

## Spherically symmetric random walks. III. Polymer adsorption at a hyperspherical boundary

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A recently developed model of random walks on a  $D$ -dimensional hyperspherical lattice, where  $D$  is *not* restricted to integer values, is used to study polymer growth near a  $D$ -dimensional attractive hyperspherical boundary. The model determines the fraction  $P(\kappa)$  of the polymer adsorbed on this boundary as a function of the attractive potential  $\kappa$  for all values of  $D$ . The adsorption fraction  $P(\kappa)$  exhibits a second-order phase transition with a universal, nontrivial scaling coefficient for  $0 < D < 4$ ,  $D \neq 2$ , and exhibits a first-order phase transition for  $D > 4$ . At  $D = 4$  there is a tricritical point with logarithmic scaling. This model reproduces earlier results for  $D = 1$  and 2, where  $P(\kappa)$  scales linearly and exponentially, respectively. A crossover transition that depends on the radius of the adsorbing boundary is found. [S1063-651X(96)05806-0]

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### I. INTRODUCTION

In previous papers [1–4] we analyzed a class of models of  $D$ -dimensional spherically symmetric random walks, where  $D$  is *not* restricted to integer values. In Ref. [1] we introduced the notion of spherically symmetric random walks and in Ref. [2] we studied a simplified model of spherically symmetric random walks that is analytically tractable for all values of  $D$ . In Ref. [3] we considered random walks that allow for the creation and annihilation of random walkers and demonstrated that these extended models exhibit critical behavior as a function of the birth rate of walkers. In Ref. [4] we summarized the results of this and the previous papers and discuss the universality of the critical behavior using analytical methods and numerical calculations for different lattice configurations. This critical behavior exhibits an interesting dependence on the dimension  $D$ . In this paper we apply these ideas specifically to the study of polymer growth near a  $D$ -dimensional hyperspherical adsorbing boundary [5].

Polymers have inspired many experimental and theoretical investigations [6,7]. Because polymers are complex objects constructed from simple building blocks, they serve as a laboratory for the development of scaling methods [8], renormalization-group theory [9], and Monte Carlo simulation [10]. Formulating simplified statistical models of polymer growth is useful for understanding aspects of critical phenomena exhibited by actual polymers. Polymer growth in a disordered environment such as directed polymers in random media (DPRM) is also used to describe phenomena ranging from crack propagation to flux-line pinning in superconductors [11(a)]. Subtle effects for the adsorption transition arise when the disorder is confined to a random potential on an adsorbing boundary [11(b)], and extending the study of these effects to dimensions  $D > 1$  is of practical importance [11(a),11(c)].

The simplest polymer system is an unbranched chain of

monomers. Such systems are easy to model by means of self-avoiding random walks [12,13]. In this paper, we examine such a polymer growing in the neighborhood of an attractive  $D$ -dimensional hyperspherical boundary. Special

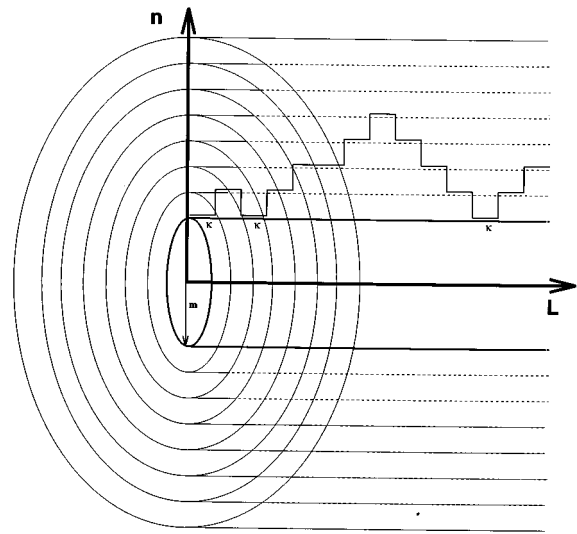


FIG. 1. Random walk on a lattice consisting of concentric cylindrical surfaces of unit radii. Such a walk serves as model for a polymer growing at an attractive cylindrical boundary such as a cell membrane with radius  $m$  (thickened lines). The polymer is initially grafted to the boundary and is growing to the right. Every time a monomer gets added at the boundary, the polymer gains in potential energy by an amount  $\kappa$ . The walk consists of  $N = 26$  monomer links, but only  $L = 14$  random steps were required because every random step in the radial direction is followed by a deterministic step in the axial direction. This requirement ensures that the random walk advances exactly one unit in the axial direction for each random step.

cases of this polymer system have already been investigated for planar ( $D=1$ ) [14] and cylindrical ( $D=2$ ) [15,16] boundaries.

The spherically symmetric random-walk model introduced in Ref. [1] was used in Ref. [15] to determine the critical properties of a polymer growing near an attractive  $D$ -dimensional hyperspherical boundary. However, that model was mathematically intractable except for  $D=1$  and 2. Here we use the model of hyperspherical random walks introduced in Ref. [2] to solve the  $D$ -dimensional polymer growth model for arbitrary  $D>0$ . Specifically, we consider

an ensemble of polymers near an attractive  $D$ -dimensional hyperspherical boundary of radius  $m$ , where  $m \geq 0$  is measured in discrete monomer units. We derived the adsorption fraction  $P(\kappa)$  as a function of the attractive potential  $\kappa$  in the limit where the average length of a polymer reaches infinity. The parameter  $\kappa$  is closely related to the birth rate  $a$  used in Ref. [3].

We find that if the attractive potential  $\kappa$  drops below a critical value  $\kappa_c$ , which in general depends on  $D$ , the adsorption fraction vanishes. As  $\kappa - \kappa_c \rightarrow 0+$  for fixed radius  $m$ , the asymptotic behavior of  $P(\kappa)$  is given by

$$P(\kappa) \sim \begin{cases} C_1(D,m)(\kappa - \kappa_c)^{D/(2-D)} & (0 < D < 2) \\ C_2(2,m)(\kappa - \kappa_c)^{-2} \exp\left[-\frac{8}{9(m+1)(\kappa - \kappa_c)}\right] & (D=2) \\ C_3(D,m)(\kappa - \kappa_c)^{(4-D)/(D-2)} & (2 < D < 4) \\ C_4(4,m) \frac{1}{\ln(\kappa - \kappa_c)} & (D=4) \\ C_5(D,m) & (D > 4), \end{cases} \quad (1.1)$$

where  $C_i(D,m)$  are constants that depend on the dimension  $D$  and the radius  $m$  of the adsorbing boundary.

Equation (1.1) ceases to be valid as  $m \rightarrow \infty$ . When

$$\kappa - \kappa_c \sim \frac{B(D)}{m}, \quad (1.2)$$

where  $B(D)$  is a constant of order 1, we observe a *crossover* transition to linear scaling behavior in  $P(\kappa)$  as  $\kappa - \kappa_c \rightarrow 0+$ .

In Sec. II we discuss the theory of polymer growth near an attractive  $D$ -dimensional spherically symmetric boundary. In Sec. III we solve the eigenvalue problem that results from a transfer-matrix description of this growth process. Finally, in Sec. IV we determine for all  $D > 0$  the adsorption fraction  $P(\kappa)$  near the critical point  $\kappa_c$ .

## II. DIRECTED-WALK MODEL FOR POLYMER ADSORPTION

We model polymer growth as a nonintersecting (directed), random walk in  $(D+1)$ -dimensional space. This random walk takes place on the union of a one-dimensional semi-infinite lattice and a  $D$ -dimensional lattice consisting of a set of concentric hyperspherical surfaces labeled  $S_n$ . The hyperspherical surfaces are equally spaced in units of one monomer length. The innermost surface  $S_m$ ,  $m \geq 0$ , is the attractive boundary, which has a radius of  $m$  in monomer units. The next surface  $S_{m+1}$  has a radius of  $m+1$  and so on. The extra axial dimension is introduced to ensure that the random walk is nonintersecting; thus we are actually studying a cylindrically-symmetric random walk in  $D+1$  dimensions.

At each step the random walker has a probability of moving one monomer unit radially outward, moving one monomer unit radially inward, or staying on the same radial surface. (When the walker is on the boundary surface  $S_m$  the

walker's probability of moving inward is zero.) Regardless of whether the walker moves radially or remains on the same radial surface, we then require the walker to move one additional monomer unit in the axial direction in the  $D+1$  dimension. This deterministic axial motion guarantees that the random walk will never cross itself. (A similar requirement is imposed in restricted solid-on-solid models.) Hence, at each step the polymer grows by adding either one or two monomers, but always advances exactly one unit in the axial direction. The growth of such a polymer is illustrated in Fig. 1 for the case  $D=2$ .

The dynamics of the polymer growth is regulated by a balance between energy and entropy. There is one energy associated with the addition of a new monomer and another associated with adsorption on the attractive boundary. Each addition of a monomer is characterized by a factor of  $z$  and each addition of a monomer on the attractive boundary  $S_m$  is associated with an additional factor of  $\kappa$ . The factor  $\kappa$  is shown in Fig. 1, but the factor of  $z$  is not indicated because there is one such factor for each line segment (monomer). As the dimension  $D$  increases there is a corresponding increase in the available volume for the polymer to occupy as it grows away from the adsorbing boundary. For any given  $D$  this configurational entropy balances the binding potential on the attractive boundary. Thus one might anticipate that the critical properties of this system will vary in an interesting way as a function of the curvature of the boundary.

While this random walk model is only a crude description of an actual polymer growing in a continuum, one might hope that the critical properties of the polymer system in the infinite chain limit are universal and well approximated by such a model.

We consider next the probabilities that define the radial motion of the random walk. We have introduced a hyper-

spherical lattice because spherical symmetry reduces a  $D$ -dimensional problem to a one-dimensional problem. The probability distribution of a spherically symmetric random walk is described completely by a one-dimensional recursion relation [1]. The coefficients in this recursion relation are dependent on the location of the walker and express the radial bias (or entropy) of the spherical geometry; that is, a random walker tends to move outward rather than inward because more volume is available in the outward direction when  $D > 1$ . In Ref. [1] inward and outward walk probabilities were proposed that express this radial bias. Unfortunately, for arbitrary  $D$ , these probabilities are so complicated that an analytical solution to the recursion relation is impossible except for a few special values of  $D$ .

In a recent paper [2] it was shown that the recursion relation *can* be solved analytically for all  $D > 0$  by replacing the outward and inward walk probabilities for region  $S_n$  with a uniform approximation for all  $n$ . In Ref. [2] it was shown that this simplified random walk exhibits the usual scaling properties of a random walk model. For example, walks on this lattice have a Hausdorff dimension  $D_H = 2$ . In comparison with random walks on other lattices, such as a hypercubic lattice, the random walk model studied in this paper is remarkable because it is analytically tractable. Numerical and analytical studies in Ref. [3] suggest that, despite the simplicity of the model, the nontrivial phenomena obtained in this paper are indeed universal.

We represent the probabilities that define the random walk considered in this paper by  $P_{\text{stay}}(n)$ , the probability that a walker stays on the surface  $S_n$  and just moves in the axial direction,  $P_{\text{out}}(n)$ , the probability that the walker moves outward from the surface  $S_n$  to the surface  $S_{n+1}$  (and then moves in the axial direction on the surface  $S_{n+1}$ ), and  $P_{\text{in}}(n)$ , the probability that the walker moves inward from the surface  $S_n$  to the surface  $S_{n-1}$  (and then moves in the axial direction on the surface  $S_{n-1}$ ). Generalizing the probabilities used in Ref. [2] to include the possibility of staying on the surface  $S_n$ , we express the *relative* probabilities as

$$P_{\text{stay}}(n) \equiv 1, \quad P_{\text{in}}(n) = \frac{2n}{2n+D-1},$$

$$P_{\text{out}}(n) = \frac{2(n+D-1)}{2n+D-1} \quad (n > m). \quad (2.1)$$

Note that the walker is more likely to move outward as  $D$  increases. However, as  $m$  increases with  $D$  held fixed, the outward and inward probabilities become equal; this happens because at large radius our nested spheres appear locally (on the scale of a monomer length) to be equally spaced parallel planes.

On the boundary  $S_m$  we enforce the condition that the walker is prohibited from moving inward by requiring that

$$P_{\text{stay}}(m) = 1, \quad P_{\text{in}}(m) = 0, \quad P_{\text{out}}(m) = 1. \quad (2.2)$$

The probabilities for the special one-dimensional case considered in Ref. [14] are obtained if we set  $D = 1$  in Eqs. (2.1) [17].

A single random walk can represent only one of the many configurations that a growing polymer can attain. To obtain

the critical properties of polymer growth at an attractive boundary, we must investigate the average behavior of an ensemble of walkers. Thus we derive a partition function for random walks and use it to generate ensemble averages that describe, for example, the fraction of a growing polymer that is adsorbed on the boundary. From the above probabilities and the parameters  $z$  and  $\kappa$  associated with adding monomers, we construct a transfer matrix  $T_{j,i}$  that expresses the probability of the walker moving from the  $i$ th to the  $j$ th surface at each step:

$$T_{j,i} = z^{|j-i|} \kappa^{\delta_{m,j}} [P_{\text{stay}}(i) \delta_{j,i} + P_{\text{out}}(i) \delta_{j-1,i} + P_{\text{in}}(i) \delta_{j+1,i}]. \quad (2.3)$$

A particular polymer configuration generated by a random walk consisting of  $L$  steps is characterized by a set of  $L$  integers  $\{h_i\}_{i=1}^L$  that specify the surface  $S_{h_i}$  reached on the  $i$ th step in the axial direction. The total statistical weight of such a polymer is expressed as a product of  $L$  elements of the transfer matrix:

$$z^L \delta_{m,h_0} T_{h_1,h_0} T_{h_2,h_1} \cdots T_{h_L,h_{L-1}},$$

where the Kronecker delta ensures that the polymer is initially grafted to the boundary. The partition function  $Z_L$  for all polymers having axial length  $L$  is then

$$Z_L = z^L \vec{b}^{(t)T} T^L \vec{e},$$

where  $\vec{b}^{(t)}$  and  $\vec{e}$  are vectors accounting for beginning and end effects. Hence  $Z = \sum_{L=1}^{\infty} Z_L$ , the total partition function for configurations of all axial lengths, is given by

$$Z(z, \kappa) = \vec{b}^{(t)T} z T (1 - zT)^{-1} \vec{e}. \quad (2.4)$$

Let  $\lambda_{\text{max}}(\kappa, z)$  be the largest eigenvalue of the transfer matrix  $T$  and define  $z_{\infty}(\kappa)$  by

$$1 = z_{\infty}(\kappa) \lambda_{\text{max}}[\kappa, z_{\infty}(\kappa)]. \quad (2.5)$$

Letting  $\Delta z = z_{\infty}(\kappa) - z$ , note that the partition function  $Z$  in Eq. (2.4) diverges as  $\Delta z \rightarrow 0+$ .

We can express the average length of a polymer in terms of the partition function  $Z$ :

$$\langle N(z, \kappa) \rangle = z \frac{\partial}{\partial z} \ln Z(z, \kappa).$$

Similarly, the average number of monomers adsorbed on the boundary is given by

$$\langle N_{S_m}(z, \kappa) \rangle = \kappa \frac{\partial}{\partial \kappa} \ln Z(z, \kappa).$$

As  $\Delta z \rightarrow 0+$ , both  $\langle N \rangle$  and  $\langle N_{S_m} \rangle$  diverge; that is, the average length of a polymer chain diverges. In this paper we study the fraction of adsorbed monomers  $P(\kappa)$  as a function

of the binding potential  $\kappa$  for an ensemble of polymers of all possible lengths. The adsorption fraction is given by

$$P(\kappa) = \lim_{\Delta z \rightarrow 0^+} \frac{\langle N_{S_m}(z, \kappa) \rangle}{\langle N(z, \kappa) \rangle} = - \frac{\kappa}{z_\infty(\kappa)} \frac{dz_\infty(\kappa)}{d\kappa}. \quad (2.6)$$

Note that the adsorption fraction  $P(\kappa)$  is defined only on the line  $z_\infty(\kappa)$  in the  $(\kappa, z)$  plane.

### III. EIGENVALUES OF THE TRANSFER MATRIX FOR ARBITRARY $D$

In this section we obtain an eigenvalue condition whose solution yields the spectrum  $\lambda$  of the transfer matrix  $T$  defined in Eq. (2.3). Inserting the probabilities in Eqs. (2.1) and (2.2) into Eq. (2.3), we obtain the difference-equation eigenvalue problem [18]

$$\lambda g_n = \sum_{i=m+1}^{\infty} T_{n,i} g_i = \begin{cases} g_n + 2z \frac{n+D-2}{2n+D-3} g_{n-1} + 2z \frac{n+1}{2n+D+1} g_{n+1} & (n \geq m+2) \\ g_{m+1} + z g_m + 2z \frac{m+2}{2m+D+3} g_{m+2} & (n = m+1) \\ \kappa g_m + 2\kappa z \frac{m+1}{2m+D+1} g_{m+1} & (n = m). \end{cases} \quad (3.1)$$

This problem has a continuous spectrum for all values of  $\kappa$ , but the spectrum contains bound states only for a certain range of  $\kappa$ . The continuous spectrum, and thus the value of its upper limit, does not vary as a function of  $\kappa$ . If  $\kappa$  is in a range such that the upper limit of the continuous spectrum is the largest eigenvalue of the transfer matrix, the adsorption fraction as defined in Eq. (2.6) vanishes because, by the chain rule, it is proportional to the derivative of  $\lambda_{\max}$  as a function of  $\kappa$ . On the other hand, if the value of  $\kappa$  is such that a bound state exists, the bound-state eigenvalue usually *does* vary as a function of  $\kappa$  and its value is larger than the upper limit of the continuous spectrum, which leads to a nonvanishing adsorption fraction. Thus the emergence of bound states is the criterion for the appearance of an adsorbed phase for the polymer.

In the Appendix we show that the eigenvalue condition for the bound states of the eigenvalue problem Eqs. (3.1) is given by

$$0 = \frac{2m+D-1}{m} {}_2F_1\left(\frac{m}{2}, \frac{m+1}{2}; m + \frac{D-1}{2}; \epsilon^2\right) + \epsilon A {}_2F_1\left(\frac{m+1}{2}, \frac{m}{2} + 1; m + \frac{D+1}{2}; \epsilon^2\right), \quad (3.2)$$

where we have defined

$$\epsilon = \frac{2z}{\lambda - 1}, \quad A = \frac{m+D-1}{m} \left[ \frac{1}{\kappa} \left( \frac{2}{\epsilon} + \frac{1}{z} \right) - \frac{1}{z} \right] - \frac{2m+D-1}{m\epsilon}. \quad (3.3)$$

Using  $z = z_\infty(\kappa)$  as defined in Eq. (2.5), the eigenvalue condition in (3.2) yields an implicit relation for  $z_\infty(\kappa)$  and thus we obtain the adsorption fraction  $P(\kappa)$  as defined in Eq. (2.6).

### IV. CRITICAL POINT ANALYSIS

The numerical value of  $P(\kappa)$  for any  $\kappa$  can be obtained from the implicit equation for  $z_\infty(\kappa)$ . However, using asymptotic analysis we can determine the behavior near the critical point explicitly. We showed that the critical transition is associated mathematically with the onset of bound states. Thus the critical point is located at  $\epsilon = 1$ . Using [19]

$$\begin{aligned} {}_2F_1(a, b; c; x) &= \frac{\Gamma(c)\Gamma(c-a-b)}{\Gamma(c-a)\Gamma(c-b)} \\ &\times {}_2F_1(a, b; a+b-c+1; 1-x) \\ &+ (1-x)^{c-a-b} \frac{\Gamma(c)\Gamma(a+b-c)}{\Gamma(a)\Gamma(b)} \\ &\times {}_2F_1(c-a, c-b; c-a-b+1; 1-x), \end{aligned}$$

we rewrite the eigenvalue condition (3.2) as

$$\begin{aligned} K \frac{m+1}{m+D-1} \left( \frac{1-\epsilon^2}{12} \right)^{D/2-1} &\left[ {}_2F_1\left(\frac{m+D-1}{2}, \frac{m+D-2}{2}; \frac{D}{2}; 1-\epsilon^2\right) + \epsilon A {}_2F_1\left(\frac{m+D}{2}, \frac{m+D-1}{2}; \frac{D}{2}; 1-\epsilon^2\right) \right] \\ &= \frac{m+D-2}{m} {}_2F_1\left(\frac{m}{2}, \frac{m+1}{2}; \frac{4-D}{2}; 1-\epsilon^2\right) + \epsilon A {}_2F_1\left(\frac{m+1}{2}, \frac{m}{2} + 1; \frac{4-D}{2}; 1-\epsilon^2\right), \end{aligned} \quad (4.1)$$

with

$$K = -3^{D/2-1} \frac{\Gamma\left(1 - \frac{D}{2}\right) \Gamma(m+D)}{\Gamma\left(\frac{D}{2} - 1\right) \Gamma(m+2)}. \quad (4.2)$$

Observe that the special cases of even integer  $D > 2$  require special attention; we consider these special cases later. The case  $D = 2$  has already been studied in Ref. [16] and will not be discussed here.

We now substitute

$$z = z_\infty(\kappa_c) - \Delta z \quad (\Delta z \rightarrow 0+),$$

$$\kappa = \kappa_c + \Delta \kappa \quad (\Delta \kappa \rightarrow 0+).$$

We will determine  $\kappa_c$  later from asymptotic analysis of the eigenvalue condition. However, using  $\epsilon|_{z_\infty(\kappa_c)} = 1$  and  $\lambda = 1/z_\infty(\kappa)$  and the definition of  $\epsilon$  in Eqs. (3.3), it is easy to determine that

$$z_\infty(\kappa_c) = \frac{1}{2}.$$

Retaining terms to sufficient order for the subsequent analysis,

$$\epsilon \sim 1 - 6\Delta z + \dots,$$

$$A \sim \frac{m+D-1}{m} \left[ \left( \frac{4}{\kappa_c} - 3 - \frac{m}{m+D-1} \right) - \frac{4}{\kappa_c^2} \Delta \kappa + 2 \left( \frac{8}{\kappa_c} - \frac{8m+5D-5}{m+D-1} \right) \Delta z + \dots \right],$$

we obtain from the eigenvalue condition in (4.1)

$$\mathcal{A} + \mathcal{B}\Delta\kappa + \mathcal{C}\Delta z + \dots \sim \Delta z^{D/2-1} (\mathcal{X} + \mathcal{Y}\Delta\kappa + \dots), \quad (4.3)$$

where

$$\mathcal{A} = 3 - \frac{4}{\kappa_c} - \frac{D-2}{m+D-1},$$

$$\mathcal{B} = 4 \frac{m+D-1}{(m+1)\kappa_c^2},$$

$$\mathcal{C} = \frac{2}{(m+1)(4-D)} \left[ 2(D-1)(2D+1) + m(28D-13) + 6m^2(D+5) + 9m^3 - \frac{4}{\kappa_c} (m+D-1)(3m^2+9m + D+2) \right],$$

$$\mathcal{X} = \left( 3 - \frac{4}{\kappa_c} \right) K,$$

$$\mathcal{Y} = \frac{4K}{\kappa_c^2},$$

where,  $K$  is given in Eq. (4.3).

In the following subsections, we determine the critical point  $\kappa_c$  and the asymptotic relation between  $\Delta z$  and  $\Delta \kappa$  by balancing terms in Eq. (4.3) order by order in the limits  $\Delta z \rightarrow 0+$ ,  $\Delta \kappa \rightarrow 0+$ . The asymptotic behavior of the adsorption transition near the critical point is then obtained from

$$P(\kappa) \sim \frac{\kappa_c}{z_\infty(\kappa_c)} \frac{d\Delta z}{d\Delta \kappa}. \quad (4.4)$$

#### A. Case $0 < D < 2$

In this case we eliminate a divergent term in Eq. (4.3) by imposing the condition  $\mathcal{X} = 0$ , which gives

$$\kappa_c = \frac{4}{3}. \quad (4.5)$$

To balance the terms in next order we demand that

$$\mathcal{A} \sim \mathcal{Y} \Delta z^{D/2-1} \Delta \kappa.$$

Thus we find that

$$\Delta z \sim \left( \frac{\mathcal{Y}}{\mathcal{A}} \right)^{2/(2-D)} \Delta \kappa^{2/(2-D)}$$

and, according to Eq. (4.4),

$$P(\kappa) \sim \frac{16}{3(2-D)} \left[ \frac{9(m+1)}{4(2-D)} K \right]^{2/(2-D)} (\kappa - \kappa_c)^{D/(2-D)} \quad (\kappa \rightarrow \kappa_c^+). \quad (4.6)$$

#### B. Case $2 < D < 4$

Here, to balance the most dominant terms in Eq. (4.3), we set  $\mathcal{A} = 0$ , which yields

$$\kappa_c = \frac{4}{3 - \frac{D-2}{m+D-1}}. \quad (4.7)$$

Note that  $\kappa_c$  in Eq. (4.7) joins continuously onto the value of  $\frac{4}{3}$  in Eq. (4.5) at  $D = 2$  for all  $m$ , rises with  $D$  for  $D > 2$ , and levels off at  $\kappa_c = 2$  as  $D \rightarrow \infty$ . On the other hand, as  $m \rightarrow \infty$  for fixed  $D > 2$  we regain the value of the critical point for  $D = 1$ .

To next order in the asymptotic analysis we obtain

$$\Delta z \sim \left( \frac{\mathcal{B}}{\mathcal{C}} \right)^{2/(D-2)} \Delta \kappa^{2/(D-2)}$$

or

$$P(\kappa) \sim \frac{16(m+D-1)}{(D-2)(3m+2D-1)} \left[ \frac{(3m+2D-1)^2}{4K(D-2)(m+1)} \right]^{2/(D-2)} \times (\kappa - \kappa_c)^{(4-D)/(D-2)} \quad (\kappa \rightarrow \kappa_c^+). \quad (4.8)$$

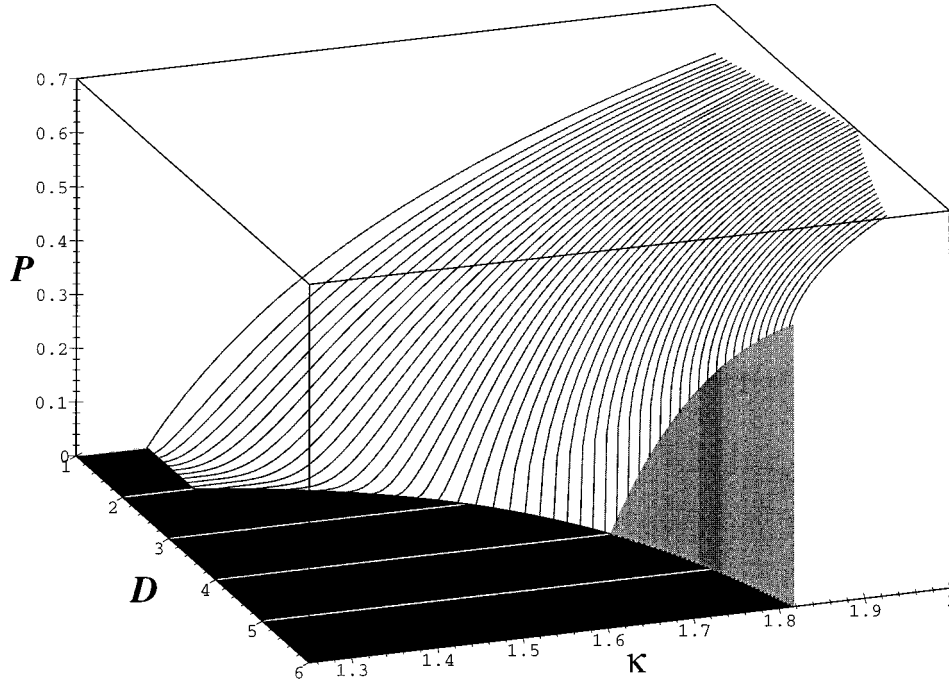


FIG. 2. Plot of the adsorption fraction  $P(\kappa)$ . For increasing  $D < 2$  the scaling exponent increases and the transition becomes weaker until for  $D = 2$  exponential scaling is obtained. For increasing  $D > 2$  the scaling exponent decreases and the transition itself becomes stronger again, which is compensated for by an increase in the critical binding potential  $\kappa_c$  that is required to bring about the transition. At  $D = 4$  we observe a tricritical point with logarithmic scaling and for  $D > 4$  the transition is first order, indicated by a discontinuity (green shaded region) in  $P(\kappa)$  across the critical point.

### C. Case $D > 4$

As in the preceding subsection we must set  $\mathcal{A} = 0$  and obtain the same value for  $\kappa_c$  as in Eq. (4.7). Higher-order asymptotic analysis then gives

$$\Delta z \sim -\frac{\mathcal{B}}{\mathcal{C}} \Delta \kappa.$$

Thus, to leading order the adsorption fraction is asymptotically a constant:

$$P(\kappa) \sim \frac{(D-4)(3m+2D-1)}{(2m+D)(3m+2D-5)} \quad (\kappa \rightarrow \kappa_c^+). \quad (4.9)$$

The discontinuity in the adsorption fraction across the critical point indicates a first-order phase transition.

The higher-order correction to this jump discontinuity is given by a term of order  $\Delta \kappa^{(D/2)-2}$ . This correction dominates for  $D < 6$ . When  $D \geq 6$ , the dominant correction becomes a term of order  $\Delta \kappa$ , scaling independently of  $D$ . Note that the jump discontinuity disappears as  $m \rightarrow \infty$ .

### D. Special case $D = 4$

The case  $D = 4$  is special because here a line of first- and second-order phase transitions meet. Our analysis must proceed somewhat differently because certain coefficients in Eq. (4.3) diverge as  $D \rightarrow 4$ . To investigate this case we return to Eq. (3.2), evaluated at  $D = 4$ , and use the relation (see formula 15.3.11 in Ref. [19])

$${}_2F_1\left(\frac{m}{2}, \frac{m+1}{2}; m + \frac{3}{2}; \epsilon^2\right) \sim \frac{2^{m+1}\Gamma(m + \frac{3}{2})}{\sqrt{\pi}\Gamma(m+2)} \times [1 + 3m(m+1)\Delta z \ln \Delta z + O(\Delta z)]$$

and the relation obtained by shifting  $m$  to  $m + 1$ .

The leading asymptotic contribution to the eigenvalue condition in (3.2) in this case is balanced when again

$$\kappa_c = \frac{4}{3 - \frac{D-2}{m+D-1}} \Big|_{D=4} = \frac{4(m+3)}{3m+7}.$$

The remaining terms to higher order are

$$\Delta \kappa \sim -\frac{24(m+1)(m+2)(m+3)}{(3m+7)^2} \Delta z \ln \Delta z + O(\Delta z).$$

Inverting this relation then yields

$$\Delta z \sim -\frac{(3m+7)^2}{24(m+1)(m+2)(m+3)} \frac{\Delta \kappa}{\ln \Delta \kappa} \times \left[ 1 + O\left(\frac{\ln \ln \frac{1}{\Delta \kappa}}{\ln \Delta \kappa}\right) \right].$$

Finally, we obtain a logarithmic scaling relation for the adsorption fraction

$$P(\kappa) \sim -\frac{3m+7}{3(m+1)(m+2)} \frac{1}{\ln(\kappa - \kappa_c)} \quad (\kappa \rightarrow \kappa_c^+). \quad (4.10)$$

The behavior of the adsorption fraction is summarized in Fig. 2, where we have plotted the adsorption fraction  $P(\kappa)$  for  $0 \leq D \leq 6$  and for  $1.25 \leq \kappa \leq 2$  by solving numerically the eigenvalue equation in (3.2). In this plot we chose  $m = 0$  because the critical phenomena derived in this section are most prominent for small values of the radius  $m$ .

### E. Crossover transition

In the limit of large radius  $m$  we intuitively expect that the attractive boundary will be effectively planar on the length scale of monomer units. In this limit the asymptotic behavior of the adsorption fraction near the critical point should thus be linear. Hence, for  $m \gg 1$  there must be a *crossover* region such that the scaling coefficient obtained for the adsorption fraction  $P(\kappa)$  changes from being dimensionally dependent and sensitive to the curvature of the boundary to the value 1, which is obtained for the case  $D=1$ . To be precise, if we allow the binding potential to vary in a small neighborhood above  $\kappa_c$ ,

$$\kappa = \kappa_c + \Delta\kappa \quad (\Delta\kappa \ll 1)$$

for some fixed radius  $m \gg 1$ , we find that the relations given in Eqs. (4.6)–(4.10) hold when  $\Delta\kappa \ll 1/m$ . However, for  $1 \gg \Delta\kappa \gg 1/m$  linear scaling is obtained. Consequently, the crossover between these two regimes occurs for any  $D > 0$  when  $\Delta\kappa = O(1/m)$  (aside from possible logarithmic corrections for even integer  $D$ ), as stated in Eq. (1.2).

To locate the crossover region analytically it is useful to study the eigenvalue condition in (3.2) asymptotically in the limits  $\Delta z \ll 1$ ,  $\Delta\kappa \ll 1$ , and  $1/m \ll 1$ . There are three distinct cases to consider: (i)  $\Delta z \gg m^{-2}$ , (ii)  $\Delta z \sim m^{-2}$ , and (iii)  $\Delta z \ll m^{-2}$ . As was found in Ref. [16] for the particular case  $D=2$ , we find here that for all  $D > 0$  cases (i) and (ii) lead immediately to linear scaling. For case (iii) we find, to leading order, that

$$\Delta\kappa \sim \frac{8\Gamma\left(\frac{D}{2}\right)}{3^{1+D/2}\Gamma\left(1-\frac{D}{2}\right)m} (m^2\Delta z)^{1-D/2} - \frac{16}{3D} m\Delta z \quad (0 < D < 2) \quad (4.11)$$

and

$$\Delta\kappa \sim \frac{8\Gamma\left(2-\frac{D}{2}\right)}{3^{3-D/2}\Gamma\left(\frac{D}{2}-1\right)m} (m^2\Delta z)^{D/2-1} - \frac{16}{3(4-D)} m\Delta z - \frac{64}{(D-4)^2(D-6)} m^3\Delta z^2 \quad (D > 2, \quad D \neq 4, 6, \dots). \quad (4.12)$$

For all  $D > 0$  we therefore find that the  $D$ -dependent scaling relations derived in Secs. IV A–IV D hold for case (iii). The crossover transition happens when all the terms in Eqs. (4.11) and (4.12) are of equal order, that is, where case (iii) borders on case (ii). Hence the crossover occurs when  $m^2\Delta z = O(1)$ , which verifies Eq. (1.2).

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### APPENDIX: CALCULATION OF THE EIGENVALUE CONDITION

A bound state of Eqs. (3.1) must satisfy a condition ensuring that the likelihood of finding the walker in remote regions  $n \rightarrow \infty$  is diminishing sufficiently fast:

$$g_n \rightarrow 0 \quad (n \rightarrow \infty). \quad (A1)$$

To find such a condition it is convenient to define

$$g_n = \begin{cases} (2n+D-1)h_n & (n > m) \\ 2(m+D-1)h_m & (n = m). \end{cases}$$

Then, Eqs. (3.1) reduce to

$$0 = (1-\lambda)(2n+D-1)h_n + 2z(n+D-2)h_{n-1} + 2z(n+1)h_{n+1} \quad (n > m), \quad (A2)$$

supplemented by the boundary condition

$$0 = (\kappa - \lambda)(m+D-1)h_m + \kappa z(m+1)h_{m+1}. \quad (A3)$$

To simplify the analysis of this problem, we define the generating functions

$$G(x) = \sum_{n=m}^{\infty} g_n x^n$$

and

$$H(x) = \sum_{n=m}^{\infty} h_n x^n.$$

Using the identity

$$\sum_n n x^n h_n = x \frac{\partial}{\partial x} \sum_n x^n h_n, \quad (A4)$$

$G(x)$  can be formally obtained from  $H(x)$ :

$$G(x) = 2x \frac{\partial}{\partial x} H(x) + (D-1)[H(x) + x^m h_m]. \quad (A5)$$

A differential form of the eigenvalue problem may now be obtained by multiplying Eq. (A2) by  $x^n$  and summing from  $n=m+1$  to  $n=\infty$ . After shifting indices and applying the identity in Eq. (A4), we obtain

$$\begin{aligned} & \left[ (1-\lambda) \left( D-1 + 2x \frac{\partial}{\partial x} \right) + 2zx \left( D-1 + x \frac{\partial}{\partial x} \right) \right. \\ & \quad \left. + 2z \frac{\partial}{\partial x} \right] H(x) \\ & = \left[ (1-\lambda)(2m+D-1) + m \frac{2z}{x} \right] h_m x^m \\ & \quad + 2z(m+1)h_{m+1} x^m. \end{aligned}$$

We eliminate  $h_{m+1}$  by applying the boundary condition in Eq. (A3) and divide both sides by  $2z$  to obtain

$$Q^2(x)H'(x) + (D-1)Q(x)Q'(x)H(x) = (1+Ax)mh_mx^{m-1}, \quad (\text{A6})$$

where we have defined

$$\gamma = \frac{1}{\epsilon} (1 - \sqrt{1 - \epsilon^2}), \quad Q(x) = \sqrt{(x-\gamma)(x-1/\gamma)} \quad (\text{A7})$$

and  $A$  and  $\epsilon$  are given in Eqs. (3.3).

It is easy to solve Eq. (A6) because it is a linear first-order differential equation. We multiply by the integrating factor  $Q(x)^{D-3}$  to get

$$[Q^{D-1}(x)H(x)]' = (1+Ax)Q^{D-3}(x)mh_mx^m.$$

Requiring that

$$\lim_{x \rightarrow 0} x^{-m}H(x) = h_m$$

gives

$$H(x) = mh_m Q^{1-D}(x) \int_0^x dt t^{m-1} Q^{D-3}(t)(1+At).$$

Thus, from Eq. (A5) the generating function  $G(x)$  is given by

$$G(x) = (D-1)mh_m \left\{ x^m \left[ 1 + \frac{2(1+Ax)}{(D-1)Q^2(x)} \right] + \frac{(1-x^2)}{Q^{D+1}(x)} \int_0^x dt t^{m-1} Q^{D-3}(t)(1+At) \right\}. \quad (\text{A8})$$

The behavior of  $g_n$  as  $n \rightarrow \infty$  is determined by the singularities of  $G(x)$ . It is evident from the definition of  $Q(x)$  in

Eqs. (A7) that  $G(x)$  in general has singularities at  $x = \gamma$  and  $x = 1/\gamma$ . If  $\gamma$  is complex, then  $\gamma = 1/\gamma^*$  and both singularities are located on the unit circle. Thus condition (A1) cannot be satisfied and there is no bound state. The largest value of the transfer matrix is given by the upper limit of the continuous spectrum,  $\lambda_{\max}(\kappa) = 2$ . Hence the adsorption fraction vanishes and the polymer is in the desorbed phase.

To obtain a nonzero adsorption fraction  $P(\kappa)$  we must find bound states in the spectrum  $\lambda$ . Bound states (discrete values of  $\lambda$ ) appear for values of  $\kappa$  and  $z$  such that  $\gamma$  is real and  $\gamma < 1$ . We must eliminate growing solutions of the form  $g_n \propto \gamma^{-n}$ . This is accomplished by imposing the finiteness condition

$$\lim_{x \rightarrow \gamma} |G(x)| < \infty.$$

A local analysis of  $G(x)$  for  $x \rightarrow \gamma^-$  reveals that  $G(x)$  is finite at  $x = \gamma$  if the following eigenvalue condition is satisfied:

$$0 = \int_0^1 dt t^{m-1} (1+At) [(1-t)(1-\gamma^2 t)]^{(D-3)/2}. \quad (\text{A9})$$

This integral is divergent for  $D \leq 1$  (or for  $D \leq 2$  when  $\gamma = 1$ ). Therefore, to study this integral for all values of  $D$  we observe that when it converges it defines a hypergeometric function  ${}_2F_1(a, b; c; z)$  [19]. We then rely on the analytic continuation provided by the hypergeometric function to rewrite Eq. (A9) as

$$0 = \frac{2m+D-1}{2m} {}_2F_1\left(\frac{3-D}{2}, m; m + \frac{D-1}{2}; \gamma^2\right) + \gamma A {}_2F_1\left(\frac{3-D}{2}, m+1; m + \frac{D+1}{2}; \gamma^2\right).$$

Finally, we use the quadratic transformation formula for hypergeometric functions 15.3.26 in Ref. [19] to obtain the form of the eigenvalue condition given in Eq. (3.2).

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- Note that this constant is smaller on the boundary ( $n=m$ ) than in open space. At the boundary the probability to jump inward is effectively lost. In the more general case of a permeable boundary, the polymer can also grow into the interior of the hypersphere where it might encounter another medium having a different fugacity  $z'$ . Our treatment here corresponds to the special case of an excluded interior  $z'=0$ .
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