

Polymers undergoing inhomogeneous adsorption: Order parameters for a partially directed walk model

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We consider partially directed walk models of polymers undergoing inhomogeneous adsorption. The inhomogeneity can be in the polymer, in the surface, or in both. For the cases where the polymer is either a homopolymer or a strictly alternating copolymer and where the surface is either homogeneous or has stripes of width 1, we calculate detailed order parameters and show that these provide important information about the ways in which the polymer adsorbs.

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I. INTRODUCTION

The theory of polymer adsorption at an impenetrable surface has a long history [1]. Various models have been considered, including random walks [1–3] for which we have essentially complete solutions available. Self-avoiding walk models are considerably more difficult, but some rigorous results are available [4,5] and there are many numerical studies [6,7] including recent and very precise estimates by Beaton *et al.* [8]. Other types of models that have proved to be very useful are directed and partially directed walks [9–11]. These models have the distinct advantage that they are often exactly solvable by combinatorial techniques.

Originally the models considered were for homopolymers adsorbing on homogeneous surfaces but these can be extended to heterogeneous systems where the heterogeneity can be in the polymer or in the surface or in both. The heterogeneity can be random [12–15] or regular [16–18]. When the heterogeneity is random it can be annealed or quenched [14].

Some theoretical work has been carried out on copolymer adsorption on inhomogeneous surfaces [13,16,17,19–28] and this situation serves as a simple model of the biological process of recognition [15,18–20]. The basic idea is that a particular monomer sequence leads to more favorable adsorption on a surface with a particular pattern of adsorption sites so that the polymer is recognized by the surface. This is connected with the phenomenon of frustration where other monomer sequences are not easily adsorbed on the patterned surface. This raises questions about the conformation of the adsorbed polymer and how the conformation depends on the details of the copolymer sequence and the surface heterogeneity. This question can be addressed by considering how the adsorbed polymer responds to the application of a force, desorbing the polymer [3,29–34], especially when the angle at which the force is applied can be varied [35–40]. An alternative way to investigate this question is to compute more detailed information about the adsorbed polymer and this is the approach that we take in this paper. The adsorbed polymer can be regarded [41,42] as a sequence of trains (or incursions [4]) where the successive edges are all in the surface, loops where the first and last vertices, but no others in the sequence, are in the surface, and tails which have exactly one vertex in the surface. We calculate various train statistics and, for our model, we also obtain loop statistics from these results. At temperatures above the critical adsorption temperature,

essentially all of the monomers are in tails, while below this temperature trains and loops dominate. In the adsorbed phase the fraction of monomers in tails goes to zero in the thermodynamic limit and, as the temperature decreases further, the proportion of monomers in trains increases. In the infinite- n limit it can be shown that the limiting free energy of walks that start and end in the surface is the same as that of walks that start in the surface but are not restricted to end there. This follows from some very general arguments [4].

In addition, for the case of a copolymer with two types of monomers or for a striped surface with two types of stripes, we compute the statistics of the different possible types of visits to the surface. These quantities are sensitive to the energy parameters associated with the various types of visits and give information about the conformation of the adsorbed polymer.

Any such calculations will, unavoidably, be model dependent in a quantitative way. In earlier work [17,39] we compared results for the partially directed walk model and for the self-avoiding walk model and showed that the behavior is qualitatively very similar. As a result, the general features of the behavior of the partially directed walk model studied here are expected to be very close to those of the self-avoiding walk model.

In Sec. II we define the models that we consider and outline the techniques by which these models can be solved exactly. In Sec. III we describe our principle results and we discuss our results further in Sec. IV.

II. MODELS AND METHOD OF SOLUTION

The basic conformational model that we use throughout this paper is a partially directed walk (PDW) on the simple cubic lattice. With the obvious coordinate system (x_1, x_2, x_3) (so that vertices of the lattice have integer coordinates) we consider walks that start at the origin, are confined to the half space $x_3 \geq 0$, and have their last vertex in the plane $x_3 = 0$. The plane $x_3 = 0$ represents an impenetrable surface at which adsorption can occur. We write $x_i(j)$ for the i th coordinate of the j th vertex, $i = 1, 2, 3$, $j = 0, \dots, n$, so $x_1(0) = x_2(0) = x_3(0) = 0$ and $x_3(j) \geq 0$, $j = 0, \dots, n$. Partially directed walks are a subset of self-avoiding walks with the added restriction that they cannot take steps in the negative x_1 or x_2 directions. The restriction of having the last vertex in $x_3 = 0$ does not affect our results for the adsorbed phase since it can be shown that tails

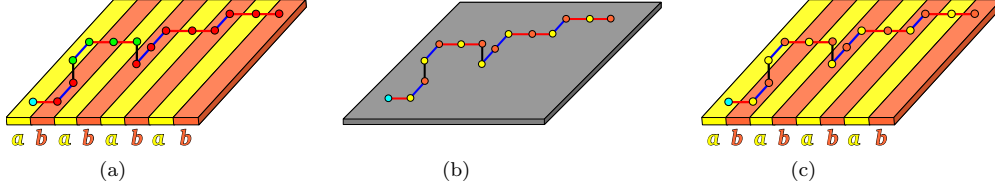


FIG. 1. (Color online) Schematic examples of the three different models studied in this paper: (a) the HS model, (b) the CH model, and (c) the CS model. For clarity, the steps in the x_1 and x_2 directions are coloured red and blue, respectively.

are negligible in this phase in the thermodynamic ($n \rightarrow \infty$) limit.

We shall be primarily concerned with three types of heterogeneity [17] (see Fig. 1).

(i) A homopolymer interacting with a striped surface (the HS model). The polymer is homogeneous but the surface has stripes of two types a and b . The type of stripe is determined by the parity of the x_2 coordinate. A monomer on an a stripe contributes an energy ϵ_a and a monomer on a b stripe contributes an energy ϵ_b . We sometimes write $-\epsilon_a/k_B T = \alpha$ and $-\epsilon_b/k_B T = \beta$, where k_B is Boltzmann's constant and T is the absolute temperature.

(ii) A strictly alternating copolymer interacting with a homogeneous surface (the CH model). The polymer has two comonomers A and B that strictly alternate along the polymer. The surface is homogeneous. Each A monomer in the surface contributes energy ϵ_A and each B monomer on the surface contributes energy ϵ_B . We sometimes write $-\epsilon_A/k_B T = \alpha$ and $-\epsilon_B/k_B T = \beta$.

(iii) A strictly alternating copolymer interacting with a striped surface (the CS model). The polymer is strictly alternating as in the CH model and the surface is striped as in the HS model. Here A monomers on a stripes contribute energy ϵ_{Aa} , etc. To simplify the situation we set $\epsilon_{Ab} = \epsilon_{Ba} = 0$ and we sometimes write $-\epsilon_{Aa}/k_B T = \alpha$ and $-\epsilon_{Bb}/k_B T = \beta$.

We extract the thermodynamic quantities from these models by considering the singularity structure of the generating function for all walks in a particular class. In general, we write

$$G = \sum_n Z_n z^n, \quad (1)$$

where Z_n is the n -step partition function for the model given by

$$Z_n = \sum_{v_\mu, v_\nu} c_n \exp(-H/kT), \quad (2)$$

where $c_n = c_n(v_\mu, v_\nu)$ is the number of n -step walks with v_μ (v_ν) interactions of type μ (ν), respectively, and

$$H = v_\mu \epsilon_\mu + v_\nu \epsilon_\nu. \quad (3)$$

Here μ can be A or a or Aa and ν can be B or b or Bb depending on which model we are considering. Irrespective of the model, we note that the thermodynamic limit $\lim_{n \rightarrow \infty} n^{-1} \ln Z_n \equiv \kappa$ exists and the generating function can be written as

$$G = \sum_n e^{\kappa n + o(n)} z^n. \quad (4)$$

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

We can further decorate the generating function with variables conjugate to the number of edges in the surface t , out of the surface l , and the number of loops l_N in a particular walk. Depending on the model of the inhomogeneity and the associated geometry, we also make use of a number of auxiliary generating functions that keep track of the parity of the total number of steps, as well as steps in the x_2 direction. In order to obtain these functions, as well as the solutions to the full problem, we employ methods related to *wasp-waist factorization*. (This term seems to have been first used by Bousquet-Mélou [43].)

When dealing with inhomogeneous walk models we shall use a set of coupled equations satisfied by the different generating functions, but we start with the case of a homopolymer interacting with a homogeneous impenetrable surface. Due to the nature and geometry of the inhomogeneous models, we shall need to keep track of the parity of the total number of steps and steps in the x_2 direction. As a result, we introduce variables s_1 and s_2 that are conjugate to steps in the x_1 and x_2 directions, respectively. In this case, the generating function $P(s_1, s_2, z)$ satisfies the equation

$$P = 1 + (s_1 + s_2)zP + z^2 P^* + (s_1 + s_2)z^3 P^* P, \quad (5)$$

where $P^*(s_1, s_2, z) = P(s_1, s_2, z) - 1$ represents all PDWs with at least one step.

The factorization scheme above partitions all possible PDWs according to their first steps. The walk can be a single vertex, contributing 1, or its first step can be in either the x_1 or x_2 direction along 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 $z^2 P^*$, or after returning to the surface for the first time, it can take a step in either the x_1 or x_2 direction and then be continued in all possible ways. The factorization scheme is sketched in Fig. 2.

Solving the resulting quadratic equation for $P(s_1, s_2, z)$, one finds that the physically relevant solution (i.e., the solution with positive coefficients in its z expansion) has a square root singularity at

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

where $s_{12} = s_1 + s_2$. When $s_1 = s_2 = 1$, this quantity reduces to $z_1 = (\sqrt{17} - 3)/4$, which agrees with a result of Orlandini *et al.* [31]. The singularity z_1 dominates in the desorbed phase

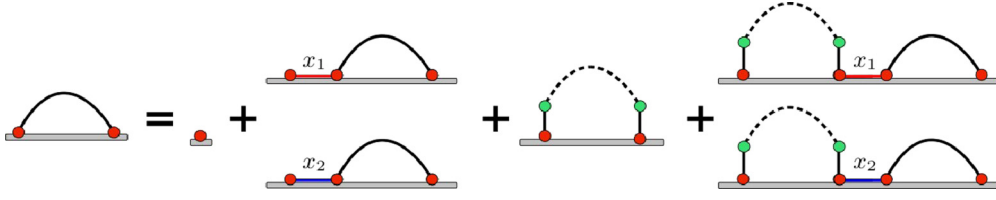


FIG. 2. (Color online) General factorization argument for loops interacting with a surface.

where the walk has a zero density of visits to the surface in the $n \rightarrow \infty$ limit.

As part of the factorization scheme used for the remaining models considered in this paper we make use of several auxiliary generating functions. When considering the CH model (alternating copolymer and a homogeneous surface), we need to keep track of the parity of the total number of steps. We write $Q^E(s_1, s_2, z) = [P(s_1, s_2, z) + P(s_1, s_2, -z)]/2$ and $Q^O(s_1, s_2, z) = P(s_1, s_2, z) - Q^E(s_1, s_2, z)$ for the generating functions of walks having an even or odd total number of steps. On the other hand, for the HS model (a homopolymer and a striped surface), we need to keep track of the parity of the steps that cross stripes. In this case we can write $Q^e(s_1, s_2, z) = [P(s_1, s_2, z) + P(s_1, -s_2, z)]/2$ and $Q^o(s_1, s_2, z) = P(s_1, s_2, z) - Q^e(s_1, s_2, z)$ for the functions with an even or odd number of steps in the x_2 direction, respectively. For the CS model (alternating copolymer and a striped surface) we combine this procedure to determine the functions that keep track of the parity of the total number of steps as well as the parity of the steps in the x_2 direction. Here we get

$$Q^{Ee}(s_1, s_2, z) = \frac{Q^E(s_1, s_2, z) + Q^E(s_1, -s_2, z)}{2}, \quad (7)$$

$$Q^{Eo}(s_1, s_2, z) = Q^E(s_1, s_2, z) - Q^{Ee}(s_1, s_2, z), \quad (8)$$

$$Q^{Oe}(s_1, s_2, z) = \frac{Q^O(s_1, s_2, z) + Q^O(s_1, -s_2, z)}{2}, \quad (9)$$

and

$$Q^{Oo}(s_1, s_2, z) = Q^O(s_1, s_2, z) - Q^{Oe}(s_1, s_2, z), \quad (10)$$

where Q^{Ms} is the generating function of walks with parity $M \in \{E, O\}$ with respect to total number of steps and parity $s \in \{e, o\}$ with respect to steps in the x_2 direction.

With these auxiliary functions in hand, we can start to build up the equations for the various models that include an inhomogeneity. We start with the CH model, where we consider a strictly alternating copolymer interacting with a homogenous surface. We define P_A and P_B to be the generating functions for walks that start with an A vertex and a B vertex, respectively. In this scenario, the set of coupled equations satisfied by the generating functions can be written as

$$P_A = 1 + (s_1 + s_2)btzP_B + al_N l^2 z^2 (\bar{Q}^E - 1)[1 + (s_1 + s_2)btzP_B] + bl_N l^2 z^2 \bar{Q}^O [1 + (s_1 + s_2)atzP_A], \quad (11)$$

$$P_B = 1 + (s_1 + s_2)atzP_A + bl_N l^2 z^2 (\bar{Q}^E - 1)[1 + (s_1 + s_2)atzP_A] + al_N l^2 z^2 \bar{Q}^O [1 + (s_1 + s_2)btzP_B], \quad (12)$$

where $\bar{Q}^E = Q^E(1, 1, lz)$ and $\bar{Q}^O = Q^O(1, 1, lz)$ are the generating functions of loops with even and odd total step parity, respectively. This factorization argument follows a modification of the scheme sketched in Fig. 2 in that we are now keeping track of the parity of steps for the portion of the walk that is out of the surface, as well as keeping track of more than just the total number of steps. In this scheme, we also introduce the variables a, b, l, l_N , and t , as defined above, and obtain solutions $P_A = P_A(a, b, l, l_N, t, z)$ and $P_B = P_B(a, b, l, l_N, t, z)$. Both P_A and P_B have the same singularity structure, namely, a square root singularity that we have already seen in (6) along with a simple pole at $z = z_2^{\text{CH}}(a, b, l, l_N, t)$.

In a similar way we can obtain the generating functions for the HS model. This time the generating functions that we use will keep track of walks that start on an a stripe and b stripe, respectively, via P_a and P_b . The full set of equations, including auxiliary functions and variables that keep track of contacts with the various stripes, as well as the remaining parameters that appear in the model, can be written as

$$P_a = 1 + s_1 atzP_a + s_2 btzP_b + al_n l^2 z^2 (\bar{Q}^e - 1)[1 + s_1 atzP_a + s_2 btzP_b] + bl_n l^2 z^2 \bar{Q}^o [1 + s_2 atzP_a + s_1 btzP_b], \quad (13)$$

$$P_b = 1 + s_2 atzP_a + s_1 btzP_b + al_n l^2 z^2 \bar{Q}^o [1 + s_1 atzP_a + s_2 btzP_b] + bl_n l^2 z^2 (\bar{Q}^e - 1)[1 + s_2 atzP_a + s_1 btzP_b], \quad (14)$$

where $\bar{Q}^s = Q^s(1, 1, lz)$ for $s \in \{e, o\}$ represent the generating function of loops with an even or odd number of steps in the x_2 direction. We can solve this system of equations to obtain the generating functions $P_a = P_a(a, b, l, l_N, t, z)$ and $P_b = P_b(a, b, l, l_N, t, z)$. Both of these functions are singular for $z = z_1$ and along $z = z_2^{\text{HS}}(a, b, l, l_N, t)$, with the first singularity arising due to a square root and the second from a zero of the denominator in P_a and P_b .

Following this line of thinking, we can see that for the CS model we require four generating functions P_{Ms} , where $M \in \{A, B\}$ and $s \in \{a, b\}$ represent the nature of the starting vertex and the type of stripe under that vertex, respectively. These generating functions will be a part of system of four coupled equations that depend on the usual variables along with four auxiliary generating

functions $\bar{Q}^{Ms} = Q^{Ms}(1,1,lz)$,

$$P_{Aa} = 1 + s_2btzP_{Bb} + s_1tzP_{Ba} + al_n l^2 z^2 (\bar{Q}^{Ee} - 1)(1 + s_2btzP_{Bb} + s_1tzP_{Ba}) + bl_n l^2 z^2 \bar{Q}^{Oo}(1 + s_2atzP_{Aa} + s_1tzP_{Ab}) + l_n l^2 z^2 \bar{Q}^{Eo}(1 + s_2tzP_{Ba} + s_1btzP_{Bb}) + l_n l^2 z^2 \bar{Q}^{Oe}(1 + s_2tzP_{Ab} + s_1atzP_{Aa}), \quad (15)$$

$$P_{Ab} = 1 + s_2tzP_{Ba} + s_1btzP_{Bb} + l_n l^2 z^2 (\bar{Q}^{Ee} - 1)(1 + s_2tzP_{Ba} + s_1btzP_{Bb}) + l_n l^2 z^2 \bar{Q}^{Oo}(1 + s_2tzP_{Ab} + s_1atzP_{Aa}) + al_n l^2 z^2 \bar{Q}^{Eo}(1 + s_2btzP_{Bb} + s_1tzP_{Ba}) + bl_n l^2 z^2 \bar{Q}^{Oe}(1 + s_2atzP_{Aa} + s_1tzP_{Ab}), \quad (16)$$

$$P_{Ba} = 1 + s_2tzP_{Ab} + s_1atzP_{Aa} + l_n l^2 z^2 (\bar{Q}^{Ee} - 1)(1 + s_2tzP_{Ab} + s_1atzP_{Aa}) + l_n l^2 z^2 \bar{Q}^{Oo}(1 + s_2tzP_{Ba} + s_1btzP_{Bb}) + bl_n l^2 z^2 \bar{Q}^{Eo}(1 + s_2atzP_{Aa} + s_1tzP_{Ab}) + al_n l^2 z^2 \bar{Q}^{Oe}(1 + s_2btzP_{Bb} + s_1tzP_{Ba}), \quad (17)$$

$$P_{Bb} = 1 + s_2atzP_{Aa} + s_1tzP_{Ab} + bl_n l^2 z^2 (\bar{Q}^{Ee} - 1)(1 + s_2atzP_{Aa} + s_1tzP_{Ab}) + al_n l^2 z^2 \bar{Q}^{Oo}(1 + s_2btzP_{Bb} + s_1tzP_{Ba}) + l_n l^2 z^2 \bar{Q}^{Eo}(1 + s_2tzP_{Ab} + s_1btzP_{Ba}) + l_n l^2 z^2 \bar{Q}^{Oe}(1 + s_2tzP_{Ba} + s_1btzP_{Bb}). \quad (18)$$

This system of equations can be solved to produce a set of generating functions that all share the same singularity structure: a square root singularity at $z = z_1$ and a simple pole along $z = z_2^{CS}(a,b,l,l_N,t)$.

For each of the models considered here, we can study the change in the dominant singularity as the contact parameters a and b are varied. The result is a curve in the $(\ln a, \ln b)$ plane along which the singularities are equal. We refer to this collection of points as the phase boundary between the adsorbed and desorbed regimes. The associated phase boundaries for the HS, CH, and CS models can be seen in Fig. 3. See Ref. [17] for a more detailed discussion on the nature and shape of these curves.

III. RESULTS

A. Train and loop statistics

Every walk can be regarded as a sequence of trains, loops, and tails [41,42]. The models considered in this paper are required to start and end in the same plane and as such they are composed of a sequence of trains and loops, exclusively.

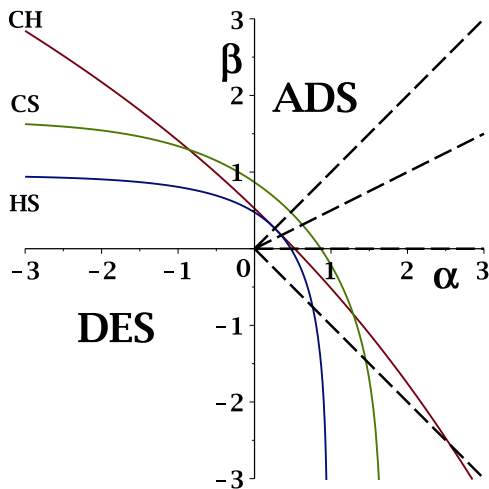


FIG. 3. (Color online) Phase diagram of the HS, CS, and CH models. The rays along which walk statistics are collected are shown as dashed lines.

From this we can see that the number of trains and the number of loops are either equal or differ by ± 1 and the fraction of edges in loops plus the fraction of edges in trains is 1.

For our models, we obtain the required walk statistics by evaluating exactly various first derivatives of the free energy. For example, the mean fraction of edges in a train and edges in a loop can be calculated from

$$\rho_{\text{train}} = \frac{\partial \kappa}{\partial \ln t}, \quad \rho_{\text{loop}} = \frac{\partial \kappa}{\partial \ln l}, \quad (19)$$

where $\kappa = -\ln z_c$ for the dominant singularity z_c . In a similar way we can also calculate the number of trains per edge ρ_{l_N} in the $n \rightarrow \infty$ limit from $\rho_{l_N} = \frac{\partial \kappa}{\partial \ln l_N}$ and the fact that in the thermodynamic limit $\rho_{l_N} = \rho_{l_N}$. We have exact expressions for these quantities, though they are too complex to report here in detail.

In Figs. 4(a)–4(l) we show the α dependence of various quantities along the three rays $\beta = 0$, $\beta = \alpha/2$, and $\beta = -\alpha$. In Figs. 4(a), 4(e), and 4(i) we show the α dependence of the limiting fraction of edges in trains in the $n \rightarrow \infty$ limit, ρ_{train} , for three cases: $\beta = 0$, $\beta = \alpha/2$, and $\beta = -\alpha$. The last case corresponds to a type of frustration. Each of the figures has three curves, one for each of the HS, CH, and CS models. In each case ρ_{train} is zero for values of α below the critical value (i.e., in the high-temperature desorbed phase) and increases monotonically above this critical value. Of course, the critical value of α and the rate of increase depends on the model and on how β depends on α . For $\beta = 0$, $\beta = \alpha/2$, and $\beta = \alpha$ (not shown), ρ_{train} approaches unity as α goes to infinity, i.e., as the temperature goes to zero. (When $\beta = \alpha$ both the HS and CH models reduce to homopolymer adsorption on a homogeneous surface.) For $\beta = -\alpha$ the limiting behavior is the same for the HS and CS models, but for the CH model the limiting value of ρ_{train} is $1/3$. This reflects the fact that while it is energetically advantageous for A monomers to adsorb on the homogeneous surface, it is disadvantageous for B monomers to adsorb on the surface. Because of the geometry of the walk, an A visit implies a B visit for the CH model and we have a kind of frustration. Contrast this with the HS model, where the adsorbed walk can follow an a stripe and the CS model where the walk can follow an a stripe and avoid Bb contacts, so avoiding disadvantageous energy contributions. These results

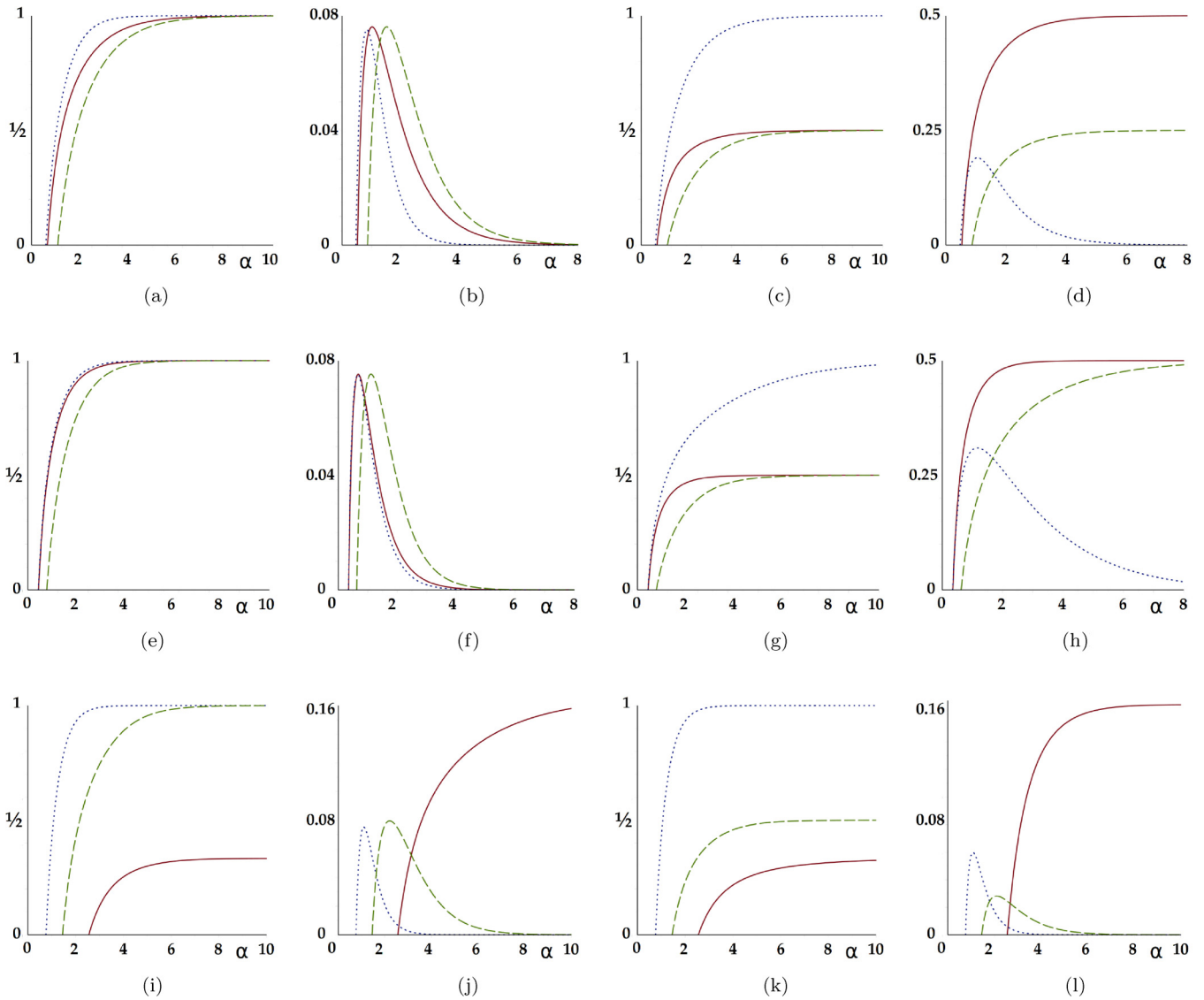


FIG. 4. (Color online) Order parameters along various rays in the (α, β) plane for the HS (dotted lines), CH (solid lines), and CS (dashed lines) models for the rays (a)–(d) $\beta = 0$, (e)–(h) $\beta = \alpha/2$, and (i)–(l) $\beta = -\alpha$: (a), (e), and (i) mean fraction of edges in a train; (b), (f), and (j) mean number of trains; (c), (g), and (k) mean fraction of *A*-type contacts; and (d), (h), and (l) mean fraction of *B*-type contacts.

suggest that the (degenerate) ground state of the CH model when $\beta = -\alpha$ is an alternating sequence of loops with four edges and trains with two edges. See Fig. 5 for a sketch. We shall see further evidence for this in the next section.

In Figs. 4(b), 4(f), and 4(j) we show the α dependence of the scaled number of trains, i.e., the number of trains per edge in the $n \rightarrow \infty$ limit. For all of the cases this quantity is zero until after the adsorption transition and, except for the CH model when $\beta = -\alpha$, the curve is then unimodal, going to zero as $\alpha \rightarrow \infty$. For the CH model when $\beta = -\alpha$ the curve

increases monotonically and tends to $1/6$ as $\alpha \rightarrow \infty$. This is consistent with the ground state described above where loops of four edges and trains of two edges alternate so there is one loop for every six edges.

We observe that the different models, corresponding to different physical situations, give rise to strong quantitative differences in the density of monomers in trains and to qualitative differences in the mean number of trains. These might be experimentally accessible by NMR techniques, such as solvent relaxation NMR [44].

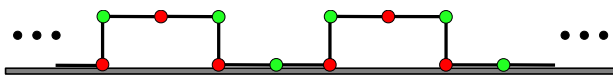


FIG. 5. (Color online) Sketch of the proposed ground state for the CH model. Steps perpendicular to the x_3 direction can be in either the x_1 or the x_2 direction so the ground state is degenerate.

B. Visits of different types

In this section we examine the statistics of various kinds of visits to the surface. For the HS model we are interested in the fraction of vertices that are on an *a* stripe and the fraction that are on a *b* stripe. In the $n \rightarrow \infty$ limit we call these two limiting fractions ρ_1^{HS} and ρ_2^{HS} , respectively. In a similar way we define

ρ_1^{CH} , ρ_2^{CH} , ρ_1^{CS} , and ρ_2^{CS} . The α dependences of the various ρ_1 quantities are shown in Figs. 4(c), 4(g), and 4(k) and we show those of the ρ_2 quantities in Figs. 4(d), 4(h), and 4(l).

For $\beta = 0$ and $\beta = \alpha/2$ both ρ_1^{CH} and ρ_1^{CS} approach $1/2$ as $\alpha \rightarrow \infty$. For the copolymer on a homogeneous surface (the CH model) this suggests that all the vertices are on the surface, while for a copolymer on a striped surface (the CS model) all the A vertices are on a stripes. For the CS model this could be achieved by simply following an a stripe or by crossing from one stripe to the next at each step, or by some combination of these two strategies. The behavior is different at $\beta = 0$, where $\rho_2^{\text{CS}} \rightarrow 1/4$ so that the walk maximizes entropy by having only half of the B vertices on b stripes, and at $\beta = \alpha/2$, where there is an energetic advantage to having B vertices on b stripes and $\rho_2^{\text{CS}} \rightarrow 1/2$ (so all B vertices are on b stripes).

For the homopolymer on a striped surface (the HS model) $\rho_1^{\text{HS}} \rightarrow 1$ and $\rho_2^{\text{HS}} \rightarrow 0$ for $\beta = 0$ and for $\beta = \alpha/2$. The walk follows an a stripe since this is the strategy that optimizes the energy.

When $\beta = \alpha$, the HS and CH models become homopolymers adsorbing on a homogeneous surface. The walk lies entirely in the surface in the $\alpha \rightarrow \infty$ limit and ρ_1 and ρ_2 approach $1/2$ for both models. For the CS model, $\rho_1^{\text{CS}} \rightarrow 1/2$ and $\rho_2^{\text{CS}} \rightarrow 1/2$, but now it is energetically advantageous for A monomers to be on a stripes and B monomers to be on b stripes so the walk crosses from stripe to stripe at each step.

When $\beta = -\alpha$, for the HS model, $\rho_1^{\text{HS}} \rightarrow 1$ and $\rho_2^{\text{HS}} \rightarrow 0$ so again the walk follows an a stripe for energetic reasons. There is no energetic advantage in visiting a b stripe. For the CS model, $\rho_1^{\text{CS}} \rightarrow 1/2$ and $\rho_2^{\text{CS}} \rightarrow 0$. Again the walk follows an a stripe to avoid the energetic penalty of having a B vertex on a b stripe. For the CH model it is impossible to avoid entirely having B vertices in the surface if A vertices are to be on the surface. The optimum strategy seems to be a configuration of alternating loops with four edges and trains with two edges as discussed above, so $\rho_1^{\text{CH}} \rightarrow 1/3$ and $\rho_2^{\text{CH}} \rightarrow 1/6$. For every six edges in this repeating structure there are two A vertices and one B vertex in the surface. See Fig. 5.

Again there are strong qualitative and quantitative differences in the behavior of the different models, especially along the ray $\beta = -\alpha$ where we have frustration. These quantities should be experimentally accessible by NMR techniques (e.g., different chemical shifts [45]) or by infrared spectroscopy where stretching frequencies will be affected differently depending on which and where monomers adsorb [45].

C. Spans in the x_1 and x_2 directions

We have also calculated the mean spans in the x_1 and x_2 directions. Since the walks are directed in these two directions, the limits $S_i = \lim_{n \rightarrow \infty} \langle x_i(n)/n \rangle$, $i = 1, 2$, are positive. For the CH model where the surface is homogeneous $S_1 = S_2$, but for the HS and CS models the presence of the stripe destroys the symmetry and S_1 and S_2 are not necessarily equal. The difference between S_1 and S_2 reflects the conformation of the adsorbed polymer and in particular gives information about the average conformation with respect to the stripe direction.

Detailed results as a function of α are given in Fig. 6 for the HS and CH models. We were unable to compute the corresponding quantities for the CS model. For values of α

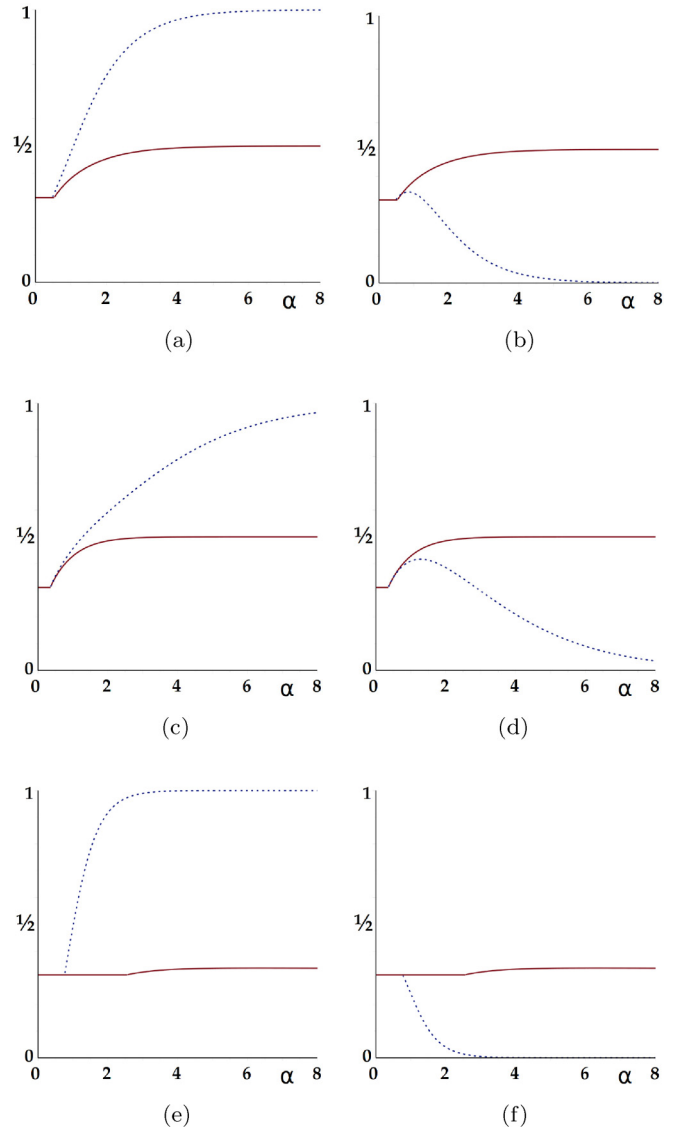


FIG. 6. (Color online) Plots of the average span in the (a), (c), and (e) x_1 and (b), (d), and (f) x_2 directions along various rays in the (α, β) plane for the HS (dotted lines) and CH (solid lines) models for the rays (a) and (b) $\beta = 0$, (c) and (d) $\beta = \alpha/2$, and (e) and (f) $\beta = -\alpha$.

less than the critical value for adsorption the values of S_1 and S_2 are constant and equal for all the cases because the walk is in the desorbed phase. In this phase, the dominant singularity is given by $z = z_1(s_1, s_2)$ as shown in (6), irrespective of the inhomogeneity. Using this expression for the singularity in the definition of S_1 and S_2 above, we find that when α is less than the critical value

$$S_1 = S_2 = \frac{17 + \sqrt{17}}{68} = 0.31063\dots \quad (20)$$

In this phase the presence of the impenetrable plane $x_3 = 0$ means that the walk is entropically repelled from this plane. The details of the surface are essentially irrelevant since the number of visits to the surface is $o(n)$ and this leads to $S_1 = S_2 < 1/3$.

When α is larger than the critical value the behavior depends on both the model and on the ray in the (α, β) plane. For the HS model S_1 increases monotonically to 1 though the details of the rate of change depend on the ray; S_2 decreases monotonically to zero for $\beta = -\alpha$ but for $\beta = 0$ and for $\beta = \alpha/2$, S_2 first increases as the walk is pulled into the surface and then decreases as the walk starts to follow the a stripes. For the CH model the values of S_1 and S_2 are identical since the surface is homogeneous. For $\beta = 0$ and for $\beta = \alpha/2$ the values increase monotonically to $1/2$, while for $\beta = -\alpha$ they increase slightly to $1/3$.

The large- α behavior reflects the ground states and we first consider the HS model. In each case, for $\beta = 0$, $\alpha/2$, and $-\alpha$ the walk follows an a stripe in the ground state and $S_1 = 1$ while $S_2 = 0$.

For the CH model, when $\beta = 0$ and $\alpha/2$ the walk is entirely adsorbed in the ground state and, since there is no surface inhomogeneity, we have $S_1 = 1/2$ and $S_2 = 1/2$. When $\beta = -\alpha$ the ground state is as sketched in Fig. 5 with only $2/3$ of the edges parallel to the surface. Since there is no surface inhomogeneity, half of these edges are in the x_1 direction and half in the x_2 direction, so $S_1 = S_2 = 1/3$.

The ground state of the CS model depends strongly on the ray being followed in the (α, β) plane. When $\beta = 0$ there is no advantage or disadvantage to having B vertices on b stripes, but all A vertices should be on a stripes. The walk can follow a stripes or cross from one a stripe to another in two steps, or any combination. Hence $S_1 = S_2 = 1/2$. Moreover, the ground state will be degenerate with entropy $(k_B/2) \ln 2$. When $\beta = \alpha/2$ it is energetically favorable to have A vertices on a stripes and b vertices on B stripes so the walk will cross from stripe to stripe at each step, so $S_1 = 0$ and $S_2 = 1$. When

$\beta = -\alpha$, B vertices will avoid B stripes and the walk will follow an a stripe so $S_1 = 1$ and $S_2 = 0$.

IV. DISCUSSION

We have considered partially directed walk models, in three dimensions, of three kinds of inhomogeneous polymer adsorption: a homopolymer adsorbing on a striped surface, an alternating copolymer adsorbing on a homogeneous surface, and an alternating copolymer adsorbing on a striped surface. In each case we have obtained complete solutions in the infinite- n limit. We have computed detailed statistics about the fraction of monomers in trains, the mean number of trains, and the densities of various types of vertex-surface contacts. These quantities give useful information about the way in which the polymer lies on the surface, especially at low temperatures when the polymer is strongly adsorbed, and could be experimentally accessible by NMR methods. Such measurements are a useful alternative to atomic force microscopy in probing the conformations of the adsorbed polymer.

The conformations are very dependent on both the nature of the inhomogeneity and the relative values of the energy parameters. By making one energy term attractive and the other repulsive we observe a kind of frustration and this can play a role in the recognition process where one monomer sequence is much more readily adsorbed than another on a particular surface.

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