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LETTER TO THE EDITOR

Unbinding transition of flexible Gaussian polymers in two dimensions

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Abstract. The unbinding of Gaussian polymers with bending energy and external tension parallel to the wall is studied by scaling arguments and transfer matrix methods in two spatial dimensions. Unbinding transitions occur as the strength of the wall potential or the external tension is varied. Three different scaling regimes can be distinguished: (i) a stiff-rod regime; (ii) a semi-flexible regime; and (iii) a crumpled regime. Scaling functions are calculated numerically for the crossover behaviour.

The unbinding transition of polymers in two spatial dimensions has been studied recently [1-3] in two different limits. A polymer is considered here as a flexible string of monomers, with fluctuations controlled by the bending energy. On length scales small compared to the persistence length [4], ξ_p, it behaves like a flexible rod (semi-flexible regime) [1, 2]. On length scales much larger than ξ_p, the bending energy becomes irrelevant. In this crumpled state, the polymer can be treated as an elastic spring [1, 3, 5]. In both cases, unbinding transitions are found to depend on the long-range tail of the wall potential, which falls off as z^{-p} for large distances z. Potentials with $p > p_c$ belong to the same universality class, while potentials with $p < p_c$ are strong enough to always bind the polymer, where $p_c = \frac{2}{3}$ in the semi-flexible limit, $p_c = 2$ for Gaussian polymers, and $p_c = \frac{4}{3}$ for polymers with excluded volume interactions [2, 3]. In this paper we (i) study the crossover from the rod-like to the crumpled polymer in the vicinity of an attractive wall, and (ii) discuss the effect of an external tension parallel to the wall.

We consider a continuum model for a Gaussian polymer near a wall. The configuration of the chain will be described by $(x(s), z(s))$ and $\vartheta(s)$, where x and z are coordinates parallel and perpendicular to the wall, ϑ is the local angle between the polymer and the wall, and s measures the distance on the chain. $x(s)$ and $z(s)$ are related to $\vartheta(s)$ by $\mathrm{d}x/\mathrm{d}s = \cos(\vartheta)$ and $\mathrm{d}z/\mathrm{d}s = \sin(\vartheta)$. The partition function is then defined by the path integral

$$Z_l(\vartheta, z, x|\vartheta_0, z_0, x_0) = \int \mathrm{D}\vartheta \exp\left\{ -\int_0^l \mathrm{d}s \left[\frac{\kappa}{2}\left(\frac{\mathrm{d}\vartheta}{\mathrm{d}s}\right)^2 - \sigma \frac{\mathrm{d}x}{\mathrm{d}s} + V(z) \right] \right\}. \qquad (1)$$

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Here, κ is the bending modulus, and σ an external tension along the x axis. At $s=0$ and $s=l$ the position and angle of the polymer are fixed at the values x, z, ϑ and x_0, z_0, ϑ_0, respectively. The path integral implies the Schrödinger-like equation

$$\left[\frac{\partial}{\partial l}-\frac{1}{2\kappa}\frac{\partial^2}{\partial\vartheta^2}+\sin(\vartheta)\frac{\partial}{\partial z}+\cos(\vartheta)\frac{\partial}{\partial x}-\sigma\cos(\vartheta)+V(z)\right]Z_l(\vartheta, z, x|\vartheta_0, z_0, x_0)=0. \qquad (2)$$

Potentials of the form

$$V(z)=\begin{cases}-wz^{-p} & z>a_0\\ -u & 0\leqslant z<a_0\\ \infty & z<0\end{cases} \qquad (3)$$

will be considered. If information about the distribution of x is not required, integration over x leads to a similar, but somewhat simpler equation for $Z_l(\vartheta, z|\vartheta_0, z_0)$. Finally, for the free polymer, (2) can be reduced to

$$\left(\frac{\partial}{\partial l}-\frac{1}{2\kappa}\frac{\partial^2}{\partial\vartheta^2}-\sigma\cos(\vartheta)\right)Z_l(\vartheta|\vartheta_0)=0. \qquad (4)$$

Equation (4) can be used to calculate various quantities analytically in terms of Matthieu functions. For a free polymer with $\vartheta_0=0$, we find that without tension

$$\langle x\rangle=2\kappa(1-\mathrm{e}^{-l/2\kappa}) \qquad (5)$$

and $\langle x(\vartheta)\rangle=(\kappa/\pi)(1+\cos(\vartheta))$ for $l\to\infty$. An expansion for small tensions yields

$$\frac{\langle x\rangle}{l}=\kappa\sigma-\frac{7}{4}(\kappa\sigma)^3+\mathrm{O}((\kappa\sigma)^5) \qquad (6)$$

again for $l\to\infty$.

On length scales less than the persistence length, only angles $\vartheta\ll 1$ contribute to the partition function. The trigonometric functions can then be expanded, and one obtains the semi-flexible limit

$$\left(\frac{\partial}{\partial l}-\frac{1}{2\kappa}\frac{\partial^2}{\partial\vartheta^2}+\vartheta\frac{\partial}{\partial z}+\frac{1}{2}\sigma\vartheta^2+V(z)\right)Z_l(\vartheta, z|\vartheta_0, z_0)=0 \qquad (7)$$

which generalizes the Schrödinger-type equation of [1, 2] to a polymer with tension. We can introduce rescaled variables $\tilde z=z/a_0$, $\tilde\vartheta=(2\kappa/a_0)^{1/3}\vartheta$, $\tilde l=(2\kappa a_0^2)^{-1/3}l$, and $\tilde u=(2\kappa a_0^2)^{1/3}u$, $\tilde w=(2\kappa)^{1/3}w$, $\tilde\sigma=2\kappa\sigma(a_0/2\kappa)^{4/3}$. Then (7) reads

$$\left(\frac{\partial}{\partial\tilde l}-\frac{\partial^2}{\partial\tilde\vartheta^2}+\tilde\vartheta\frac{\partial}{\partial\tilde z}+\frac{1}{2}\tilde\sigma\tilde\vartheta^2+\tilde V(\tilde z)\right)Z_{\tilde l}(\tilde\vartheta, \tilde z|\tilde\vartheta_0, \tilde z_0)=0 \qquad (8)$$

where the potential is now given by

$$\tilde V(\tilde z)=\begin{cases}-\tilde w\tilde z^{-p} & \tilde z>1\\ -\tilde u & 0\leqslant\tilde z<1\\ \infty & \tilde z<0.\end{cases} \qquad (9)$$

For $\sigma=0$, three different scaling regimes [6, 7] can be defined by comparing the asymptotic decay z^{-p} of the potential $V(z)$ and the fluctuation-induced repulsion $V_{\mathrm{FL}}\sim z^{-\tau}$, with $\tau=-2(d-1)/(d-5)$. The conditions $p>\tau$, $p=\tau$ and $p<\tau$, with $\tau=\frac{2}{3}$ for $d=2$, correspond to the strong, intermediate and weak-fluctuation regimes, respectively.

For polymers much longer than the persistence length, the effective Hamiltonian [3]

$$H\{x, z\} = \int_0^l \mathrm{d}s \left[\frac{1}{2}\Sigma\left(\frac{\mathrm{d}x}{\mathrm{d}s}\right)^2 + \frac{1}{2}\Sigma\left(\frac{\mathrm{d}z}{\mathrm{d}s}\right)^2 + V_{\mathrm{eff}}(z)\right] \tag{10}$$

can be used to describe the critical behaviour of the polymer. Again three different scaling regimes [6] can be defined by comparing the asymptotic decay z^{-p} of the potential $V(z)$ and the fluctuation-induced repulsion $V_{\mathrm{FL}} \sim z^{-\tau}$, but now $\tau = -2(d-1)/(d-3)$. The effective Hamiltonian (10) is obtained by integrating out fluctuations on length scales shorter than the persistence length $\xi_p = \kappa$. For a *free* polymer (with $\sigma = 0$) this yields the effective tension $\Sigma = \Sigma_0/\kappa$, with a constant $\Sigma_0 = \mathrm{O}(1)$. However, near a wall this integration also leads from the bare potential V to the renormalized potential V_{eff}, which cannot be obtained easily. Only when *all* length scales are much larger than ξ_p is $V_{\mathrm{eff}} = V$. With rescaled variables $\hat{z} = z/a_0$, $\hat{x} = x/a_0$, $\hat{l} = l/(2\Sigma a_0^2)$, and $\hat{u} = 2\Sigma a_0^2 u$, $\hat{w} = 2\Sigma w$, all parameters can then be absorbed in the two variables $\hat{u}$ and $\hat{w}$.

For a numerical study, we consider a discrete version of the model (2), which is defined by the following recurrence relation for the partition function:

$$\begin{aligned} Z_{l+1}(\vartheta, z, x) = {} & [(1-2q)Z_l(\vartheta, z - b\sin(\vartheta), x - b\cos(\vartheta)) \\ & + qZ_l(\vartheta - \Delta\vartheta, z - b\sin(\vartheta), x - b\cos(\vartheta)) \\ & + qZ_l(\vartheta + \Delta\vartheta, z - b\sin(\vartheta), x - b\cos(\vartheta))] \\ & \times \exp[-V(z) + \sigma b\cos(\vartheta)]. \end{aligned} \tag{11}$$

The angle ϑ changes in discrete units 0, $\pm\Delta\vartheta$. q is the probability of the polymer to have a bend of angle $\Delta\vartheta$ at the lth monomer. To implement the recursion numerically, we take discrete integer variables x, z, and a monomer length b, which is considerably larger than unity. If $(z - b\sin(\vartheta))$ or $(x - b\cos(\vartheta))$ do not coincide with a lattice point, the nearest integer is used.

The free polymer without tension is easily solved for the discrete model too, by transfer matrix methods. For large l and $(\Delta\vartheta) \ll 1$ (so that sums can be replaced by integrals) we obtain the same behaviour as in the continuum limit (5), with

$$\kappa = \frac{b}{2q(\Delta\vartheta)^2}. \tag{12}$$

This relation defines κ for the discrete model.

We consider first the unbinding problem with short-range interactions, i.e. $w = 0$ in (3). As u approaches a critical value, u_c, critical unbinding is observed with $\langle z \rangle \sim (u - u_c)^{-\nu_\perp}$, with $\nu_\perp = 1$. This is exactly the behaviour expected from (10). However, for the critical potential strength u_c we find three different scaling regimes, depending on the relative size of the length scales $\xi_p = \kappa$, a_0 and the effective step size perpendicular to the wall, $b_\perp = q^{-1} b \Delta\vartheta$: (i) the stiff-rod regime, where $a_0 \ll \kappa$ and $b_\perp \gg a_0$, (ii) the semi-flexible regime, where $1 \ll a_0 \ll \kappa$ and $b_\perp \ll a_0$ and (iii) the crumpled regime, where all length scales are large compared to the persistence length.

In order to predict the behaviour in the *stiff-rod regime*, we use the necklace approach of Fisher and Huse [8, 9]. For $a_0 = 1$, this approach is exact. The critical strength u_c of the wall potential can be expressed in terms of the partition functions $Z_l^{\mathrm{HW}}(\vartheta = 0, z = 1|0, 1)$ and $Z_l^{\mathrm{HW}}(\vartheta = \pi, z = 1|0, 1)$ of polymers, which start parallel to the (hard) wall at $z = 1$ and end parallel to the wall at $z = 1$, but never touch the wall otherwise. The only quantity needed is $G_c = \Sigma_l Z_l^{HW}(0|0) + Z_l^{HW}(\pi|0)$. A little thought shows that u_c is determined by [9]

$$v(1-2q) = 1 - v^2 G_c \tag{13}$$

where $v = \exp(u_c)$. The left-hand side of this equation is the free energy per monomer of a completely bound polymer. For large κ, $G_c \sim \kappa^{-2} \to 0$, so that simply $u_c = -\ln(1-2q) \simeq 2q$. Together with (12), this implies

$$\kappa u_c = \frac{b}{(\Delta\vartheta)^2} \qquad \text{for } a_0 = 1. \tag{14}$$

In the *semi-flexible regime*, the polymer fluctuates *inside* the potential well, but is still essentially parallel to the wall. Therefore, the free energy of the bound state is given by the free energy (per monomer), $f \sim a_0^{-2/3}$, of a semi-flexible polymer between two hard walls with separation a_0 [1]. Then, (13) reads $v\,e^f = 1 - v^2 G_c$, which implies

$$\kappa u_c = c\left(\frac{\kappa}{a_0}\right)^{2/3} \tag{15}$$

with a constant c. This is exactly the behaviour of u_c in the case of semi-flexible polymers (7) although the divergence of $\langle z \rangle$ is determined by the effective Hamiltonian (10). Finally, in the *crumpled regime*, the critical strength is given by $u_c \sim (\Sigma a_0^2)^{-1} \sim \kappa / a_0^2$.

For the continuum model, only regimes (ii) and (iii) exist. Therefore, in the continuum limit, u_c has the scaling form

$$u_c = \frac{1}{\kappa}\,\Omega(\kappa/a_0) \tag{16}$$

where $\Omega(y) \sim y^{2/3}$ for $y \to \infty$, and $\Omega(y) \sim y^2$ for $y \to 0$. The results obtained from the discrete model for various values of p, a_0 and $\Delta\vartheta$ are shown in figure 1. The results agree very well with (14), (16).

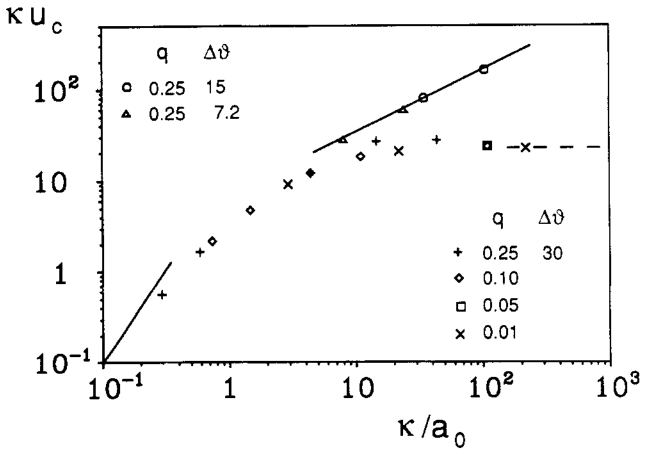

Figure 1. Scaled critical potential strength κu_c as a function of the scaled inverse width $(a_0/\kappa)^{-1}$ of the short-range potential. The scaling function Ω in the continuum limit (16) is given by the upper envelope of the data points. Its asymptotic behaviour is indicated by the full lines. The broken line shows the stiff-rod result (14) for $\Delta\vartheta = 30°$. The step length used is $b = 6$ for $\Delta\vartheta = 30°$ and $b = 8$ otherwise.

We study now the effect of a lateral tension σ, which stretches the polymer parallel to the wall. Then, the critical strength of the potential depends on σ. In the stiff-rod regime (i), we find that u_c has a scaling form,

$$u_c = \frac{1}{\kappa}\,\Xi(\kappa\sigma) \tag{17}$$

as displayed in figure 2, with $\Xi(y) \sim y^{-1}$ for large y. For small σ, Ξ should be analytic, so that $\Xi(y) \to \Xi(0) - \Xi_2 y^2$ for $y \to 0$, with $\Xi(0) = b(\Delta\vartheta)^{-2}$, see (14), and a positive constant Ξ_2. This implies that for 'relaxation induced critical unbinding' (RICU), with $\sigma \to 0$ at $u = u_c$ ($\sigma = 0$),

$$\langle z\rangle \sim \sigma^{-2\nu_\perp}. \tag{18}$$

In the semi-flexible regime (ii), scaling as in (7) leads to the σ dependence of u_c given by

$$u_c = (\kappa a_0^2)^{-1/3}\Theta\left(\kappa\sigma\left(\frac{a_0}{\kappa}\right)^{4/3}\right). \tag{19}$$

The data for different values of κ and a_0 obtained from model (11) indeed show the expected scaling behaviour, see figure 3. Since u_c should again be an analytical function of σ at $\sigma = 0$, $\Theta(y) \to \Theta(0) - \Theta_2 y^2$ for $y \to 0$, with $\Theta(0) = c$, see (15), and a positive constant Θ_2. For large σ, u_c should become independent of κ, which implies $u_c \sim (\sigma a_0^2)^{-1}$, and $\Theta(y) \to y^{-1}$ for $y \to \infty$. In the crumpled regime (iii), $u_c \sim (\sigma a_0^2)^{-1}$, see (10).

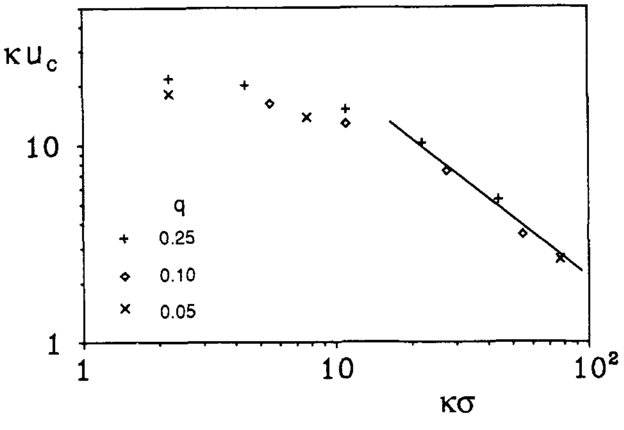

Figure 2. Scaling function Ξ of the critical potential strength as a function of the tension σ in the stiff-rod regime (17). The asymptotic behaviour is indicated by the full line. All data points have been calculated with $a_0 = 1$, $b = 6$, and $\Delta\vartheta = 30°$.

Finally, we want to consider the unbinding transition in the case of long-range potentials with $p = p_c = 2$. The transition now depends on the details of the potential $V(z)$. It can be characterized by the asymptotic behaviour of the probability Z_l of an *unbound* polymer to return to the wall after l steps [9]. For large l, $Z_l \sim l^{-\psi(w)}$, where ψ is a function of the amplitude w of the tail, but does *not* depend on any other details of the potential. Three subregimes are found [3, 10]. For $w > w_A > 0$, $\psi < 1$ and the tail itself is strong enough to always bind the polymer. As $w \to w_A^+$ a transition *may* occur, where the polymer unbinds with an essential singularity in the parallel correlation

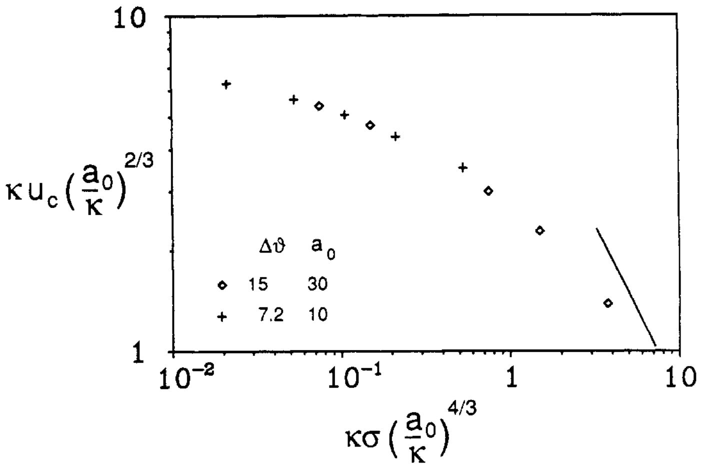

Figure 3. The scaling function $\Theta(\kappa\sigma(a_0/\kappa)^{4/3}) = u_c(\kappa a_0^2)^{1/3}$ of the critical potential strength as a function of the tension σ, in the semi-flexible regime (19). The asymptotic behaviour for large σ is indicated by the full line. All data points have been calculated with $b=8$ and $q=0.25$.

length (subregime A). For $w_A > w > w_{BC}$, $1 < \psi < 2$; *if* a transition occurs as u is varied, it is continuous and the correlation length diverges with a power law, $\xi \sim (\hat{u} - \hat{u}_c(\hat{w}))^{-\nu_\parallel}$, with $\nu_\parallel = (\psi - 1)^{-1}$ and $\nu_\perp = \zeta\nu_\parallel$, where $\zeta = \frac{1}{2}$ is the wandering exponent [6] (subregime B). Finally, for $w < w_{BC} < 0$, the transition is first order with $\nu_\parallel = 1$ (subregime C). The phase diagram for the crumpled regime has been calculated in [10]; it shows all three subregimes A, B, C.

The behaviour in the regimes (i) and (ii) is more complex, however. In this case, there is a minimal value, $\psi^* = \psi(w^*)$, of ψ, which can be reached by varying w, with $\frac{3}{2} > \psi^* > 1$. For $w > w^*$, the polymer is bound. This implies, in particular, that there is no subregime A in this case. In order to investigate this point further, we introduce a slightly generalized potential

$$V(z) = \begin{cases} -w(z+z_0)^{-p} & z > a_0 \\ -u & 0 \leq z < a_0 \\ \infty & z < 0. \end{cases} \tag{20}$$

The phase diagram for $a_0 = 1$ and $z_0 = 10$ is shown in figure 4. For $w/\kappa > 0.91$, the polymer is always bound, although ψ (calculated with a sufficiently large value of z_0 in (20)) reaches its 'critical' value $\psi = 1$ only at $w/\kappa = 1.48$. It is numerically rather difficult to obtain precise values for $\psi(w)$, but the results are consistent [10] with $\psi = 1 + \sqrt{\frac{1}{4} - \hat{w}}$, where $\hat{w} = 2\Sigma_0 w/\kappa$. For $b = 6$, $\Delta\vartheta = 30°$ and $p = 0.25$, we obtain $w_A/\kappa \approx 1.48$, $w_{BC}/\kappa \approx -4.55$, and $\Sigma_0 = 0.082$. This value of Σ_0 is *not* the same as the value which appears in other properties, like the end-to-end distance of a free polymer.

If fluid membranes in $d = 3$ are crumpled, as it is presently believed, similar phenomena are to be expected at unbinding transitions. In particular, it would be interesting to study relaxation induced unbinding (RIU) transitions (see [11] and references therein). For attractive potentials with a power-law tail z^{-p}, the membrane is always bound as long as an external tension is present. If the potential is weak enough and $p > p_c$, it unbinds as $\sigma \to 0$ (complete RIU), whereas it remains bound for

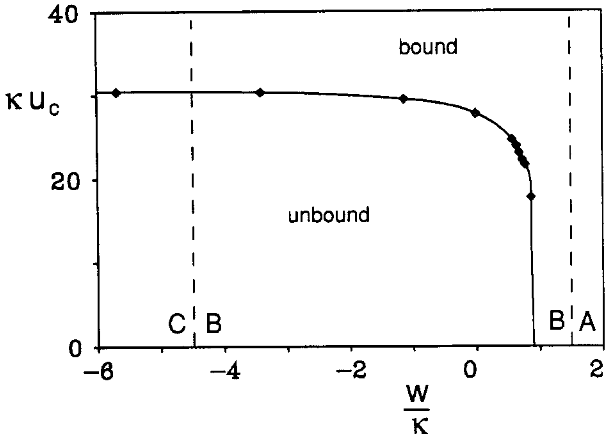

Figure 4. Phase diagram for the discrete model (11) with the potential (20), with $b = 6$, $\Delta\vartheta = 30°$, $q = 0.25$, $a_0 = 1$, and $z_0 = 10$. The broken lines indicate the boundaries between the subregimes A and B, and between B and C. The full line is a guide to the eye.

stronger potentials. For the potential which separates these regimes, RICU should be observed.

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