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Force-Induced Desorption and Unzipping of Semiflexible Polymers

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The thermally assisted force-induced desorption of semiflexible polymers from an adhesive surface or the unzipping of two bound semiflexible polymers by a localized force are investigated. The phase diagram in the force-temperature plane is calculated both analytically and by Monte Carlo simulations. Force-induced desorption and unzipping of semiflexible polymers are first order phase transitions. A characteristic energy barrier for desorption is predicted, which scales with the square root of the polymer bending rigidity and governs the initial separation process before a plateau of constant separation force is reached. This leads to activated desorption and unzipping kinetics accessible in single molecule experiments.

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Peeling an adhesive fiber from a surface or separating two adhesive fibers are two basic experimental tests of elastic and adhesive fiber properties. Over the past decade, experimental force spectroscopy techniques such as atomic force microscopy (AFM) and optical or magnetic tweezers have been developed, which allow us to perform analogous manipulation experiments on *individual polymers* with spatial resolution in the nm range and force resolution in the pN range [1]. Particularly suited for single polymer manipulation experiments are large rodlike polymers, e.g., biopolymers such as DNA, cytoskeletal filaments, or protein fibers, dendronized, or charged polymers. These polymers are *semiflexible*, i.e., governed by their bending energy with typical persistence lengths in the nm or μm regime. Quantitative analysis of force spectroscopy on semiflexible polymers requires theoretical models that take into account the *combined* effects of external force, temperature, and polymer bending energy. In this Letter, I present a theory and simulations for the force-induced desorption and unzipping of semiflexible polymers. Force-induced desorption experiments with single semiflexible polymers have recently been realized by attaching adsorbed polyelectrolytes to an AFM tip [2–7]. The most recent experiments [5–7] give access to the *single* polymer force-distance curve. Force-induced desorption is assisted by thermal fluctuations and, thus, also gives additional insight into the fundamental problem of polymer adsorption, which has been studied intensively both analytically [8–10] and by simulations [11] for semiflexible polymers.

A closely related problem is the unzipping of two semiflexible polymers, e.g., the unzipping of stiff protein fibers [12] or of cytoskeletal filaments or bundles of filaments [13,14]. The unzipping of DNA [15], where single strands are modeled as *flexible* polymers, has been extensively studied [16–20], and two barrier effects have been reported: (i) *Finite* DNA can unzip below the critical force by overcoming a free energy barrier, which is proportional to its total length [16]. This effect is also present for unzipping semiflexible polymers, but we will focus on the limit of long polymers such that the bound state becomes thermodynamically stable below the critical force. (ii) A free energy barrier arises from the enhanced stiffness of the double-stranded DNA helix [19]. In this Letter, I rather focus on the situation where each of the unzipping polymers is semiflexible, and point out a generic barrier effect governed by their *intrinsic* bending rigidity.

I show that the desorption and unzipping of semiflexible polymers by localized forces are first order transitions and obtain the full phase diagram in the force-temperature plane, i.e., the critical force as a function of temperature both analytically and by Monte Carlo simulations. For semiflexible polymers, force-induced desorption or unzipping require thermal activation over a characteristic *energy barrier* that scales with the square root of the bending rigidity κ and is absent for flexible polymers. This energy barrier governs the initial separation process before a plateau of constant desorption or unzipping force is reached and has important consequences for experiments. The energy barrier is a generic bending rigidity effect and gives rise to an enhanced stability against external forces.

Force-induced desorption at zero temperature.—First, we will focus on force-induced desorption and discuss the related problem of unzipping in the end. In the absence of thermal fluctuations ($T = 0$), force induced desorption becomes a classical mechanics problem similar to fracture. At $T = 0$, polymer excursions parallel to the adhesive surface are suppressed, and the configuration of a polymer segment of contour length L_c can be parameterized by tangent angles $\phi(s)$ with respect to the adhesive surface, where s is the arc length ($0 < s < L_c$), see Fig. 1(a). The bending energy is given by $E_b = (\kappa/2)\int_0^{L_c} ds(\partial_s\phi)^2$, where κ is the bending rigidity. The adsorption energy is $E_a = \int_0^{L_c} ds V[z(s)]$, where $z(s)$ is the distance of polymer segments from the adsorbing surface at $z = 0$ and $V(z)$ is a generic square well adhesion potential of small range ℓ with $V(z) = W < 0$ for $z < \ell$, $V(z) = 0$ for $z > \ell$, and $V(z) = \infty$ for $z < 0$ due to the hard wall. For van der Waals forces or screened electrostatic interactions the potential range ℓ is comparable to the polymer thick-

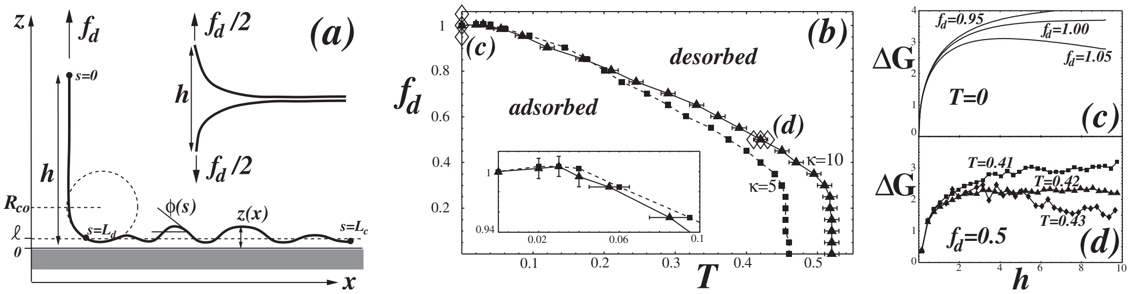

FIG. 1. (a) Force-induced desorption and unzipping of semiflexible polymers (inset); f_d is the desorbing (unzipping) force and h the height (separation) at the end point. (b) Phase diagrams in the plane of desorbing force f_d and temperature T from Monte Carlo simulations for bending rigidities $\kappa = 10$ (triangles) and $\kappa = 5$ (squares), adsorption potential range $\ell = 0.1$, and contour length $L_c = 100$ (all lengths in units of Δs, energies in units of the adhesion energy $|W|\Delta s = 1$; lines are guides to the eye). Inset shows the reentrance region at low temperatures. (c),(d) Free energy landscapes $\Delta G(h)$ as a function of the height h for $\kappa = 10$ and forces and temperatures as indicated by diamonds in the phase diagram (b); (c) at $T = 0$ according to the analytical result, see Eq. (1); (d) for $f_d = 0.5$ from Monte Carlo simulations in agreement with Eqs. (4) and (5). In the desorbed phase $\Delta G(h)$ exhibits an energy barrier.

ness or the Debye-Hückel screening length, respectively. For the discussion at $T = 0$, we consider a contact potential, i.e., the limit of small ℓ. In the absence of a desorbing force the polymer lies flat on the adhesive surface [$\phi(s) = 0$ for all s] gaining an energy $-|W|L_c$. The semiflexible polymer is peeled from the adhesive surface by a localized desorbing force $\mathbf{f}_d$ that is applied in the z direction at the end point $s = 0$. Under the influence of the force, a polymer segment $0 < s < L_d$ desorbs, which costs a potential energy $|W|L_d$. In order to map out the energy landscape of the desorption process, we consider a *constrained* equilibrium and minimize the sum of bending and potential energy of the polymer, $E = |W|(L_d - L_c) + E_b$, under the constraint of a fixed height $h = \int_0^{L_d} ds \sin\phi(s)$ of the polymer end at $s = 0$. Minimizing with respect to L_d gives the transversality condition $\partial_s\phi(L_d) = -(2|W|/\kappa)^{1/2} \equiv 1/R_{\rm co}$ which determines the contact curvature radius $R_{\rm co}$ [21]; the boundary conditions are $\phi(L_d) = 0$ and $\partial_s\phi(0) = 0$ corresponding to a free tangent. Solving the resulting shape equation, we find the scaling form $\Delta E(h) \equiv E(h) - E(0) = (\kappa|W|)^{1/2}\mathcal{F}_E(h/R_{\rm co})$ for the total energy, which has the limits

$$\Delta E(h) \approx \begin{cases} 2^{7/4}3^{-1/2}h^{1/2}\kappa^{1/4}|W|^{3/4} & \text{for } h \ll R_{\rm co} \\ |W|[h + 4(\sqrt{2} - 1)R_{\rm co}] & \text{for } h \gg R_{\rm co} \end{cases}. \quad (1)$$

The result (1) can be corroborated by a scaling argument starting from the estimate $\Delta E(h, L_d) \sim \kappa h^2/L_d^3 + |W|L_d$ of the energy cost to desorb a segment of length L_d. For $h \ll R_{\rm co}$, energy minimization with respect to the desorbed length L_d gives $L_d \sim h^{1/2}\kappa^{1/4}|W|^{-1/4}$ and an energy cost $\propto h^{1/2}$ as in (1). For $h \gg R_{\rm co}$ essentially the whole desorbed length L_d is lifted straight and perpendicular to the substrate except for a curved segment of length $\sim R_{\rm co}$ around the contact point, which leads to $L_d \approx h + \mathcal{O}(R_{\rm co})$ and an energy cost $\propto h$ as in (1).

Including the energy gain for a constant desorbing force f_d, we obtain the energy landscape $\Delta G(h) \equiv \Delta E(h) - f_d h$ at $T = 0$ as a function the height h, see Fig. 1(c). The equilibrium height minimizes $\Delta G(h)$, and we find a first order desorption transition from $h = 0$ to infinite h above the critical force $f_{d,c} = |W|$. For *all* force values $f_d > |W|$, there remains a local minimum at $h = 0$ corresponding to the firmly adsorbed state, which is separated by an *energy barrier* ΔG_b from the desorbed equilibrium state. The energy barrier is given by $\Delta G_b \approx 2^{3/2}\kappa^{1/2}|W|^{3/2}/3f_d$ for all $f_d > |W|$, i.e., it decays as $1/f_d$ and scales with $\kappa^{1/2}$ and, hence, is a consequence of the bending rigidity of the polymer. The scaling behavior of ΔG_b also follows from equating the energy cost $\Delta E(h) \propto h^{1/2}\kappa^{1/4}|W|^{3/4}$ and the gain $f_d h$. Because of the energy barrier, force-induced desorption requires thermal activation or an h-dependent force $f_d(h) = \partial_h\Delta E(h)$, which diverges as $h^{-1/2}$ for small h.

Thermal desorption.—In the absence of a desorbing force ($f_d = 0$), a semiflexible polymer can undergo thermal desorption, which we describe using a model connecting length scales below and above the persistence length $L_p \equiv 2\kappa/T$ ($k_B \equiv 1$) [22]. At the desorption transition, the correlation length $\xi_\parallel$ diverges. For $\xi_\parallel < L_p$, we apply results for a weakly bent *semiflexible* polymer [10], whereas we use standard results for the adsorption of *flexible* Gaussian polymers in combination with an effective adsorption potential for $\xi_\parallel > L_p$. In the latter flexible regime, desorbed segments of typical length $\xi_\parallel$ decay into uncorrelated persistent Kuhn segments of length L_p. The strength of the effective renormalized adsorption potential for these Kuhn segments is given by the free energy of adsorption $f_{W,{\rm SF}}$ of a semiflexible segment. This construction connects the semiflexible and flexible regime. Using this approach [22], we find the critical potential strength for desorption, $W_c \approx -\frac{\sqrt{3}\pi}{2}(T/\ell^{2/3}L_p^{1/3})[1 - \frac{\pi^2}{24}(\ell/L_p)^{2/3}]$, and a free energy of adsorption

$$|f_W| \approx \begin{cases} 3(W - W_c)^2L_p/2T & \text{for } |W - W_c| \ll T/L_p \\ |f_{W,{\rm SF}}| \sim |W - W_c| & \text{for } |W - W_c| \gtrsim T/L_p \end{cases}, \quad (2)$$

which is related to the correlation length by $|f_W| = T/\xi_\parallel$.

The first line in (2) is the free energy of adsorption in the flexible regime; the second line is the free energy of adsorption in the semiflexible regime, which holds for $|f_W| \gtrsim T/L_p$ or outside a window of adhesion strengths of width T/L_p around the critical value W_c.

Phase diagram.—In the presence of thermal fluctuations the free energy of adsorption f_W replaces the bare potential strength W and the free energy per length $g(f_d)$ of a thermally fluctuating, stretched semiflexible polymer replaces the force $-f_d$. For small stretching forces $f_d \ll T/L_p$, the polymer is effectively flexible and entropic elasticity gives $g(f_d) \approx -f_d^2 L_p/6T$, whereas for strong stretching $f_d \gg T/L_p$, we have $g(f_d) \approx -f_d + (2Tf_d/L_p)^{1/2}$, where the square root contribution is typical for semiflexible behavior [23]. The polymer desorbs if the stretching free energy $g(f_d)$ compensates for the free energy cost of desorption, i.e., for $|g(f_d)| > |f_W|$. This gives a first order force-induced desorption transition (similar to DNA unzipping [17,20], where the single strands are flexible polymers), at a critical force

$$f_{d,c} \approx \begin{cases} (6T|f_W|/L_p)^{1/2} & \text{for } |f_W| \ll 2T/L_p \\ |f_W| + (2T|f_W|/L_p)^{1/2} & \text{for } |f_W| \gg 2T/L_p \end{cases} \tag{3}$$

and, thus, the phase boundary of the adsorbed phase in the f_d-$|W|$ or f_d-T plane. The line of first order force-induced desorption transitions ends in the critical point of thermal desorption at zero force.

The results for the phase diagram were confirmed by Monte Carlo (MC) simulations of a discretized semiflexible polymer consisting of $N = L_c/\Delta s$ beads with heights z_i (i.e., $h = z_N$) and $N - 1$ connecting segments of length Δs with unit tangent vectors $\mathbf{t}_i$ using the Hamiltonian $\mathcal{H} = E_b + \sum_{i=1}^{N} \Delta s V(z_i) - f_d h$, where $E_b = (\kappa/2) \times \sum_{i=1}^{N-1} (\mathbf{t}_{i+1} - \mathbf{t}_i)^2/\Delta s$ is the bending energy. The MC simulation uses the Metropolis algorithm with a combination of local displacement, pivot, and reptation moves. The resulting MC phase diagrams in the f_d-T plane are shown in Fig. 1(b). The analytical result (3) correctly describes three main features of the simulation results: (i) A characteristic square-root dependence $f_{d,c} \sim |f_{W,\mathrm{SF}}|^{1/2} \sim |T - T_c|^{1/2}$ close to the thermal desorption transition typical for flexible behavior. (ii) A broad *linear* regime $f_{d,c} \approx |f_W| \sim |T - T_c|$ at lower temperatures, which is absent for flexible polymers and due to the bending rigidity effects. (iii) At low temperatures $T < |W|\ell^{2/3} L_p^{1/3}$, we find $f_{d,c} \sim |W| - T^{4/3}/\ell^{2/3}\kappa^{1/3} + T|W|^{1/2}/\kappa^{1/2}$, which gives a small *reentrant* region of the desorbed phase because thermal fluctuations weaken the adhesion strength less than the pulling force. Such "cold desorption or unzipping" has been reported previously for flexible polymers like DNA [20,24].

Free energy landscape.—The energy landscape of the desorption process can be mapped by calculating the *constrained* free energy $\Delta F(h) = -T \ln[Z(h)/Z(0)]$, where $Z(h)$ is the restricted partition sum over all polymer configurations with a given height h of the end point. The transfer matrix treatment of the weakly bent semiflexible polymer [10,22] gives the constrained free energy

$$\Delta F(h) = -\frac{T}{2} \ln\left(\frac{h}{L_p}\right) + \frac{2^{7/4}}{3^{1/2}} h^{1/2} \kappa^{1/4} |f_W|^{3/4} \tag{4}$$

for the semiflexible regime $|f_W| \gtrsim T/L_p$. This is the exact generalization of the $T = 0$ result (1) for small h to finite temperatures, where the free energy of adsorption of a semiflexible polymer f_W replaces the bare contact potential W and a logarithmic entropic repulsion from the hard wall occurs. For large h, the free energy cost (4) is *always* exceeded by the linear energy gain $-f_d h$, which suggests the absence of a phase transition and a desorption instability even for small forces f_d [9].

However, the weak bending approximation breaks down upon increasing h if typical tangent angles $h/L_d > 1$ become large for $h > R_{\mathrm{co}} \equiv (\kappa/2|f_W|)^{1/2}$. Then the whole desorbed tail of length L_d becomes lifted perpendicular to the substrate except for a curved segment of length $\sim R_{\mathrm{co}}$, i.e., $L_d \approx h + \mathcal{O}(R_{\mathrm{co}})$. In this limit the full free energy $\Delta G(h) = \Delta F(h) - hf_d$ in the presence of the desorbing force can be written as

$$\Delta G(h) \approx h[|f_W| + g(f_d)] + cR_{\mathrm{co}}|f_W|, \tag{5}$$

where c is a numerical constant [$c = 4(\sqrt{2} - 1)$ at $T = 0$, see (1)]. Equation (5) is in accordance with our above free energy criterion $|g(f_d)| = |f_W|$ for the desorption transition.

Therefore, also for $T > 0$, the free energy landscape $\Delta G(h) = \Delta F(h) - hf_d$, as given by (4) for $h \lesssim R_{\mathrm{co}}$ and (5) for $h \gg R_{\mathrm{co}}$, exhibits a *barrier* for $f_d > f_{d,c}$, which arises from the bending rigidity although the microscopic adhesion potential is purely attractive. In the MC simulation, $\Delta G(h)$ can be calculated from the logarithm of the end point distribution function, which clearly confirms the existence of a barrier, see Fig. 1(c). In the semiflexible regime for $|f_W| \gtrsim T/L_p$, we find an energy barrier $\Delta G_b \sim \kappa^{1/2}|f_W|^{3/2}/f_d$ for all forces $f_d > f_{d,c} \approx |f_W|$. The barrier scales with $\kappa^{1/2}$ and decreases as $1/f_d$ starting from $\Delta G_b \sim (\kappa|f_W|)^{1/2}$. The barrier is attained for a height $h \sim \Delta G_b/f_d$, which approaches $h \sim R_{\mathrm{co}}$ for $f_d = |f_W|$. In the semiflexible regime $|f_W| \gtrsim T/L_p$, we have $\Delta G_b \gtrsim T$ and $R_{\mathrm{co}} \lesssim L_p$. Upon entering the flexible regime the barrier becomes smaller than the thermal energy T and can thus be overcome quasispontaneously by thermal activation; the contact radius becomes larger than the Kuhn segment length L_p.

Desorption kinetics in experiments.—The existence of a barrier in the semiflexible regime $|f_W| \gtrsim T/L_p$ has important consequences for single polymer desorption experiments. In equilibrium, the necessary desorption force $f_d(h) = \partial_h \Delta F(h) \sim h^{-1/2}\kappa^{1/4}|f_W|^{3/4}$ *diverges* for small h, before a plateau $f_d = f_{d,c} \approx |f_W|$ is reached at large

h. This is indeed observed in experimental force-distance curves [4–7]. Measurements of the shape of the $h^{-1/2}$ divergence together with the plateau force $f_{d,c}$ allow us to determine the bending rigidity κ and the free energy of adsorption f_W of the semiflexible polymer using the results (3) and (4). If the desorption experiment is performed out of equilibrium at constant desorption force larger than the threshold force, $f_d > f_{d,c}$, the energy barrier ΔG_b has to be overcome by thermal activation with an Arrhenius-type desorption rate $k_d \sim \tau^{-1}e^{-\Delta G_b/T} \sim \tau^{-1}e^{-f_0/f_d}$, where $f_0 \equiv L_p^{1/2}|f_W|^{3/2}/T^{1/2}$ is a characteristic force and τ a microscopic time scale of the polymer dynamics. This has a strong influence on the kinetics of *initial* desorption. The force dependence of $k_d \sim 1/f_d$ is qualitatively different from other thermally activated single molecule processes such as bond dissociation [25]. The probability P of finding the polymer still adsorbed at time t fulfills $dP/dt = -k_d P$. For a constant force f_d this simply gives $P(t) = e^{-k_d t}$. Also for a time-ramped desorption force $f_d(t) = r_d t$ with a sufficiently slow constant loading rate $r_d \ll f_0/\tau$ the dynamics is thermally activated, and we find $t^* \sim (f_0/r_d)/\ln(f_0/r_d\tau)$ and $f_d^* \sim r_d t^*$ for the most frequent time and force for initial desorption, respectively [22]. Because $f_d^* \sim f_0 \gtrsim |f_W|$ initial desorption of a semiflexible polymer requires larger forces than the critical force $f_{d,c} \approx |f_W|$.

Unzipping.—The unzipping of two bound semiflexible polymers by a force $\mathbf{f}_d$ pulling apart the polymer ends [see Fig. 1(a)] can be studied in the same way as force-induced desorption. The component $\mathbf{f}_d \cdot \mathbf{z}$ of the three-dimensional polymer separation vector $\mathbf{z}$ is the analogue of the height coordinate z for desorption. The systems differ in the attractive potential which is a function of the absolute value $|\mathbf{z}|$, $V = V(|\mathbf{z}|)$, for unzipping. Apart from numerical prefactors, our main results (1)–(5) remain unchanged.

For the unzipping (or desorption) of single cytoskeletal filaments or bundles of filaments [12–14] typical persistence lengths are $L_p \sim 100\ \mu$m. Cross-linker-mediated adhesion [26] gives rise to typical potentials strengths of the order of $|f_W| \sim |W| \sim 10^{-2}$ T/nm $\gg T/L_p$ corresponding to cross-linker energies of T and spacings along the filament of the order of 100 nm. This leads to $f_{d,c} \approx |f_W| \sim 4 \times 10^{-2}$ pN, curvature radii $R_{\rm co} \sim 2\ \mu$m, and a typical force scale for the initial unzipping process of $f_0 \sim 2$ pN, much larger than $f_{d,c}$.

Conclusion.—In summary, I found the phase diagram for force-induced desorption of semiflexible polymers and predict the existence of a characteristic energy barrier which is a consequence of the bending rigidity and absent for flexible polymers. The results for the phase diagram and the energy barrier are confirmed by Monte Carlo simulations. The energy barrier gives rise to activated desorption or unzipping kinetics and leads to an enhanced dynamic stability of the bound state of stiff adhesive polymers or fibers under force. This effect plays a role for biological polymers under force, e.g., in DNA, protein, or filament unzipping and desorption as well as for numerous materials science applications ranging from the delamination of thin sheets to the peeling of adhesive hairs, e.g., wet hair [27]. The results can also shed new light on the zipping or adsorption dynamics of semiflexible filaments, which plays an important role in cytoskeletal networks [13,14].

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