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Polymer-chain adsorption transition at a cylindrical boundary

S. Boettcher
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

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In a recent paper [S. Boettcher and M. Moshe, Phys. Rev. Lett. **74**, 2410 (1995)], a simple method was proposed to generate solvable models that predict the critical properties of statistical systems in hyperspherical geometries. To that end, it was shown how to reduce a random walk in D dimensions to an anisotropic one-dimensional random walk on concentric hyperspheres. Here I construct such a random walk to model the adsorption-desorption transition of polymer chains growing near an attractive cylindrical boundary such as that of a cell membrane. I find that the fraction of adsorbed monomers on the boundary vanishes exponentially when the adsorption energy decreases towards its critical value. When the adsorption energy rises beyond a certain value above the critical point whose scale is set by the radius of the cell, the adsorption fraction exhibits a crossover to a linear increase characteristic of polymers growing near planar boundaries.

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I. INTRODUCTION

The study of polymers is rightfully popular with experimentalist and theorist alike [1,2]. Their diversity and practical importance in biology and chemistry makes experimental investigations rewarding. The variety and complexity of polymeric systems rising from a few simple building blocks inspires much theoretical and numerical work using techniques such as scaling [3], renormalization group [4], and Monte Carlo calculations [5]. While we are far from a solvable first-principles model of polymer systems resembling reality, the conception of simplified statistical models might allow us to capture elementary aspects of some of the critical phenomena exhibited by real polymers. Thus, even simple models of polymers, such as any solvable statistical model with nontrivial behavior, warrants attention because of the insight granted into the interplay of fundamental properties such as the range of forces, the symmetries of the system, and geometrical constraints [6].

The simplest polymer system is that of an unbranched chain of monomers embedded in some volume. While practically difficult to obtain, it is simple to model this system by a self-avoiding random walk [7]. The properties of random walk models can easily be studied numerically and in some cases even analytically [8]. In this paper, I present the study of a polymer growing in the neighborhood of an attractive boundary. The properties of this polymer can be derived analytically when modeled as a directed self-avoiding random walk on a lattice that only allows for rectangular turns. Earlier investigations have focused on a polymer growing in the neighborhood of a planar boundary [9]. Here I use a recently proposed model for random walks on a hyperspherical lattice to extend the theory to D-dimensional hyperspherical boundaries [10]. I then give a detailed discussion of the solution for the adsorption fraction of an infinitely long polymer $P(\kappa)$ at an attractive cylindrical boundary with a potential κ [11]. The adsorption fraction is nonvanishing only if the attractive potential on the boundary is larger than a critical value κ_c. I show that the critical properties of the adsorption fraction in this case are profoundly different from those found near planar boundaries. While the adsorption fraction scales linearly at a planar boundary, I find for a cylinder of radius $m \geq 0$ in monomer units and for $\Delta\kappa \equiv \kappa - \kappa_c \searrow 0^+$ that the asymptotic behavior of $P(\kappa)$ is given by

$$P(\kappa) \sim \frac{4}{81} \frac{e^{-8/[9(m+1)\Delta\kappa]}}{(m+1)\Delta\kappa^2} . \tag{1}$$

If the radius m of the boundary is large compared to the length of a monomer, one would expect to recover the scaling behavior that is characteristic of a planar boundary, except for the immediate neighborhood of the critical point. In fact, I find for $m \ll 1$ that there is a crossover between linear and exponential scaling when $m\Delta\kappa = \mathcal{O}(1)$. That is, if $m\Delta\kappa \ll 1$, then Eq. (1) holds, while linear scaling is obtained as soon as $m\Delta\kappa \gg 1$.

The simplicity of the dynamics in this random walk model and the nontrivial phenomena obtained from it raise interesting questions regarding the universal properties of this lattice. According to universality [12], at the critical transition only a few fundamental properties of the system determine its behavior. In this model, the critical behavior arises from the balance between a short-range attractive potential and the entropy of walk configurations in space. I argue that the entropy at the critical point is sufficiently well represented by a hyperspherical lattice. It has been shown that such a lattice reproduces all the universal features expected of lattices [10]. The critical behavior obtained on this lattice for rotationally symmetric systems should therefore reflect the universal critical behavior of the system. The advantage of random walks on hyperspheres is to describe the critical behavior in a minimal and tractable way in comparison, for example, to a far more structured hypercubic lattice.

In the following section, I generalize the theory for a polymer growing at an attractive boundary in a D-dimensional hyperspherical geometry. In Sec. III, I discuss the theory for the special cases $D=1,2$ and 3. In Sec. IV, I analyze in detail the solution obtained for $D=2$, the case of an attractive cylindrical boundary. I evaluate the solution asymptotically near the critical point to derive Eq. (1). Finally, in Sec. V, I discuss some implications of my findings.

II. DIRECTED WALK MODEL FOR THE POLYMER ADSORPTION TRANSITION

In this paper I want to describe the growth of a single-stranded polymer at an attractive hyperspherical boundary. The boundary is considered to be impenetrable. The first monomer in this polymer chain is grafted to the boundary. New monomers are added to the end of the existing polymer chain in a random fashion. The addition of each monomer obtains a fugacity of z, while the addition of a monomer on the boundary yields an energy gain for the system of $\kappa \geq 1$. For simplicity, I want the polymer to be stretched out (directed) along the boundary to avoid self-interaction and excluded-volume effects.

Polymers in solution at an attractive boundary undergo an adsorption-desorption transition at a critical value of the attractive potential κ_c [13]. From the theory for a single-stranded polymer it is found that $P(\kappa)$, the fraction of adsorbed monomers in the limit of an infinitely long polymer, attains a finite value only for κ larger than κ_c [9]. Here I am interested in the critical properties of the adsorption fraction for a polymer as a function of the curvature of the attractive boundary.

The growth process of a polymer can be modeled as a directed, $(D+1)$-dimensional random walk in a D-dimensional hyperspherical geometry. (The extra dimension refers to the time coordinate of the walk, which corresponds to the length L of the polymer extending alongside the D-dimensional hyperspherical boundary.) I choose for this random walk to occur on a lattice consisting of a set of concentric hyperspherical surfaces S_n equally spaced in units of a monomer length. The innermost surface S_m, $m \geq 0$, representing the attractive boundary, has an integer radius of m in monomer units, the next surface S_{m+1} has a radius of $m+1$, and so on. The (virtual) surface area of the nth surface is

$$S_n = \frac{2\pi^{D/2}}{\Gamma(D/2)} n^{D-1} . \tag{2}$$

The walker resides before each step in some region $n \geq m$ between the surface S_n and the surface S_{n+1}. In general, the statistical weights for proceeding are dependent on the location of the walker and the direction of the next step due to the anisotropy of the spherical geometry. A step parallel to the boundary to stay in region n is taken with some weight $P_{\text{stay}}(n)$, while the weights for the walker to either move outward to region $n+1$ or move inward to region $n-1$ may be given by $P_{\text{out}}(n)$ and $P_{\text{in}}(n)$, respectively. For the case of a cylindrical boundary $D=2$ such a walk is shown in Fig. 1.

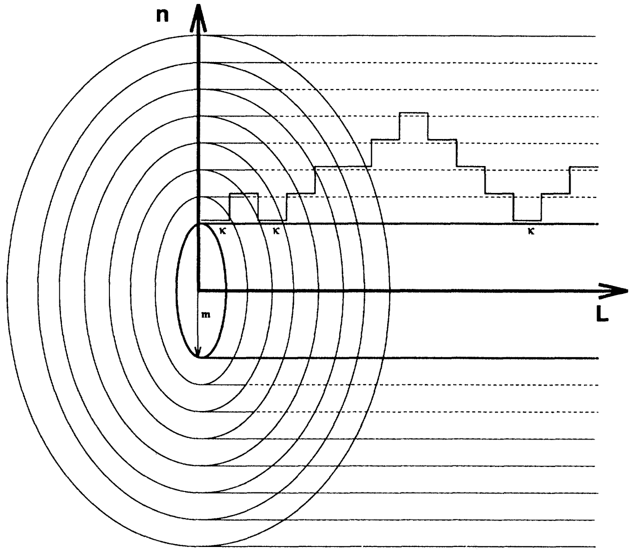

FIG. 1. Random walk on a lattice consisting of concentric cylindrical surfaces of unit radii. Such a walk serves as a model for a polymer growing at an attractive cylindrical boundary with radius m (bold lines). The polymer is initially grafted to the boundary and is growing to the right. Every time a monomer is added at the boundary, the polymer gains in potential energy by an amount κ.

For a growing polymer or a random walker above a convex boundary like that of a D-dimensional hypersphere, there is on each step always more "open space" (i.e., accessible states) available in proceeding outward than in proceeding inward. This anisotropy is more pronounced for stronger curved boundaries, i.e., increasing D. A walker anywhere in region n has for an inbound step a number of target states available that is proportional to the virtual surface area S_n that is traversed. For an outbound step, the number of states available is proportion to the area S_{n+1}. Using Eq. (2), this effect can be accounted for by assigning for all $n>m$

$$\begin{aligned} P_{\text{stay}}(n) &\equiv 1 , \\ P_{\text{in}}(n) &= \frac{2S_n}{S_n+S_{n+1}} = \frac{2n^{D-1}}{n^{D-1}+(n+1)^{D-1}} , \\ P_{\text{out}}(n) &= \frac{2S_{n+1}}{S_n+S_{n+1}} = \frac{2(n+1)^{D-1}}{n^{D-1}+(n+1)^{D-1}} , \end{aligned} \tag{3}$$

whereas on the boundary S_m, I choose

$$P_{\text{stay}}(m)=1 , \quad P_{\text{in}}(m)=0 , \quad P_{\text{out}}(m)=1 . \tag{4}$$

(Overall factors are chosen to conform to Ref. [9] when $D=1$ or $m \rightarrow \infty$.) Note that the walk is prohibited from reaching inward from region m by setting $P_{\text{in}}(m)=0$. The walk starts in region m. Every step is further weighted with a factor z and each parallel step inside the region m acquires an additional factor of κ.

A walk with $L>0$ parallel steps has reached L levels $\{h_i\}_{i=1}^{L+1}$, $h_i \geq m$, above or at the boundary. I want to restrict these walks such that $|h_{i+1}-h_i| \leq 1$, $0 \leq i \leq L$. This restriction on the directed walk, in the spirit of a restricted solid-on-solid model, has no impact on the critical behavior of the system for an ensemble average of walks of all length L. But this restriction implies that each random step that leads into a radial direction must be followed by a *deterministic* parallel step. Thus, while the walk in Fig. 1 consists of $N=26$ links, only $L=14$ random choices of levels h_i, $1 \leq i \leq L$, were required.

A transfer matrix T_{h_{i+1},h_i} that describes the transition of the walker from the ith to the $(i+1)$st level is then given by

$$T_{j,i}=z^{|j-i|}\kappa^{\delta_{m,j}}[P_{\text{stay}}(i)\delta_{j,i}+P_{\text{out}}(i)\delta_{j-1,i}+P_{\text{in}}(i)\delta_{j+1,i}] \ . \tag{5}$$

The transfer matrix T is in general asymmetric because of the anisotropy of the hyperspherical geometry. It is symmetric only for the case of a planar geometry, $D=1$, where $P_{\text{in}} \equiv P_{\text{out}}$. The total statistical weight of a certain walk configuration is then given by

$$z^L\delta_{m,h_0}T_{h_1,h_0}T_{h_2,h_1}\cdots T_{h_L,h_{L-1}} \tag{6}$$

such that the partition function Z_L for all walks extending L parallel steps away from the starting point is

$$Z_L=z^L\vec{b}^{(t)}T^L\vec{e} \ , \tag{7}$$

where $\vec{b}^{(t)}$ and $\vec{e}$ are vectors accounting for beginning and end effects. The total partition function for walks of all length $Z=\sum_{L=1}^{\infty}Z_L$ then evaluates to

$$Z(z,\kappa)=z\vec{b}^{(t)}T(1-zT)^{-1}\vec{e} \ . \tag{8}$$

For any given κ, if $\lambda_{\max}(\kappa,z)$ is the largest eigenvalue of T, then Z diverges for $z\nearrow z_\infty(\kappa)$, where $z_\infty(\kappa)$ is defined by

$$1=z_\infty(\kappa)\lambda_{\max}(\kappa,z_\infty(\kappa)) \ . \tag{9}$$

The average length of a walk is usually defined to be

$$\langle N(z,\kappa)\rangle=z\partial_z \ln Z(z,\kappa) \ , \tag{10}$$

whereas the average number of steps taken on the boundary can be obtained through

$$\langle N_s(z,\kappa)\rangle=\kappa\partial_\kappa \ln Z(z,\kappa) \ . \tag{11}$$

Both $\langle N\rangle$ and $\langle N_s\rangle$, diverge like some power of $1/[z_\infty(\kappa)-z]$ for $z\nearrow z_\infty(\kappa)$. Thus, for $z\nearrow z_\infty(\kappa)$, the limit is obtained where the average polymer is infinitely long. At the same time, $\langle N_s\rangle$ refers to the number of monomers that are adsorbed on the boundary as a function of the attractive boundary potential κ. The fraction of adsorbed monomers $P(\kappa)$ is given by

$$P(\kappa)=\lim_{z\nearrow z_\infty(\kappa)}\frac{\langle N_s(z,\kappa)\rangle}{\langle N(z,\kappa)\rangle}=-\frac{\kappa}{z_\infty(\kappa)}\frac{dz_\infty(\kappa)}{d\kappa} \ . \tag{12}$$

Thus $z_\infty(\kappa)$ marks a line in the (κ,z) plane for which $P(\kappa)$ is defined.

While this random walk model is *in its details* only a crude description of a polymer growing in a continuum, it can be expected that the critical properties of the polymer system in the infinite chain limit is well approximated by such a model. The critical properties of the polymer system arise from the balance between the entropy of all possible polymer (or walk) configurations in the space above the boundary and the energy gained in the attractive potential on the boundary. 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. For instance, the more the boundary is curved, the larger the space available for walk configurations away from the boundary and therefore the larger the entropy. I will show that for a curved boundary the critical transition is substantially weaker than in the case of a planar boundary.

III. THE ADSORPTION PROBLEM FOR PLANAR, CYLINDRICAL, AND SPHERICAL BOUNDARIES

In this section, I use generating function techniques to derive a differential equation that has to be solved to obtain the spectrum of the transfer matrix T. First, I discuss the differential operator for arbitrary D. Then, I examine the differential equation for the special cases of $D=1,2$, and 3.

To determine the spectrum λ of the transfer matrix T, I insert the weights in Eqs. (3) and (4) into Eq. (5), leading to the eigenvalue problem

$$\lambda g_n=\sum_{i=m+1}^{\infty}T_{n,i}g_i$$

$$=\begin{cases} g_n+z\dfrac{2n^{D-1}}{(n-1)^{D-1}+n^{D-1}}g_{n-1}+z\dfrac{2(n+1)^{D-1}}{(n+1)^{D-1}+(n+2)^{D-1}}g_{n+1} \ , & n\geq m+2 \\ g_{m+1}+zg_m+z\dfrac{2(m+2)^{D-1}}{(m+2)^{D-1}+(m+3)^{D-1}}g_{m+2} \ , & n=m+1 \\ \kappa g_m+\kappa z\dfrac{2(m+1)^{D-1}}{(m+1)^{D-1}+(m+2)^{D-1}}g_{m+1} \ , & n=m \ . \end{cases} \tag{13}$$

This system always has a continuous spectrum, independent of κ, but the spectrum contains bound states only for a certain range of κ. If for a neighborhood of a value of κ the largest eigenvalue $\lambda_{\max}$ is given by the upper bound on the continuous spectrum, then the adsorption fraction vanishes due to Eq. (12), since $\lambda_{\max}$—and thus z_∞—does not vary with κ. On the other hand, if a bound state exists, its eigenvalue usually varies as a function of κ and is larger than the continuous spectrum, which leads to a nonvanishing adsorption fraction. Thus the existence of bound states will prove to be the criterion for the appearance of an adsorbed phase for the polymer. A bound state has to satisfy a condition ensuring that the likelihood of finding the walker in far-out regions $n \to \infty$ is diminishing sufficiently fast, i.e.,

$$g_n \to 0 \quad \text{for } n \to \infty \; . \tag{14}$$

It is convenient to define

$$g_n = \begin{cases} [n^{D-1}+(n+1)^{D-1}]h_n \; , & n > m \\ 2(m+1)^{D-1}h_m \; , & n = m \; . \end{cases} \tag{15}$$

Then, Eqs. (13) reduce to

$$0=(1-\lambda)[n^{D-1}+(n+1)^{D-1}]h_n+2zn^{D-1}h_{n-1} +2z(n+1)^{D-1}h_{n+1} \; , \quad n>m \tag{16}$$

and

$$0=(\kappa-\lambda)h_m+\kappa z h_{m+1} \; . \tag{17}$$

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

$$G(x)=\sum_{n=m}^{\infty} g_n x^n \tag{18}$$

and

$$H(x)=\sum_{n=m}^{\infty} h_n x^n \; . \tag{19}$$

Using the identity

$$\sum_n n^i x^n h_n = (x\partial_x)^i \sum_n x^n h_n \; , \tag{20}$$

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

$$G(x)=\left[(x\partial_x)^{D-1}+\frac{1}{x}(x\partial_x)^{D-1}x\right]H(x) - \left[(x\partial_x)^{D-1}-\frac{1}{x}(x\partial_x)^{D-1}x\right]x^m h_m \; , \tag{21}$$

when D is a positive integer. Note that $(x\partial_x)^{D-1}x^m = m^{D-1}x^m$ for $m>0$ or $D>1$, but that $(x\partial_x)^{D-1}x^m=1$ for $D=1$ and $m=0$. The eigenvalue problem can be converted from a difference equation for h_n into a differential equation for $H(x)$. The condition in Eq. (14) on g_n translates into an analyticity condition on $G(x)$: The exponentially growing solutions for g_n in Eq. (13) are averted if and only if $G(x)$ has no singularities for $|x|<1$. Thus one obtains bound states exactly when singularities of $G(x)$ appear inside the unit circle with eigenvalues that are determined by a condition that cancels these singularities.

The differential form of the eigenvalue problem is obtained by multiplying Eq. (16) with x^n and summing from $n=m+1$ to ∞:

$$0=(1-\lambda)\left[\sum_{n=m+1}^{\infty} n^{D-1}x^n h_n + \sum_{n=m+1}^{\infty}(n+1)^{D-1}x^n h_n\right] +2z\sum_{n=m+1}^{\infty} n^{D-1}x^n h_{n-1}+2z\sum_{n=m+1}^{\infty}(n+1)^{D-1}x^n h_{n+1} \; . \tag{22}$$

After shifting indices and applying the identity in Eq. (20), one gets

$$0=(1-\lambda)\left[(x\partial_x)^{D-1}+\frac{1}{x}(x\partial_x)^{D-1}x\right]\sum_{n=m+1}^{\infty} x^n h_n +2z(x\partial_x)^{D-1}x\sum_{n=m}^{\infty}x^n h_n+2z\frac{1}{x}(x\partial_x)^{D-1}\sum_{n=m+2}^{\infty}x^n h_n \; . \tag{23}$$

Completing the sum by adding and subtracting the missing terms in the definition of $H(x)$ in Eq. (19), one obtains

$$0=(1-\lambda)\left[(x\partial_x)^{D-1}+\frac{1}{x}(x\partial_x)^{D-1}x\right][H(x)-x^m h_m] +2z(x\partial_x)^{D-1}xH(x)+2z\frac{1}{x}(x\partial_x)^{D-1} \times[H(x)-x^m h_m-x^{m+1}h_{m+1}] \; . \tag{24}$$

Eliminating h_{m+1} by applying the boundary condition in Eq. (17) and separating off the inhomogeneous part gives

$$\left\{(1-\lambda)\left[(x\partial_x)^{D-1}+\frac{1}{x}(x\partial_x)^{D-1}x\right]+2z(x\partial_x)^{D-1}x+2z\frac{1}{x}(x\partial_x)^{D-1}\right\}H(x) = \left\{(1-\lambda)\left[(x\partial_x)^{D-1}+\frac{1}{x}(x\partial_x)^{D-1}x\right]+2z\frac{1}{x}(x\partial_x)^{D-1}+2\left[\frac{\lambda}{\kappa}-1\right]\frac{1}{x}(x\partial_x)^{D-1}x\right\}x^m h_m \; . \tag{25}$$

To further simplify the presentation, I multiply both sides by $x/(2z)$ and abbreviate

$$\epsilon=\frac{2z}{\lambda-1}\,,\qquad \gamma=\frac{1}{\epsilon}\left(1-\sqrt{1-\epsilon^2}\right)\,,\qquad Q(x)=\sqrt{(x-\gamma)(x-1/\gamma)} \tag{26}$$

to obtain

$$\begin{aligned}\{Q(x)^2(x\partial_x)^{D-1}+Q(x)Q'(x)[(x\partial_x)^{D-1},x]_-\}H(x)\\ =\left\{\left(1-\frac{x}{\epsilon}\right)(x\partial_x)^{D-1}+\left[\frac{1}{\kappa}\left(\frac{2}{\epsilon}+\frac{1}{z}\right)-\left(\frac{1}{\epsilon}+\frac{1}{z}\right)\right]\right.\\ \left.\times(x\partial_x)^{D-1}x\right\}x^m h_m\,,\end{aligned} \tag{27}$$

where $[\;,\;]_-$ is the usual commutator. Clearly, the operators in the inhomogeneous part are easy to evaluate but remain as a shorthand notation to avoid ambiguities for the case $D=1$, $m=0$. To proceed further in the analysis of this differential equation, it is necessary to choose a specific positive integer D. For a given D, one obtains an inhomogeneous differential equation of order $D-1$. The solution of this differential equation is uniquely determined through conditions imposed at the origin on $H(x)$ and its derivatives, using the definition of $H(x)$ in Eq. (19).

It is obvious from the differential equation in (27) that $H(x)$, and therefore $G(x)$, generically has singularities at least at $x=\gamma$ and $1/\gamma$. If γ is real and positive, then one of these singularities must be located inside of or on the edge of the disk $|x|<1$. Say that $\gamma<1$. Then, to avoid growing solutions of the form $g_n \propto \gamma^{-n}$, a discrete eigenvalue λ exists that is determined through the condition

$$\lim_{x\to\gamma}|G(x)|<\infty\,. \tag{28}$$

For specific values of D, the left-hand side of Eq. (27) can be simplified further. For instance, for the planar case $D=1$, Eq. (27) is especially simple because all differential operators disappear, the commutator vanishes, and the relation reduces to an algebraic equation

$$G(x)=2H(x)=\frac{2}{Q(x)^2}\left\{1+\left(\frac{1}{\kappa}-1\right)\left(\frac{2}{\epsilon}+\frac{1}{z}\right)x\right\}x^m h_m\,. \tag{29}$$

Applying the condition in Eq. (28) yields the relation for the eigenvalues

$$0=1+\left(\frac{1}{\kappa}-1\right)\left(\frac{2}{\epsilon}+\frac{1}{z}\right)\gamma\,, \tag{30}$$

which was discussed in Ref. [9]. Note that despite the explicit appearance of the curvature radius m in Eq. (29), the eigenvalue relation in Eq. (30) is independent of m, as it should be for the planar case. It is a necessary condition on the eigenvalue relation for any D that it reduces to Eq. (30) for a hypersphere of infinite radius $m\to\infty$.

For $D=2$, the case of a polymer growing alongside an attractive cylindrical boundary of radius m, one gets $[x\partial_x,x]_-=x$ and Eq. (27) reads

$$\begin{aligned}Q(x)\{Q(x)x\partial_x+[x\partial_x Q(x)]\}H(x)\\ =Q(x)x\partial_x\{Q(x)H(x)\}\\ =\left\{\left(1-\frac{x}{\epsilon}\right)m+\left[\frac{1}{\kappa}\left(\frac{2}{\epsilon}+\frac{1}{z}\right)-\left(\frac{1}{\epsilon}+\frac{1}{z}\right)\right]\right.\\ \left.\times(m+1)x\right\}x^m h_m\,.\end{aligned} \tag{31}$$

Requiring that $\lim_{x\to 0}x^{-m}H(x)=h_m$ determines the solution

$$H(x)=\frac{mh_m}{Q(x)}\int_0^x dt\frac{t^{m-1}}{Q(t)}(1+At)\,, \tag{32}$$

where I define for convenience

$$A=\frac{m+1}{m}\left[\frac{1}{\kappa}\left(\frac{2}{\epsilon}+\frac{1}{z}\right)-\frac{1}{z}\right]-\frac{2m+1}{m\epsilon}\,. \tag{33}$$

Thus, according to Eq. (21), $G(x)$ is given by

$$\begin{aligned}G(x)&=2x\partial_x H(x)+H(x)+x^m h_m\\ &=h_m x^m+\frac{h_m}{Q(x)^2}\left\{2m(1+Ax)x^m\right.\\ &\quad+\frac{m(1-x^2)}{Q(x)}\\ &\quad\left.\times\int_0^x dt\frac{t^{m-1}}{Q(t)}(1+At)\right\}\,.\end{aligned} \tag{34}$$

The properties of $G(x)$ will be discussed in detail in the next section.

For $D=3$, it is $[(x\partial_x)^2,x]_-=x(1+2x\partial_x)$ and one gets for Eq. (27)

$$\begin{aligned}\{Q(x)^2(x\partial_x)^2+Q(x)[x\partial_x Q(x)](1+2x\partial_x)\}H(x)\\ =Q(x)\left\{(x\partial_x)^2+\frac{\left(\frac{1}{\epsilon^2}-1\right)x^2}{Q(x)^4}\right\}\{Q(x)H(x)\}\\ =\left\{\left(1-\frac{x}{\epsilon}\right)m^2+\left[\frac{1}{\kappa}\left(\frac{2}{\epsilon}+\frac{1}{z}\right)-\left(\frac{1}{\epsilon}+\frac{1}{z}\right)\right]\right.\\ \left.\times(m+1)^2x\right\}x^m h_m\,.\end{aligned} \tag{35}$$

For this case, and any other integer $D\geq 3$, there is little hope to obtain the eigenvalue equation analytically. Local analysis for $H(x)$ is insufficient because the eigenvalue condition requires exact knowledge of $H(x)$ in the neighborhood of both the origin and $x=\gamma<1$.

IV. CRITICAL POINT ANALYSIS FOR A POLYMER NEAR A CYLINDRICAL BOUNDARY

In Eq. (34), I derived the generating function $G(x)$ for the eigenvalue problem in Eq. (13), which describes the behavior of polymers growing near a cylindrical boundary $D=2$. It is obvious that $G(x)$ in general has singularities at $x=\gamma$ and $1/\gamma$. If γ is complex, it is $\gamma=1/\gamma^*$ and both singularities are located on the unit circle. Then it is $\lambda_{\max}=2$, the value of the upper bound in the continuous spectrum of the transfer matrix T, that remains independent of κ. Thus, since $z_\infty(\kappa)\equiv 1/\lambda_{\max}$, it is $P(\kappa)\propto dz_\infty/d\kappa=0$ and the polymer is in the desorbed phase.

For $P(\kappa)\neq 0$, κ has to be such that a bound state λ exists that is larger than the continuous spectrum. A bound state emerges for real positive $\gamma<1$. It can be determined by imposing the condition in (28). A local analysis of $G(x)$ for $x \nearrow \gamma$ yields

$$G(x)\sim(\gamma-x)^{-3/2}\frac{mh_m\gamma^{m+3/2}}{\sqrt{1-\gamma^2}} \times\int_0^1 dt\, t^{m-1}(1+A\gamma t)[(1-t)(1-\gamma^2 t)]^{-1/2} +(\text{finite terms}),\ x\nearrow\gamma\ . \tag{36}$$

Thus $G(x)$ is finite at $x=\gamma$ if

$$0=\int_0^1 dt\, t^{m-1}(1+A\gamma t)[(1-t)(1-\gamma^2 t)]^{-1/2}\ . \tag{37}$$

With A given in Eq. (33), this relation defines a bound state $\lambda(\kappa,z)$. For it to exist, it is necessary that $\gamma<1$, i.e., that $\kappa>\kappa^*(z)$, where $\kappa^*(z)$ is obtained from Eq. (37) in the (carefully taken) limit $\gamma\nearrow 1,\epsilon\nearrow 1$:

$$\kappa^*(z)=\frac{1+2z}{1+z}\ . \tag{38}$$

In Eq. (12) I defined the adsorption fraction $P(\kappa)$ in the (κ,z) plane on the line $z_\infty(\kappa)$, where the polymer length approaches infinity. The function $z_\infty(\kappa)$ is obtained implicitly from Eq. (37) for $z=z_\infty(\kappa)$ and $\lambda=1/z_\infty(\kappa)$.

It is now easy to determine the critical point for the adsorption transition: Since a bound state and thus a nonzero adsorption fraction first appears for $\gamma=\epsilon=1$, I obtain from the definition of ϵ in Eq. (26), using Eq. (9), that $z_\infty(\kappa_c)=\frac{1}{2}$. Inserting this value of z into $\kappa^*(z)$ implies that

$$\kappa_c=\tfrac{4}{3} \tag{39}$$

because the critical point for $P(\kappa)$ is located where the line on which it is defined, $z_\infty(\kappa)$, intersects with the line $\kappa^*(z)$. The behavior of $\kappa^*(z)$ and $z_\infty(\kappa)$ is summarized in Fig. 2 for the case $m=0$. Note that for $1<\kappa<\kappa_c$ the boundary is already attractive, but not sufficiently attractive to adsorb the polymer.

While the value of $P(\kappa)$ for arbitrary κ can be obtained numerically from the implicit equation for $z_\infty(\kappa)$, it is simple to find the asymptotic behavior near the critical point explicitly. First, using the integral definition of the hypergeometric function F [14] I rewrite Eq. (37) as

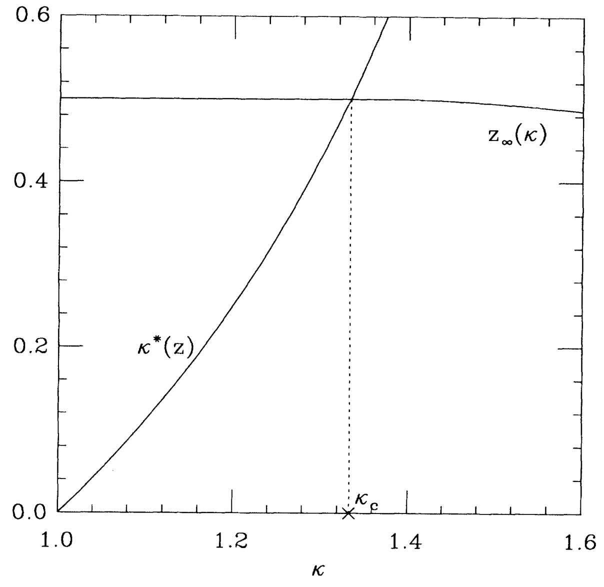

FIG. 2. The (κ,z) plane with the lines $\kappa^*(z)$ and $z_\infty(\kappa)$ for $m=0$. The adsorption fraction $P(\kappa)$ is defined only on the line $z_\infty(\kappa)$, where the average polymer length reaches infinity. An adsorbed phase $P(\kappa)\neq 0$ only exists when $\kappa>\kappa^*(z)$. Thus the critical point κ_c is given by the value of κ at the intersection of both curves.

$$\begin{aligned}&0=F_m+\gamma A F_{m+1}\ ,\\ &F_m=\frac{\Gamma(\frac{1}{2})\Gamma(m)}{\Gamma(m+\frac{1}{2})}F(\tfrac{1}{2},m;m+\tfrac{1}{2};\gamma^2)\ .\end{aligned} \tag{40}$$

If I now substitute

$$\begin{aligned}&z=z_\infty(\kappa_c)-\Delta z\ ,\quad \Delta z\searrow 0\\ &\kappa=\kappa_c+\Delta\kappa\ ,\quad \Delta\kappa\searrow 0\end{aligned} \tag{41}$$

and only keep terms to sufficient order, i.e.,

$$\begin{aligned}&\epsilon\sim 1\ ,\\ &\gamma\sim 1-2\sqrt{3}\Delta z^{1/2}\ ,\quad \Delta z\searrow 0\end{aligned} \tag{42}$$

and use formula 15.3.10 from Ref. [14]

$$F_m\sim-\ln(1-\gamma^2)-\psi(m)+2\psi(1)-\psi(\tfrac{1}{2})\ ,\quad \gamma\nearrow 1\ , \tag{43}$$

I get

$$\Delta z\sim\tfrac{1}{48}e^{-8/[9(m+1)\Delta\kappa]}\ . \tag{44}$$

With

$$P(\kappa)\sim\frac{\kappa_c}{z_\infty(\kappa_c)}\frac{d\Delta z}{d\Delta\kappa}\ , \tag{45}$$

I finally obtain Eq. (1). A more extensive calculation shows that the next-to-leading-order corrections are exponentially smaller yet.

So far, I have considered the radius m of the attractive boundary to be a fixed parameter. An interesting crossover phenomenon is revealed by investigating the asymptotic behavior of the eigenvalue condition in (40) when m is allowed to vary with respect to $\Delta\kappa$. It appears that for large m the asymptotic relation in Eq. (1) is invalid when $\Delta\kappa$ is not sufficiently small compared to $1/m$. Physically, it is clear that for $m \to \infty$ any D-dimensional spherical boundary acts like a planar ($D=1$) boundary on the scale of a monomer length. One would thus expect to find a crossover region $\Delta\kappa \sim m^{-\eta}$ for $\Delta\kappa \searrow 0^+$, $m \gg 1$, and some $\eta > 0$, such that for $\Delta\kappa \ll m^{-\eta}$ a nonlinear relation such as Eq. (1) is valid, while for $1 \gg \Delta\kappa \gg m^{-\eta}$ the linear scaling characteristic of a planar surface is obtained. (More complicated scenarios are conceivable, but do not seem to be realized.) This is in fact visible in Fig. 3: While the adsorption fraction for all $m < \infty$ initially varies exponentially, it eventually has an interval of nearly linear behavior that arises sooner the larger m gets.

I will now prove that for a cylindrical boundary $D=2$, the crossover coefficient is $\eta=1$. To that end, I will have to reanalyze the eigenvalue condition in (40) to find a relation between $\Delta\kappa$ and Δz in the limits $\Delta\kappa \searrow 0$ and $\Delta z \searrow 0$, while at the same time $m \to \infty$. Initially, it is not at all clear whether $1/m$ is smaller than, larger than, or of comparable size to $\Delta\kappa$ and Δz. It is therefore necessary to make a general dominant balance analysis [15]. It is convenient to separate the range of all possibilities into three distinct cases: (i) $m\Delta z^{1/2} = \mathcal{O}(1)$, (ii) $m\Delta z^{1/2} \ll 1$, and (iii) $m\Delta z^{1/2} \gg 1$, to localize the region in which the crossover occurs. Clearly, one should investigate case (i) first: If one finds either nonlinear or linear behavior there, then one can exclude either case (ii) or (iii) immediately because it would have just the continuation of the behavior in case (i).

For case (i), it is simpler to analyze the integral form of the eigenvalue condition in (37), which I rewrite by substituting $t = 1-(1-\gamma^2)s$ as

$$0=\int_0^{1/(1-\gamma^2)} \frac{ds}{\sqrt{s(1+s)}}[1-(1-\gamma^2)s]^{m-1} \times \left[1-(1-\gamma^2)\frac{s}{1+s}\right]^{-1/2} \times [1+\gamma A-\gamma A(1-\gamma^2)s] \ . \tag{46}$$

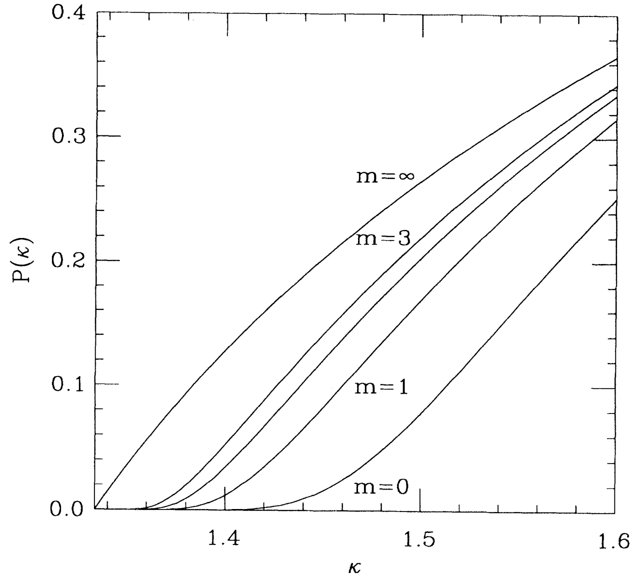

FIG. 3. The exact adsorption fraction $P(\kappa)$ plotted for $m=0,1,2,3,\infty$ and $\kappa \geq \kappa_c = \frac{4}{3}$. For finite m, $P(\kappa)$ vanishes exponentially for $\kappa \searrow \kappa_c$, while it crosses over to a linear increase when $\kappa-\kappa_c = \mathcal{O}(1/m\ln m)$. For $m=\infty$ I recover the linear behavior for $P(\kappa)$ for $\kappa \searrow \kappa_c$ that was found in Ref. [9].

Under the conditions for case (i), the integrad is sharply peeked at $s=0$ and I can use Laplace's method [15] to find the asymptotic expansion of the integral. Since $1-\gamma^2 \sim 4\sqrt{3}\Delta z^{1/2}$ and with

$$\gamma A \sim 4\left[\frac{1}{\kappa_c}-1\right]-\frac{4}{\kappa_c^2}\Delta\kappa - 8\sqrt{3}\left[\frac{1}{\kappa_c}-1\right]\Delta z^{1/2} + \left[\frac{2}{\kappa_c}-1\right]\frac{1}{m} \ , \tag{47}$$

I find that the right-hand side of Eq. (46) is in leading order asymptotic to

$$\int_0^{1/\delta} \frac{ds}{\sqrt{s(1+2)}} e^{m\ln(1-4\sqrt{3}\Delta z^{1/2}s)}[1+4\sqrt{3}\Delta z^{1/2}s]\left[1+2\sqrt{3}\frac{s}{1+s}\Delta z^{1/2}\right] \times \left[\frac{4}{\kappa_c}-3-\frac{4}{\kappa_c^2}\Delta\kappa-8\sqrt{3}\left[\frac{1}{\kappa_c}-1\right](1+2s)\Delta z^{1/2}+\left[\frac{2}{\kappa_c}-1\right]\frac{1}{m}\right] \ , \quad m\Delta z^{1/2} \gg \delta \gg m\Delta z \ . \tag{48}$$

The conditions on δ ensure that a sufficiently large integration interval is kept. They also make $1/\delta$ sufficiently small such that one can expand the exponential in Eq. (48) for all but its leading term and subsequently integrate to $s=\infty$ with exponentially small error. Then, to make terms of finite order vanish I need to set again $\kappa_c = \frac{4}{3}$. To next order I find that

$$\int_0^{\infty} \frac{ds\, e^{-cs}}{\sqrt{s(1+s)}}\left[\tfrac{9}{4}\Delta\kappa - 2\sqrt{3}(1+c+2s)\Delta z^{1/2}\right] \tag{49}$$

has to vanish, where $c = 4\sqrt{3}m\Delta z^{1/2}$ is simply some number of order unity. Disregarding numbers of order unity, I finally get that $\Delta\kappa \sim \Delta z^{1/2}$, leading to a linear scaling relation by Eq. (45). Consequently, the crossover appears to occur already for case (ii).

To analyze case (ii) I return to Eq. (40). But to obtain the desired relation, it is necessary in this case to retain one more term in formula 15.3.10 from Ref. [14] that was already used in Eq. (43). This fact only emerges after trails, each including an increasing number of terms, and is due to many cancellations among leading-order terms. It is

$$\begin{aligned} F_m &\sim -\ln(1-\gamma^2)-\psi(m)+2\psi(1)-\psi(\tfrac{1}{2})+\tfrac{1}{2}m(1-\gamma^2)[-\ln(1-\gamma^2)-\psi(m+1)+2\psi(2)-\psi(\tfrac{3}{2})] \\ &\sim -\ln(4\sqrt{3}m\,\Delta z^{1/2})+2\psi(1)-\psi(\tfrac{1}{2})-2\sqrt{3}m\,\Delta z^{1/2}\ln(4\sqrt{3}m\,\Delta z^{1/2}) \\ &\quad +2\sqrt{3}m\,\Delta z^{1/2}[2\psi(2)-\psi(\tfrac{1}{2})]+\frac{1}{2m}+\sqrt{3}\Delta z^{1/2}\ . \end{aligned} \tag{50}$$

I insert this form into Eq. (40), expand, and match terms order by order. To leading order, I find again that $\kappa_c=\frac{4}{3}$. Thereafter, many terms cancel until I finally obtain

$$\Delta\kappa \sim \frac{4}{g}\frac{1}{m\ln m}\ , \tag{51}$$

indicating that $\eta=1$ up to logarithmic corrections.

V. CONCLUSIONS

I have shown that the adsorption-desorption transition for a polymer near an attractive cylindrical boundary is substantially weaker than in the case of a planar boundary. While the adsorption fraction vanishes linearly in the planar case for attractive energies approaching the critical value, it vanishes exponentially fast in the cylindrical case.

The nonlinear (i.e., not mean-field-like) character of this result demonstrates the power of a random walk on hyperspherical lattices that was used in this model. Intuitively, it is clear that the exponential (inverted logarithmic) behavior observed in this model arises from the fraction of walks which "almost" escape to infinity, i.e., from walks that would disappear to infinity if the spatial dimension were to be $D=2+0^+$. This is a simple fact for walks in the critical dimension $D=2$, independent of the lattice. But while it is not even obvious how to model this cylindrical geometry onto a more commonly used lattice such as the square lattice, the hyperspherical lattice makes the model readily solvable. A hypercubic lattice provides far too much detail about space (which is useful for more complicated problems). A hyperspherical lattice, on the other hand, reduces any D-dimensional space to a simple one-dimensional configuration, which provides sufficient detail for spherically symmetric problems in statistical mechanics such as this. Thus it can be expected that this lattice will lead to many more insights into the critical behavior of simple problems that otherwise are intractable on hypercubic lattices.

In a future paper [16], with further simplifications in the walk model on hyperspherical lattices [17], it will be argued that the adsorption fraction scales with a critical coefficient $(2-|2-D|)/|2-D|$ for $1\leq D<4$, $D\neq 2$, while it shows a first-order transition for $D>4$.

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[1] See, for example, *Random Walks and Their Application in the Physical and Biological Sciences,* edited by M. F. Shlesinger and B. J. West (American Institute of Physics, New York, 1984).

[2] J. Des Cloizeaux and G. Jannink, *Polymers in Solution* (Clarendon, Oxford, 1990).

[3] P. G. DeGennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[4] K. F. Freed, *Renormalization Group Theory of Macromolecules* (Wiley, New York, 1987).

[5] K. Binder and K. Kremer, in *Scaling Phenomena in Disordered Systems,* edited by R. Rynn and A. Skjeltorp (Plenum, New York, 1985); K. Binder, Adv. Polymer Sci. **112**, 181 (1994); K. Binder, Nucl. Phys. B (to be published).

[6] R. J. Baxter, *Exactly Solved Models in Statistical Mechanics* (Academic, London, 1982).

[7] P. J. Flory, J. Chem. Phys. **17**, 303 (1949); E. W. Montroll, *ibid.* **18**, 734 (1950).

[8] R. Fernandez, J. Fröhlich, and A. D. Sokal, *Random Walks, Critical Phenomena, and Triviality in Quantum Field Theory* (Springer, Berlin, 1992).

[9] V. Privman, G. Forgacs, and H. L. Frisch, Phys. Rev. B **37**, 9897 (1988); V. Privman and N. M. Švrakić, *Directed Models of Polymers, Interfaces, and Clusters: Scaling and Finite-Size Properties* (Springer, Berlin, 1989).

[10] C. M. Bender, S. Boettcher, and L. R. Mead, J. Math. Phys **35**, 368 (1994); C. M. Bender, S. Boettcher, and M. Moshe, *ibid.* **35**, 4941 (1994).

[11] The results of this calculation were presented in brief by S. Boettcher and M. Moshe, Phys. Rev. Lett. **74**, 2410 (1995).

[12] See, for instance, M. Plischke and B. Bergersen, *Equilibrium Statistical Mechanics* (Prentice-Hall, Englewood Cliffs, NJ, 1989), p. 163.

[13] G. H. Weiss and R. J. Rubin, Adv. Chem. Phys. **52**, 363 (1983); A. Takahashi and M. Kawaguchi, Adv. Polymer Sci. **46**, 1 (1982); Yu. S. Lipatov and L. M. Sergeeva, *Adsorption of Polymers* (Halsted, Jersualem, 1974).

[14] F. Oberhettinger, in *Handbook of Mathematical Functions,* Natl. Bur. Stand. Appl. Math. Ser. No. 55, edited by M. Abramowitz and I. Stegun (U.S. GPO, Washington, DC, 1972), p. 555.

[15] C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers* (McGraw-Hill, New York, 1978).

[16] C. M. Bender, S. Boettcher, and P. N. Meisinger (unpublished).

[17] C. M. Bender, F. Cooper, and P. N. Meisinger (unpublished).