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Depinning of semiflexible polymers

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We present a theoretical analysis of a simple model of the depinning of an anchored semiflexible polymer from a fixed planar substrate in $1+1$ dimensions. We consider a polymer with a discrete sequence of pinning sites along its contour. Using the scaling properties of the conformational distribution function in the stiff limit and applying the necklace model of phase transitions in quasi-one-dimensional systems, we obtain a melting criterion in terms of the persistence length, the spacing between pinning sites, a microscopic effective length that characterizes a bond, and the bond energy. The limitations of this and other similar approaches are discussed. We also consider the general problem of thermal depinning in $1+d$ dimensions. In the case of force-induced unbinding, it is shown that the bending rigidity favors the unbinding through a "lever-arm effect."

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I. INTRODUCTION

For a broad category of physical problems, a free polymer is characterized by two lengths: the total contour length L and the persistence length L_p, that is the correlation length of the tangent unit vector along its contour and is proportional to its bending rigidity. When the persistence length is much smaller than the total length, the polymer is said to be flexible and it can usually be treated as a random walk. When the two lengths are of the same order, the polymer is said to be semiflexible. Some of the most important biopolymers belong to the latter class. For example, the structural elements of the cytoskeleton are microtubules, actin filaments, and intermediate filaments with persistence lengths of the order of 6 mm [1], 17 μm [2], and 2 μm [3], respectively. Although DNA filaments usually have a total length greater than the persistence length ($L_p \approx 50$ nm), the latter is long enough to affect their elastic properties [4]. Obvious biological relevance and inherent theoretical challenges have sparked great interest in the statistical mechanics of semiflexible polymers in recent years [5].

A theoretical analysis of the unbinding of semiflexible polymers from fixed surfaces or interfaces (adsorption-desorption transition) or of two semiflexible strands from each other is a particularly tricky problem. The main reason is that sharp phase transitions in statistical mechanics occur only in the thermodynamic limit and the thermodynamic limit of semiflexible polymers is ambiguous. If we keep the persistence length fixed and take the total contour length to infinity, we obtain a flexible polymer. If we take the persistence length to infinity keeping the total length fixed, we obtain a rigid rod without any fluctuations. There have been several studies of this subject over the past few years [6–13]. In all of those works, the polymer binds to a potential well which *continuously* extends over the surface (or interface). In this paper, we consider a simple model, where a weakly bending semiflexible polymer in $1+1$ dimensions is bound to a fluid surface (or interface) through a *discrete* sequence of regularly placed pinning sites ("sticky points") along its length. Such a model resembles the physical situation, where an actin filament binds to a membrane through anchoring proteins [14]. The discreteness of the binding sites allows us to employ a different kind of thermodynamic limit that avoids the inconsistencies that appear in some previous works. For fixed total length and persistence length (with $L \ll L_p$), we take the density of binding sites to infinity under the constraint that the probability of finding such a site inside the binding region remains constant. Thus, we obtain a continuous unbinding transition and a melting temperature which is a function of of the persistence length, the spacing between pinning sites, a microscopic length that characterizes a bond, and the bond energy. The paper is organized as follows: In Sec. II, we calculate the probability of finding a binding site of the polymer inside a small (microscopic) region which characterizes a bond. We then consider the simplest version of our model which is a filament with only one pinning site. In Sec. III, we use a necklace-model [15,16] type of approach which yields the thermal depinning transition. In Sec. IV, we discuss the effect of the bending rigidity on the force-induced unbinding of semiflexible polymers in the stiff limit. In Sec. V, we demonstrate the subtleties of this problem comparing our model with other approaches and we present our conclusions. Finally, in the Appendix, we present an analysis of the $(1+2)$-dimensional problem that is very similar to the $(1+1)$-dimensional one because in the weakly bending limit the transverse dimensions decouple.

II. CONFORMATIONAL PROBABILITY–FORMALISM

A widely used model that captures much of the physics of semiflexible polymers (except for their self-avoidance) is the wormlike chain (WLC) [17], where the polymer is considered to be a continuous inextensible curve $\mathbf{r}(s)$ parametrized by the arc length s measured along its contour from a fixed end. The effective free energy of a particular conformation depends only on the bending (curvature) and is given by

$$\mathcal{H} = \frac{\kappa}{2}\int_0^L ds \left[\frac{\partial \mathbf{t}(s)}{\partial s}\right]^2, \tag{1}$$

where $\mathbf{t}(s)=\partial\mathbf{r}(s)/\partial s$ is the tangent unit vector of the curve $\mathbf{r}(s)$ and κ is the bending rigidity that is related to the persistence length via $L_p=2\kappa/k_BT$ (in two dimensions).

The orientational probability distribution function for free semiflexible chains having an initial tangent vector $\mathbf{t}(0)=\mathbf{t}_0$ and a final tangent vector $\mathbf{t}(L)=\mathbf{t}_L$ is given by the path integral

$$G(\mathbf{t}_L,L|\mathbf{t}_0,0)=\mathcal{N}\int_{\mathbf{t}(0)=\mathbf{t}_0}^{\mathbf{t}(L)=\mathbf{t}_L}\mathcal{D}[\mathbf{t}(s)]\,\delta(|\mathbf{t}(s)|-1)\exp\left[-\frac{\mathcal{H}}{k_BT}\right], \tag{2}$$

where the integration is over all fluctuating "paths" $\mathbf{t}(s)$ subject to the fixed boundary conditions and the inextensibility constraint $|\mathbf{t}(s)|=1$. $\mathcal{N}$ is a normalization constant. There is a formal analogy between the classical statistical mechanics of a semiflexible polymer and the quantum statistical mechanics of a rigid rotator [17]. If we make the correspondence $\kappa\rightleftharpoons I$, $k_BT\rightleftharpoons\hbar$, and $L\rightleftharpoons\beta\hbar$ in Eqs. (1) and (2), we notice that $G(\mathbf{t}_L,L|\mathbf{t}_0,0)$ corresponds to the density matrix element, in the angle representation, of a quantum rigid rotator with moment of inertia I and inverse temperature β. As in the case of a density matrix [18], the angular probability distribution function of a free semiflexible polymer satisfies a Schrödinger equation in imaginary time:

$$\frac{\partial G}{\partial s}=\frac{1}{L_p}\frac{\partial^2 G}{\partial\theta^2}, \tag{3}$$

where $\theta(s)$ is the angle between $\mathbf{t}(s)$ and a fixed reference axis [19]. In order to obtain the complete distribution function that in addition to the tangent vector also includes the position vector $G(\mathbf{r}_s,\mathbf{t}_s,s|\mathbf{r}_0,\mathbf{t}_0,0)$, we have to replace the s derivative in the left-hand side of Eq. (3) by the "convective" derivative $\partial_s+\mathbf{t}\cdot\boldsymbol{\nabla}_{\mathbf{r}}$ along the polymer path $\mathbf{r}(s)$ with instantaneous position vector $\mathbf{r}$ and tangent vector $\mathbf{t}$ [20]. In Cartesian coordinates, the equation reads

$$\left[\frac{\partial}{\partial s}+\cos\theta\frac{\partial}{\partial x}+\sin\theta\frac{\partial}{\partial y}-\frac{1}{L_p}\frac{\partial^2}{\partial\theta^2}\right]\times G(x_s,y_s,\theta_s,s|x_0,y_0,\theta_0,0)=0, \tag{4}$$

where θ is the local slope of the polymer with respect to the x axis.

In the weakly bending limit ($L\ll L_p$), $\theta\ll1$ and we simplify Eq. (4) setting $\sin\theta\approx\theta$ and $\cos\theta\approx1$. Since we are not interested in the longitudinal fluctuations of the polymer (along the x axis), we integrate the complete probability distribution function over x to obtain a simpler equation for the reduced probability distribution

$$\left[\frac{\partial}{\partial s}+\theta\frac{\partial}{\partial y}-\frac{1}{L_p}\frac{\partial^2}{\partial\theta^2}\right]G(y_s,\theta_s,s|y_0,\theta_0,0)=0. \tag{5}$$

Using Fourier transformations [21], we solve Eq. (5) with the "initial" condition $\lim_{s\to0}G(y_s,\theta_s,s|y_0,\theta_0,0)=\delta(\theta-\theta_0)\delta(y-y_0)$ to get

$$G(y_s,\theta_s,s|y_0,\theta_0,0)=\frac{\sqrt{3}}{2\pi}\frac{L_p}{s^2}\exp\left\{-\frac{3L_p}{s^3}\left[(y-y_0-\theta_0 s)^2-s(y-y_0-\theta_0 s)(\theta-\theta_0)+\frac{1}{3}s^2(\theta-\theta_0)^2\right]\right\}. \tag{6}$$

Apart from explicitly containing the persistence length L_p, Eq. (6) is identical with that obtained in Ref. [7]. The interpretation, however, is very different. In Refs. [6,7], $G(y_s,\theta_s,s|y_0,\theta_0,0)$ is interpreted as a *dimensionless* partition function *independent* of the persistence length L_p which has been eliminated by rescaling y and θ. In those references, Eq. (6) is expected to be valid for large s and it appears that s is measured in units of an extra, "monomer" length. In contrast, we interpret it as a two-point conformational *probability distribution*, valid only in the weakly bending limit ($s\ll L_p$). Notice that $G(y_s,\theta_s,s|y_0,\theta_0,0)$ fulfills the three fundamental properties of a two-point probability distribution; its integral over y_s and θ_s is 1, it becomes a δ function when $s\to0$ and it obeys the Chapman-Kolmogorov equation [22]. The corresponding partition function differs from $G(y_s,\theta_s,s|y_0,\theta_0,0)$ by a normalization factor (related to the measure of the path integral) that should have units of length in order to render it dimensionless. (It is similar to the phase volume element $2\pi\hbar$ used in the statistical mechanics of gases.) In the calculation of several quantities, this normalization factor is unimportant as it drops out. For this type of problems, $G(y_s,\theta_s,s|y_0,\theta_0,0)$ itself can be considered as the partition function. However, as it will become clear below, the necklace model involves a sum over powers of the partition function and using a dimensionful quantity in its place would clearly be erroneous.

For fixed $y_0=\theta_0=0$, the mean square slope and transverse displacement of the free end of a filament of length L are $\langle\theta_L^2\rangle=2L/L_p$ and $\langle y_L^2\rangle=(2/3)L^3/L_p$ as can be easily calculated from Eq. (6). The *probability* of finding the free end within a very small range of slopes and transverse displacements ($-\delta<\theta_L<\delta$ and $-\epsilon<y_L<\epsilon$ with $0<\delta,\epsilon\ll1$) is

$$P(\delta,\epsilon,L,L_p)=\int_{-\delta}^{\delta}d\theta_L\int_{-\epsilon}^{\epsilon}dy_L G(y_L,\theta_L,L|0,0,0)\approx\frac{\sqrt{3}}{2\pi}\frac{L_p}{L^2}B, \tag{7}$$

where $B\equiv4\delta\epsilon$ and the approximation holds for $B\ll(\sqrt{3}/2\pi)L^2/L_p$. The *partition function* $Z(\delta,\epsilon,L,L_p)$ of a polymer which is constrained so that $y_0=\theta_0=0$ and $-\delta<\theta_L<\delta$, $-\epsilon<y_L<\epsilon$ while it is unconstrained in the longitudinal direction is related to the probability $P(\delta,\epsilon,L,L_p)$ via $Z(\delta,\epsilon,L,L_p)=Z_f(L,L_p)P(\delta,\epsilon,L,L_p)$, where $Z_f(L,L_p)$ is the partition function of a free filament. The latter has the property $Z_f(L_1+L_2,L_p)=Z_f(L_1,L_p)Z_f(L_2,L_p)$ and will be neglected as it is not going to affect any of the observable quantities, we are interested in.

The probability of finding both the free end and the point at the middle confined within a very small range of slopes and transverse displacements is

$$\int_{-\delta}^{\delta} d\theta_L \int_{-\epsilon}^{\epsilon} dy_L \int_{-\delta}^{\delta} d\theta_{L/2} \int_{-\epsilon}^{\epsilon} dy_{L/2} G\left(y_L,\theta_L,L\,\middle|\, y_{L/2},\theta_{L/2},\frac{L}{2}\right) G\left(y_{L/2},\theta_{L/2},\frac{L}{2}\,\middle|\,0,0,0\right) \approx \left(\frac{\sqrt{3}}{2\pi}\frac{L_p}{L^2}B\right)^2. \tag{8}$$

We shall use this factorization in the calculation of the partition function of our model.

We now consider the toy system of a weakly bending semiflexible polymer with its end points ($s=0$ and $s=L$) bound and a pinning site in the middle ($s=L/2$). A "bound site" in our model is defined as a point of the polymer which is constrained to fluctuate within a *microscopically* small range of slopes and transverse displacements that is characterized by the effective length B as defined above but it is free to fluctuate in the longitudinal direction. The latter situation is physically realized in the case of a fluid substrate where the "sticky points" are free to move along a one-dimensional track (membrane). A "pinning site" is defined as a point on the polymer which is energetically favorable to be bound with an associated bond energy J ($J>0$). The partition function of this system with one pinning site is

$$Z_1=[\mathcal{G}(L/2)]^2 v+\mathcal{G}(L)-[\mathcal{G}(L/2)]^2, \tag{9}$$

where

$$\mathcal{G}(l)=\frac{\sqrt{3}}{2\pi}\frac{L_p}{l^2}B \tag{10}$$

is the conformational statistical weight of a polymer segment of contour length l whose end points are bound and $v \equiv \exp(J/k_BT)$. The third term in Eq. (9) is the "counterterm" needed to prevent double counting of conformations; the conformations associated with $[\mathcal{G}(L/2)]^2$ have already been included in $\mathcal{G}(L)$.

The average fraction of intact bonds is

$$Q=\frac{\partial \ln Z_1}{\partial \ln(v-1)}. \tag{11}$$

This is a general expression valid for any number of pinning sites provided that we replace Z_1 with the corresponding Z_N and we divide the right-hand side by N. The calculation of Z_N for $N \gg 1$ is the aim of Sec. III.

III. THERMAL DEPINNING TRANSITION

The partition function of a weakly bending semiflexible polymer with its end points ($s=0$ and $s=L$) bound and N pinning sites regularly distributed along its length formally reads

$$Z_N=\sum_{n=0}^{N} v^n \mathcal{P}(n), \tag{12}$$

where $\mathcal{P}(n)$ is the probability of a conformation with exactly n bonds (*but not* $n+1$ or $n+2$ or $\cdots$ N bonds). For example, in the case of $N=2$, $\mathcal{P}(2)=[\mathcal{G}(L/3)]^3$, $\mathcal{P}(1)=2\mathcal{G}(L/3)\{\mathcal{G}(2L/3)-[\mathcal{G}(L/3)]^2\}$, and $\mathcal{P}(0)=\mathcal{G}(L)-2\mathcal{G}(L/3)\{\mathcal{G}(2L/3)-[\mathcal{G}(L/3)]^2\}-[\mathcal{G}(L/3)]^3$. Collecting terms, we obtain $Z_2=[\mathcal{G}(L/3)]^3(v-1)^2+2[\mathcal{G}(L/3)]\mathcal{G}(2L/3)(v-1)+\mathcal{G}(L)$.

Let us define a "bubble" as a polymer segment with only its ends bound. The minimum length of a bubble is $L_m=L/(N+1)$ and the maximum length is equal to the total contour length of the filament L. Notice that in our model, a bubble will always have length $\leqslant L \ll L_p$. A "chain" is defined as a sequence of minimal bubbles (each of length L_m). Figure 1 provides a pictorial definition of bubbles and chains. The partition function Z_N is a sum that consists of all products of the form $f(m_1)g(n_1)f(m_2)g(n_2)\cdots f(m_k)$, where

$$f(m)=\frac{\sqrt{3}}{2\pi}\frac{L_pB}{L_m^2m^2} \tag{13}$$

is the statistical weight of a bubble of length mL_m,

$$g(n)=[f(1)]^n(v-1)^{n+1} \tag{14}$$

is the statistical weight of a chain of length nL_m, and

$$m_1+n_1+m_2+n_2+\cdots+m_k=N+1, \quad 0<k<\left[\frac{N+1}{2}\right], \tag{15}$$

where $[(N+1)/2]$ is the integer part of $(N+1)/2$. We have

$$Z_N=\mathcal{G}(L)+\sum_{m=1}^{N} f(m)f(N+1-m)(v-1) + \sum_{k=1}^{[(N+1)/2]}\sum_{\{n_j\}}\sum_{\{m_j\}}\frac{\prod_{j=1}^{k} f(m_j)g(n_j)}{g(n_k)}. \tag{16}$$

The first two terms in Eq. (16) represent configurations with only one bond or no bond at all and we shall denote it by D_N. The curly braces indicate that the sums must satisfy the constraint of Eq. (15). As N increases, calculating the com-

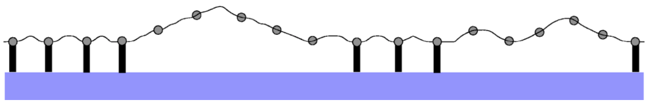

FIG. 1. A cartoon picture of a polymer conformation with a "chain" of length $3L_m$, a "bubble" of length $6L_m$, a "chain" of length $2L_m$ and a "bubble" of length $6L_m$. The dots represent pinning sites and the vertical black lines represent anchoring proteins, that bind the filament to the substrate. The weakly bending limit allows us to neglect any direct (hard wall) interaction with the substrate.

binatorial factors becomes an impossible task. That is why we use a standard trick and incorporate the constraint in the partition function via a Kronecker δ [23]:

$$Z_N=D_N+\sum_{k=1}^{[(N+1)/2]}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\delta\left[N-\sum_{j=1}^{k}(n_j+m_j)\right]\times\exp\left\{\beta\left[N-\sum_{j=1}^{k}(n_j+m_j)\right]\right\}\frac{\prod_{j=1}^{k}f(m_j)g(n_j)}{g(n_k)},\tag{17}$$

where $\Sigma_{n=1}^{\infty}\Sigma_{m=1}^{\infty}\equiv\Sigma_{n_1=1}^{\infty}\cdots\Sigma_{n_k=1}^{\infty}\Sigma_{m_1=1}^{\infty}\cdots\Sigma_{m_k=1}^{\infty}$ and the auxiliary real parameter β has been introduced to make sure that the partition function converges in later steps of the calculation.

We now introduce a complex representation of the Kronecker δ which yields

$$Z_N=D_N+\frac{1}{2\pi}\int_0^{2\pi}d\theta\exp[N(\beta+i\theta)]\times\sum_{k=1}^{[(N+1)/2]}\frac{\prod_{j=1}^{k}\Phi_j\Psi_j}{\Phi_k},\tag{18}$$

where

$$\Phi_j=\sum_{n_j=1}^{\infty}g(n_j)z^{n_j},\tag{19}$$

$$\Psi_j=\sum_{m_j=1}^{\infty}f(m_j)z^{m_j},\tag{20}$$

with $z\equiv\exp[-(\beta+i\theta)]$.

Since both Φ_j and Ψ_j are independent of j, $\Pi_{j=1}^{k}\Phi_j\Psi_j=(\Phi\Psi)^k$, and since we are interested in a very large number of pinning sites (thermodynamic limit, $N\rightarrow\infty$), we approximate $\Sigma_{k=1}^{[(N+1)/2]}(\Phi\Psi)^k\approx\Phi\Psi/(1-\Phi\Psi)$. Using analytic continuation, we transform the integral over θ to a contour integral over the complex "fugacity" z, where the contour encircles the origin $z=0$ in the counterclockwise direction once and we obtain

$$Z_N=D_N+\frac{1}{2\pi i}\oint_C dz z^{-N-1}\frac{\Psi}{1-\Phi\Psi},\tag{21}$$

where

$$\Phi=\frac{f(1)(v-1)^2z}{1-f(1)(v-1)z}\tag{22}$$

and

$$\Psi=\frac{\sqrt{3}}{2\pi}\frac{L_pB}{L_m^2}L_2(z)\tag{23}$$

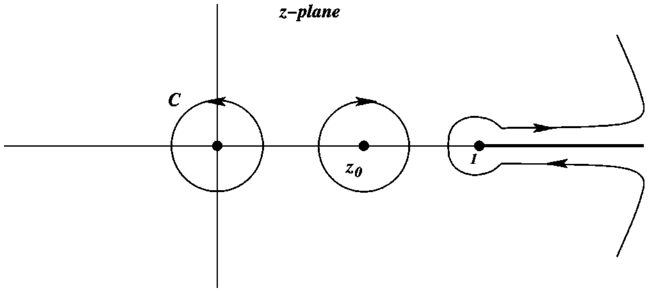

FIG. 2. The complex z plane with poles at $z=0$, $z=z_0$ and a branch cut along the positive real axis starting at $z=1$. The contour C can be deformed to a contour around z_0 and a contour around the branch cut which closes at infinity.

with $L_2(z)$ being Euler's dilogarithm function [24]. The integrand in Eq. (21) has three singularities: a pole of order $N+1$ at $z=0$; a simple pole at the solution z_0 of equation

$$\Psi(z_0)\Phi(z_0)=1;\tag{24}$$

and a branch cut along the positive real axis starting at $z=1$ due to $L_2(z)$. The contour C encircles only the singularity at the origin because of the assumptions that we had made in deriving Eq. (21). That is, $|z|$ was chosen so that the series Φ and Ψ converge and also $|\Phi\Psi|<1$. As shown in Fig. 2, the contour C can be deformed into a contour that encircles only z_0 clockwise and a loop that goes around the branch cut and closes at infinity counterclockwise [25]. At sufficiently low temperatures, $0<z_0<1$. In the thermodynamic limit, D_N vanishes and the partition function is determined by the pole at z_0: $N^{-1}\ln Z_N\approx-\ln z_0$.

As the temperature increases, v decreases and it can be seen from Eq. (24) that z_0 is shifted to the right. In the thermodynamic limit, Eq. (11) yields $Q=-[(v-1)/z_0]\times(\partial z_0/\partial v)$. This implies that the average fraction of intact bonds, which is a physically observable quantity, monotonically decreases [26]. The unbinding transition occurs when $z_0\rightarrow1$. Therefore, the unbinding criterion is $\Phi(1)\Psi(1)=1$. Given that $L_2(1)=\zeta(2)\approx1.64$, where $\zeta(z)$ is Riemann's ζ function, we obtain

$$\frac{L_pB}{L_m^2}[\exp(J/k_BT_c)-1]\approx2.\tag{25}$$

This is the main result of this paper. The transition will be continuous because the derivative of $L_2(z)$ diverges logarithmically at $z=1$ and, therefore, the average fraction of intact bonds vanishes continuously at the critical temperature T_c. Notice that in order to obtain this transition, we need the thermodynamic limit where $N\rightarrow\infty$ *and* $(\sqrt{3}/2\pi)\times(L_p/L^2)N^2B$ which is the probability of finding a pinning site within the binding region remains constant $\ll1$. This implies that $B\rightarrow0$ that is consistent with a *microscopic* effective length that characterizes the bond. Of course, real systems will have a finite number of pinning sites and the transition will not be sharp. For a sufficiently high density of pinning sites, however, we would expect a clear crossover from a low temperature phase with most of the pinning sites bound to a high temperature phase with most of the pinning sites unbound which will be described by Eq. (25). If we allow the polymer to fluctuate in two transverse dimensions, the depinning transition becomes discontinuous and the transition temperature is given by Eq. (A4). An analysis of the $(1+2)$-dimensional case is presented in the Appendix.

From the original presentation of the necklace model [15,16], it is known that the order of the transition is determined by the scaling of the statistical weight of the bubbles with their size; that is, the exponent c in $f(m) \sim 1/m^c$. As we show in the Appendix, in the case of weakly bending semiflexible polymers in $1+d$ dimensions, $c=2d$. For $c \leqslant 1$, there can be no phase transition. For $1<c<2$, the transition is continuous with critical exponents depending on c. For $c>2$, the transition is discontinuous. The $1+1$-dimensional case that we consider here is the borderline situation between continuous and discontinuous transitions. The transition is still continuous but the critical singularities are logarithmic and not algebraic. Specifically, the average fraction of intact bonds vanishes as $\sim 1/\ln(T_c - T)$ and the mean size of a given bubble diverges as $\sim \ln(T_c - T)$. For the sake of completeness, it is interesting to calculate the critical exponents for the depinning transition in $1+d$ dimensions with $d<1$. Reference [16] shows that the longitudinal correlation length $\xi_\parallel$ diverges at T_c as $\xi_\parallel \sim 1/(T_c - T)^{1/(c-1)}$. Equation (6) implies that the mean square transverse displacement of a weakly bending semiflexible polymer scales with the cube of the contour length. This scaling holds for any transverse dimensionality because in the weakly bending approximation the transverse dimensions decouple. Therefore, we expect that the transverse localization length $\xi_\perp \equiv \langle \mathbf{r}_\perp^2 \rangle^{1/2}$ will scale as $\xi_\perp \sim \xi_\parallel^{3/2}$ and its critical exponent will be $3/(4d-2)$ [that is, $\xi_\perp \sim 1/(T_c - T)^{3/(4d-2)}$]. Note that this is precisely the same as the result obtained in Ref. [12] for $2/3<d<1$ using renormalization group (RG).

IV. BENDING RIGIDITY AND FORCE-INDUCED UNBINDING

In this Section, we consider the force-induced unbinding of a weakly bending semiflexible polymer and we show that the bending rigidity facilitates the unbinding. If we apply a transverse force to the free end of a clamped semiflexible polymer, the effective free energy of Eq. (1) changes by an extra term

$$\mathcal{H}_f = \frac{\kappa}{2}\int_0^L ds \left[\frac{\partial \mathbf{t}(s)}{\partial s}\right]^2 - f\int_0^L ds \sin\theta(s), \qquad (26)$$

where, as in Sec. II, $\theta(s)$ is the slope of the tangent vector with respect to the longitudinal direction. The partition function of this system is a path integral over all possible conformations. Slicing the L length into N segments each of length a and using the small-angle approximation, we obtain

$$\mathcal{H}_f^N = \frac{\kappa}{2a}\sum_{i=1}^{N} (\theta_i - \theta_{i-1})^2 - fa\sum_{i=1}^{N} \theta_i . \qquad (27)$$

In this approximation, the path integral is Gaussian and can be easily calculated [18] yielding

$$Z_f = \exp\left[\frac{f^2 L^3}{3L_p (k_B T)^2}\right]. \qquad (28)$$

The corresponding free energy is

$$F = -\frac{f^2 L^3}{3L_p (k_B T)}. \qquad (29)$$

Note that this free energy is just minus the elastic energy of a cantilever spring, $U_{el} = f^2/2\chi$, with spring constant $\chi = 3\kappa/L^3$. The latter has been obtained in a linear response calculation in Ref. [27].

Although the original "Hamiltonian" (Eq. 26) is extensive, the free energy F of Eq. (29) is not (it grows as L^3) because Eq. (29) is an approximation, valid only in the short length scales of the weakly bending limit $(L \ll L_p)$. Given that the free energy of the bound state is always extensive, this nonextensivity leads to a "lever-arm effect" in the force-induced unbinding. That is, for a long enough total length, the unbound state will be favorable having a lower free energy. We can estimate an upper bound for this "critical" length. If $\mathcal{F}_b$ is the free energy density of the bound state, the "lever-arm" critical length L_l should satisfy the condition

$$\mathcal{F}_b L_l = \frac{f^2 L_l^3}{3L_p (k_B T)}. \qquad (30)$$

If $L>L_l$, the transverse force f will always unbind the polymer (in equilibrium). Using the model of Sec. III, we have $\mathcal{F}_b \approx (k_B T/L_m)[J/k_B T - \ln(\sqrt{3}L_p B/L_m^2 2\pi)]$. It turns out that

$$L_l \approx \sqrt{3}\,\frac{1}{f}\left[J - k_B T \ln\left(\frac{\sqrt{3}L_p B}{L_m^2 2\pi}\right)\right]^{1/2}\left(\frac{L_p}{L_m}\right)^{1/2}. \qquad (31)$$

For pulling forces of the order of pico-Newton, persistence length of the order of μm, and binding free energy per L_m of the order of $k_B T$, it turns out that $L_l \approx 10^{-3}(L_p/L_m)^{1/2} L_p$ that is an indication of the relevance of the "lever-arm effect" to biopolymers.

This is a phenomenon related to the "molecular leverage" discussed in Ref. [28]. In both cases, the bending rigidity facilitates the force-induced unbinding. The two phenomena, however, are different. We describe a situation, where a bound state with a sequence of pinned sites becomes thermodynamically unstable when the system is long enough for the "lever arm" to dominate the free energy, whereas Ref. [28] presents an estimate of the torque induced force exerted on a *single* ligand-receptor pair that turns out to be much stronger compared to that applied in traction.

V. DISCUSSION AND CONCLUSIONS

As we mentioned in the Introduction, the unbinding of semiflexible polymers is a particularly tricky problem because of the ambiguity of the relevant thermodynamic limit and also because of a lack of exact solutions of the WLC model with a binding potential. References [9–11] actually deal with the unbinding of *flexible* polymers (with $L \gg L_p$)

and consider the effect of the bending rigidity on the conformational properties of the adsorbed (low-temperature) phase. In these works, the bending rigidity enters as a perturbation to the flexible (Gaussian) chain and the inextensibility is absent. The early references [6,7] use a somewhat inconsistent approach, where the scaling behavior of a weakly bending stiff filament (valid only for $L \ll L_p$) is artificially extended to apply to any length. Another serious drawback of this approach is that it yields results that appear to be independent of the persistence length while, in principle, they should not. The idea is to solve Eq. (5) for large L with a binding potential using scaling Ansätze and then invoke the necklace model to predict the order of the unbinding transition from the scaling behavior of G. The details of the necklace model (bubbles, chains, partition function, etc.), however, are not worked out. Reference [8] employs a discrete model for stiff filaments where an extra (''monomer'') length is introduced and turns out to be relevant for the unbinding transition. It also proposes an energy-entropy melting criterion that applies to adsorbed phases similar to those discussed in Refs. [9,11]. Reference [12], using a RG treatment, demonstrates the relevance of an orientation-dependent interaction field for the unbinding transition. The RG flow implies a thermodynamic limit that carries on some of the inconsistencies of Refs. [6,7]. These inconsistencies, however, appear not to affect the universal properties of the depinning (order of the transition, critical exponents). The relevant results obtained from our necklace-model treatment turn out to be exactly the same as those from the RG treatment of Ref. [12]. Reference [13] models a semiflexible polymer as a directed self-avoiding random walk and it reiterates the inconsistencies of Refs. [6,7] because the unbinding transition occurs at the thermodynamic limit of an infinitely long walk (infinitely longer than the persistence length), where one would normally expect to recover the behavior of a flexible chain.

In conclusion, applying the necklace model, we have obtained a criterion for the depinning of anchored semiflexible polymers in the weakly bending (stiff) limit. This model has been extensively used to study the unbinding of flexible polymers [23,25,29,30]. This is its first detailed application to the unbinding of semiflexible polymers. A general and rigorous theoretical treatment of the unbinding of semiflexible polymers of arbitrary total length and persistence length, in the presence of an arbitrary binding potential, has not yet been achieved. Our model suggests an alternative way to consider the thermodynamic limit for this system and straightens out several misconceptions of previous studies.

We have also shown how the bending rigidity facilitates the force-induced unbinding of semiflexible polymers in the weakly bending limit. We have estimated a critical length as a function of the pulling force, the binding free energy density, the persistence length, and the density of pinning sites above which the polymer acts as a lever-arm and unbinds.

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APPENDIX

In this appendix, we consider the thermal depinning in $1+2$ dimensions. It is the same problem as the one we discussed in Secs. II and III with the only difference being that we now allow the polymer to fluctuate in two transverse directions (y and z). Again, we have a *line* of anchoring sites (along the x axis). All of the steps in the calculation, which yields the phase transition, can be repeated with only minor modifications. The reason is that in the approximation of a weakly bending filament (valid for $L \ll L_p$), the two transverse directions decouple.

As before, the two-point conformational probability distribution in $1+2$ dimensions is a function of the position and the slope at the two points: $G(\mathbf{r}_s,\mathbf{t}_s,s|\mathbf{r}_0,\mathbf{t}_0,0)$. We parametrize the slope using the ''Monge gauge'': $\mathbf{t}(s)=[1,\tau_y(s),\tau_z(s)]/\sqrt{1+\tau_y(s)^2+\tau_z(s)^2}$. The imaginary-time ''Schrödinger'' equation reads

$$\left[\frac{\partial}{\partial s}+\mathbf{t}\cdot\boldsymbol{\nabla}_{\mathbf{r}}-\frac{1}{L_p}\left(\frac{\partial^2}{\partial\tau_y^2}+\frac{\partial^2}{\partial\tau_z^2}\right)\right]G(\mathbf{r}_s,\mathbf{t}_s,s|\mathbf{r}_0,\mathbf{t}_0,0)=0. \tag{A1}$$

In the weakly bending approximation, $\mathbf{t}(s)\approx[1,\tau_y(s),\tau_z(s)]$ and, after integrating over x, we obtain the following equation for the reduced probability distribution:

$$\left[\frac{\partial}{\partial s}+\tau_y\frac{\partial}{\partial y}+\tau_z\frac{\partial}{\partial z}-\frac{1}{L_p}\left(\frac{\partial^2}{\partial\tau_y^2}+\frac{\partial^2}{\partial\tau_z^2}\right)\right]G=0, \tag{A2}$$

where $G=G(y_s,z_s,\tau_{ys},\tau_{zs},s|y_0,z_0,\tau_{y0},\tau_{z0},0)$. It is clear now that the two transverse directions decouple and the solution with the appropriate initial condition (δ function in the displacement and the slope) will be given by a product of two factors, each having the form given by Eq. (6). If we fix the transverse displacement and the slope at $s=0$ to be zero, the probability of finding the free end within a very small range of slopes and transverse displacements ($-\delta_y<\tau_{yL}<\delta_y$, $-\delta_z<\tau_{zL}<\delta_z$, $-\epsilon_y<y_L<\epsilon_y$, $-\epsilon_z<z_L<\epsilon_z$, with $0<\delta_{y,z},\epsilon_{y,s}\ll 1$) is $\approx(3/(2\pi)^2)L_p^2C/L^4$, where $C\equiv 2^4\delta_y\delta_z\epsilon_y\epsilon_z$.

A bond is now characterized by a binding energy J and an effective *area* C. The necklace model calculation is worked out as before but with a different bubble weight $f(m)=[3/(2\pi)^2](L_p^2C/L_m^4m^4)$. The different scaling changes Eq. (23) to

$$\Psi=\frac{3}{(2\pi)^2}\frac{L_p^2C}{L_m^4}\Phi(z,4,0), \tag{A3}$$

where $\Phi(z,4,0)$ is Euler's polylog function [24]. As before, the unbinding transition occurs when $\Psi(1)\Phi(1)=1$. Taking into account that $\Phi(1,4,0)=\zeta(4)\approx 1.08$, we obtain

$$\frac{L_p^2C}{L_m^4}[\exp(J/k_BT_c)-1]\approx 8. \tag{A4}$$

Since our calculation is based on the assumption that $[3/(2\pi)^2]L_p^2 C/L^4 \ll 1$ (in the $1+1$-dimensional case, we had $[\sqrt{3}/(2\pi)]L_p B/L^2 \ll 1$), Eq. (A4) and Eq. (25) differ only quantitatively. The derivative of $\Phi(z,4,0)$ as $z \to 1$ from below is finite. This implies a finite jump in the average fraction of intact bonds as it vanishes at the transition. The transition is therefore, discontinuous in accord with the RG prediction of Ref. [12].

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