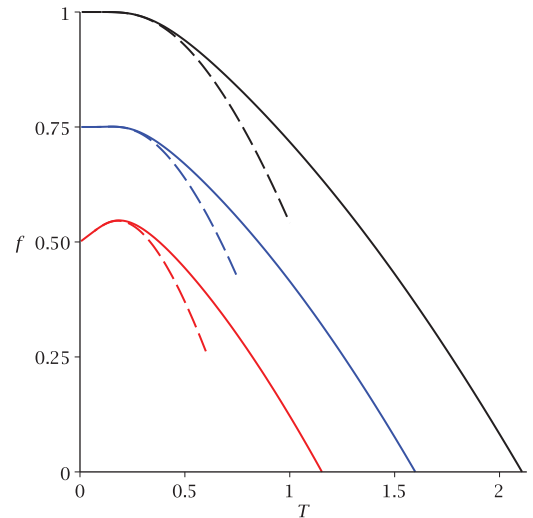


FIG. 3. (Color online) Plot of the critical force as a function of the temperature when pulling normal to the surface, $\theta = \pi/2$. The results are given in units where $k = 1$. The solid curves are for the exact treatment given in Sec. III and the dashed curves are for the low temperature approximation described in Sec. IV. The three sets of curves (top to bottom) are for $\gamma = 1, 1/2$, and zero. Note the positive limiting slope when $\gamma = 0$, indicating that the ground state is degenerate.

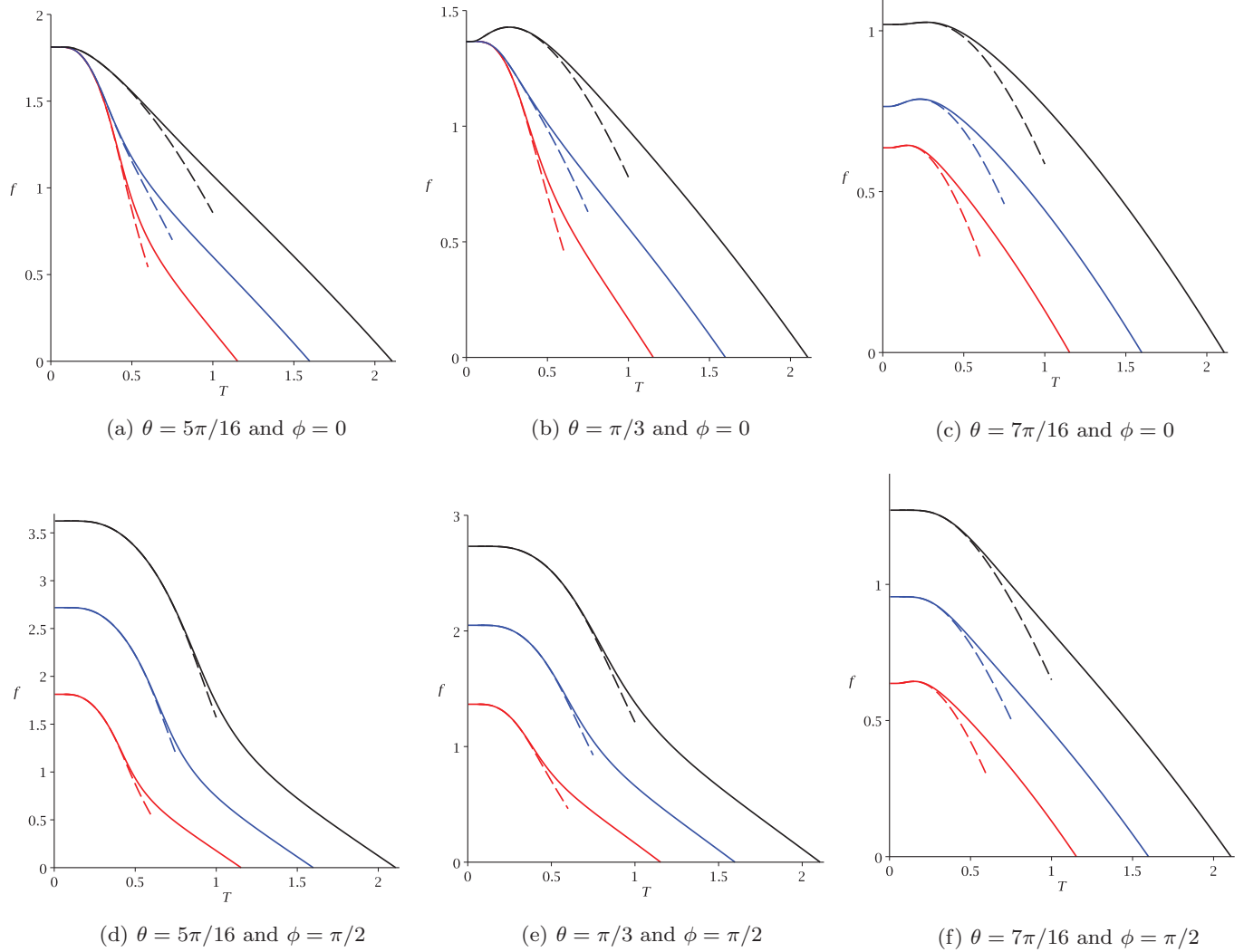


FIG. 4. (Color online) Temperature dependence of the critical force as a function of the angles θ and ϕ . The rows correspond to different values of ϕ and the columns to different values of θ . In each case the three solid curves are for $\gamma = 1, 1/2$, and zero (top to bottom) and the broken curves are the corresponding results for the low temperature treatment developed in Sec. IV.

not for the homopolymer. The limiting ($T \rightarrow 0$) slope df/dT is positive for $\gamma = 1$ for the homopolymer and positive for $\gamma = 0$ for the copolymer. This implies that the ground state is degenerate for the homopolymer when $\gamma = 1$ and for the copolymer when $\gamma = 0$. All of these differences reflect the differences in how the homopolymer and the copolymer adsorb on the striped surface, especially at low temperatures.

In Fig. 4 we show the critical force-temperature curves for $\theta = 5\pi/16, \pi/3$, and $7\pi/16$, for $\phi = 0$ and $\pi/2$, and for $\gamma = 1, 1/2$, and zero. All of the cases shown have zero limiting slope, indicating that there is no ground state entropy. In spite of this, several of the curves are reentrant. The system in the adsorbed state has entropy at low temperatures though not at zero temperature, and this entropy is lost under the influence of the force. Reentrance with zero limiting slope has been observed in other systems [39,40]. When $\phi = 0$ (i.e., when the surface component of the force is parallel to the stripe direction) the three curves show the same critical force at zero temperature for $\theta = 5\pi/16$ and $\pi/3$, so the ground state is independent of the value of γ and suggests that the

walk follows an a stripe. At $\theta = 7\pi/16$ the zero temperature forces are different so the ground state energy depends on γ . This is discussed in detail in Sec. IV and the occurrence of degenerate ground states is discussed in Sec. IV C. For $\phi = \pi/2$ the ground state energy depends on γ for all the values of γ shown and the walk is perpendicular to the stripes in the ground state. In Sec. IV we develop a low temperature approximation which helps to explain physically the disparity of shapes for the curves in Figs. 3 and 4 and the differences in behavior are discussed in more detail in that section.

There are interesting similarities to (and differences from) the corresponding curves for the case of homopolymer adsorption on a striped surface [38]. When $\theta = 7\pi/16$ the critical force at $T = 0$ is independent of γ for the homopolymer case but depends on γ for the copolymer. Compare Fig. 5 in [38] and Fig. 4 in this paper. When $\theta = 7\pi/16$ and $\phi = 0$ the curve is reentrant when $\gamma = 1$ for the homopolymer and for $\gamma = 0, 1/2$, and 1 for the copolymer. For $\theta = 7\pi/16$ and $\phi = \pi/2$ the curves are reentrant for $\gamma = 0, 1/2$, and 1 for the homopolymer and for $\gamma = 0$ for the copolymer.

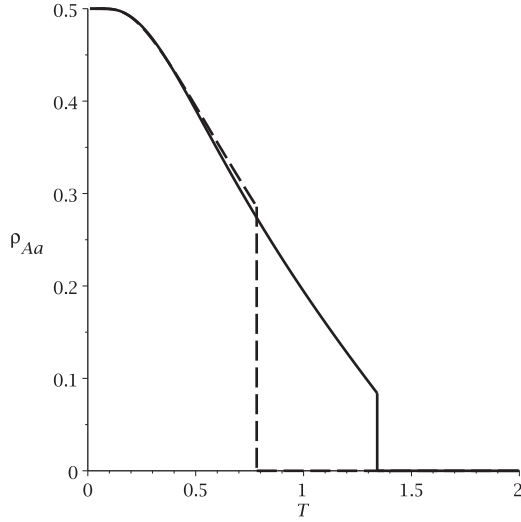


FIG. 5. Plot of the order parameter ρ_{Aa} as a function of the temperature when $\theta = \pi/3$, $\phi = 0$, and $\gamma = 1/2$. The two curves are for $f = 0.25$ (solid line) and 0.75 (dashed line).

There are several possible order parameters for the model. Define

$$\rho_{Aa} = \lim_{n \rightarrow \infty} \langle v_{Aa} \rangle / n \quad (13)$$

and

$$\rho_{Bb} = \lim_{n \rightarrow \infty} \langle v_{Bb} \rangle / n. \quad (14)$$

In Fig. 5 we plot ρ_{Aa} as a function of temperature when $\theta = \pi/3$, $\phi = 0$, $\gamma = 1/2$, and $f = 0.25$ and 0.75 . We choose these two values for the force because it will turn out that the ground state at the point when desorption occurs will be different. The order parameter ρ_{Aa} is $1/2$ at $T = 0$ and gradually decreases as the temperature increases until the desorption temperature at that force is reached and ρ_{Aa} drops discontinuously to zero. The behavior is similar at the two values of the force although, of course, the desorption occurs at different temperatures. When $f = 0.75$ the value of ρ_{Aa} is slightly larger than when $f = 0.25$ at temperatures a little below the desorption temperature. At the larger value of the force there is a larger surface component of force tending to pull A vertices into the a stripes.

In Fig. 6 we plot ρ_{Bb} as a function of temperature for the same parameter values. Now the shape of the order parameter curve is dramatically different at the two values of the force. When the force is small, ρ_{Bb} is $1/2$ at $T = 0$ while for the larger value of the force $\rho_{Bb} = 0$ at $T = 0$. This means that the ground state is different for the two force values. When $f = 0.25$ the walk is a straight line perpendicular to the stripe direction so that A vertices are in a stripes and B vertices are in b stripes. When $f = 0.75$ the component of the force along the stripe direction (recall that $\phi = 0$) is sufficient to change the ground state to a walk following an a stripe.

This suggests that conditions can be found where the two ground states are degenerate and this is explored further in Sec. IV C.

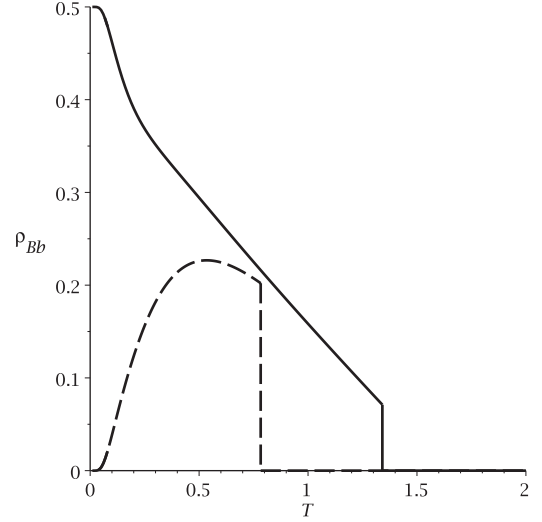


FIG. 6. Plot of the order parameter ρ_{Bb} as a function of the temperature when $\theta = \pi/3$, $\phi = 0$, and $\gamma = 1/2$. The two curves are for $f = 0.25$ (solid line) and 0.75 (dashed line).

IV. A LOW TEMPERATURE APPROXIMATION

In this section we develop an approximate treatment that is exact at zero temperature and is a very good approximation at low temperatures. In particular, it reproduces the shape of the f - T curves at low temperatures. We use this treatment in Sec. IV C to explore the occurrence of degenerate ground states at the critical force for adsorption.

The essential approximation is to consider the walk under the action of the force as having its first $n - m$ edges entirely in the surface and its final m edges out of the surface. In addition the approximation assumes that in the last m edges, there are no steps towards the surface. These approximations are expected to be reliable at low temperatures and large forces.

We first consider walks that lie entirely in the surface and solve this problem exactly. Let $S_{Aa}(a, b, y_1, y_2, z)$ be the generating function of walks that start with an A vertex on an a stripe. The quantities a and b are conjugate to the number of A visits to a sites and to the number of B visits to b sites, y_1 and y_2 are conjugate to the numbers of steps in the x_1 and x_2 directions, and z is conjugate to the total number of edges in the walk. The generating functions S_{Ab} , etc., are defined similarly. These four generating functions satisfy the four simultaneous equations

$$S_{Aa} = 1 + by_2zS_{Bb} + y_1zS_{Ba}, \quad (15)$$

$$S_{Ba} = 1 + y_2zS_{Ab} + ay_1zS_{Aa}, \quad (16)$$

$$S_{Ab} = 1 + y_2zS_{Ba} + by_1zS_{Bb}, \quad (17)$$

and

$$S_{Bb} = 1 + ay_2zS_{Aa} + y_1zS_{Ab}. \quad (18)$$

Solving these equations we find that all four generating functions have the same denominator. The thermodynamics is determined by the poles of the generating functions, i.e., by the zeros of the denominator. We are only interested in real positive zeros (so that the free energy is real). Let $z_c(a, b, y_1, y_2)$ be the appropriate zero. Then the free energy of an $n - m$ step walk in the surface is given by $F_1 = (n - m)kT \ln z_c$.

For the part of the walk out of the surface we can write the partition function as

$$Z_2 = (y_1 + y_2 + y_3)^m, \quad (19)$$

where y_3 is conjugate to the number of steps in the x_3 direction. Recall that we are assuming that there are no steps towards the surface. The free energy of a walk of m edges out of the surface is then $F_2 = -kT \ln Z_2$. The total free energy is $F = F_1 + F_2$ and to optimize the free energy we differentiate F with respect to m and set the derivative equal to zero. This determines the temperature dependence of the critical force for desorption. We convert to physical variables using (11) and (12).

A. Pulling normal to the surface

When $\theta = \pi/2$ the results are independent of ϕ . The force-temperature curves are shown in Fig. 3 and compared to the results from the full treatment in Sec. III. The three curves are for $\gamma = 0, 1/2$, and 1. When $\gamma > 0$ the ground state corresponds to the walk being a straight line in the surface, perpendicular to the stripe direction, so as to optimize Bb visits. The force-temperature curves have zero limiting slope as $T \rightarrow 0$, since there is no entropy in the ground state. When $\gamma = 0$ the energy of a walk following an a stripe is equal to that of a walk perpendicular to the stripe direction so we have a doubly degenerate ground state and the limiting slope is positive, reflecting the loss of entropy when the walk is desorbed. See Sec. IV C for further discussion of this issue.

B. Pulling at an angle

When $\theta < \pi/2$ the results depend strongly on the value of ϕ . In Fig. 4 we show the force-temperature curves for $\theta = 5\pi/16, \pi/3$, and $7\pi/16$; $\phi = 0$ and $\pi/2$; and $\gamma = 0, 1/2$, and 1. The agreement between the low temperature approximation and the full treatment is excellent. In particular, the low temperature treatment reproduces the zero temperature forces, the limiting ($T \rightarrow 0$) slopes, and the re-entrance of some of the curves.

All of the curves shown have zero limiting slope (but see Sec. IV C for exceptions). When $\phi = \pi/2$ the zero temperature force depends on γ , indicating that the ground state corresponds to walks crossing the stripes. When $\phi = 0$ and θ is relatively small the zero temperature force is independent of γ so the component of the force along the stripe direction is large enough to compensate for the energetic advantage of Bb visits. At larger values of θ the component of the force along the stripe direction is insufficient to compensate and the ground state changes. This suggests that there is an intermediate value of θ where the ground state is degenerate and this is explored in Sec. IV C. The curves are reentrant at some angles but not at others and the low temperature approximation faithfully reproduces this behavior.

C. Degenerate ground states

There are two obvious candidates for the ground state, one in which the walk follows the stripe and the other in which the walk is a straight line normal to the stripe direction. In the first case the free energy is

$$F_{\parallel} = -n/2 - nf \cos \theta \cos \phi \quad (20)$$

and in the second

$$F_{\perp} = -n(1 + \gamma)/2 - nf \cos \theta \sin \phi. \quad (21)$$

These two free energies are equal when

$$f = \frac{\gamma}{2 \cos \theta (\cos \phi - \sin \phi)}. \quad (22)$$

If a force is applied while the walk is in the first of these two ground states, then the free energy, in this model, is given by

$$F = -(n - m)/2 - (n - m)f \cos \theta \cos \phi - mf \sin \theta, \quad (23)$$

where m is the number of vertices out the surface. The critical force for adsorption at zero temperature is given by the solution of $\partial F / \partial m = 0$, i.e.,

$$f = \frac{1}{2(\sin \theta - \cos \theta \cos \phi)}, \quad (24)$$

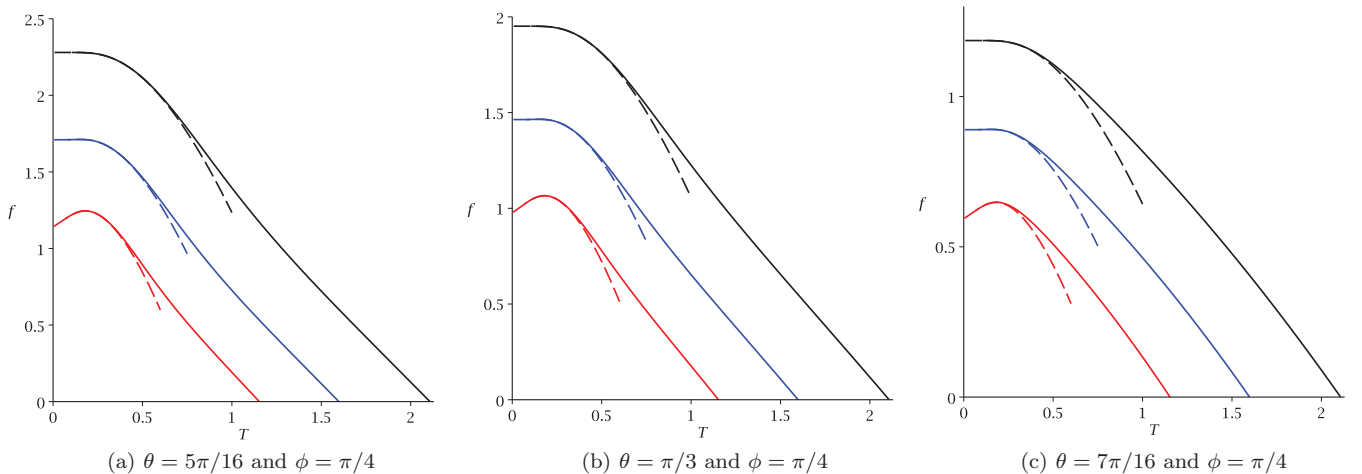


FIG. 7. (Color online) Temperature dependence of the critical force for $\phi = \pi/4$ and various values of the angle θ . In each case the three solid curves are for $\gamma = 1, 1/2$, and zero (top to bottom) and the broken curves are the corresponding results for the low temperature treatment developed in Sec. IV. Note the positive limiting slopes as $T \rightarrow 0$ when $\gamma = 0$.

so the the ground state is doubly degenerate at the desorption transition when the force given by (22) is equal to this critical force, that is, when

$$\gamma = \frac{\cos \phi - \sin \phi}{\tan \theta - \cos \phi}. \quad (25)$$

A similar calculation starting with (21), of course, gives the same result.

For instance, when $\phi = 0$ (so that the surface component of the force is parallel to the stripe direction) and $\gamma = 1$ the ground state is degenerate at the critical value of the force when $\tan \theta = 2$. Similarly, when $\phi = 0$ and $\gamma = 1/2$ the critical angle is given by $\tan \theta = 3$. This degeneracy is present exactly at the critical value of the force at zero temperature and is lifted when the force increases and the walk is pulled off the surface. There is a loss of entropy and an additional entropic term resisting desorption. This entropic term results in a positive derivative, df/dT , at $T = 0$. If we restrict to $\theta > \pi/4$ (recall that $\gamma \geq 0$) then ϕ must be at least $\pi/4$ for degeneracy [see (25)]. When $\phi = \pi/4$ the ground state is degenerate when $\gamma = 0$. This feature can be seen in the positive limiting slope of the force-temperature plots as T goes to zero in Fig. 7 whenever $\gamma = 0$.

V. DISCUSSION

We have considered a partially directed walk model of a strictly alternating copolymer adsorbing on a striped surface where monomers of type A interact with stripes of type a , monomers of type B interact with stripes of type b , and there are no Ab or Ba interactions. In addition, the walk is

subject to a force, tending to desorb the walk, and this force can be applied at various angles. We have solved the model completely at the level of generating functions and extracted the thermodynamics from the asymptotics of the generating functions. We have also developed a relatively simple low temperature treatment that is exact at zero temperature and gives a good approximation at low temperatures. This approximation faithfully reproduces the shapes of the critical force-temperature curves at low temperatures.

The model shows a number of interesting features including reentrance behavior and switches of the ground state when parameters are changed. In particular, we investigated when the ground state is degenerate and observed interesting effects on the force-temperature curves. Observing the temperature dependence of the critical force can give useful information about the orientation of the polymer on the surface, especially at low temperature.

There are some interesting extensions and questions that deserve attention. What happens if the stripes are of width greater than one [17]? What happens if the regular surface heterogeneity consists of a checkerboard pattern instead of stripes [17]? Can the treatment be extended to other regular copolymers such as AAB or $AABB$ [41]? These are interesting extensions and would throw further light on recognition questions as well as being of interest as topics in polymer adsorption.

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