Appendix to "Force-induced desorption and unzipping of semiflexible polymers"

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In this Appendix I present details on the theory of thermal desorption of semiflexible polymers and on the desorption kinetics.

Thermal desorption. In the absence of a desorbing force ($f_d = 0$), a semiflexible polymer can undergo thermal desorption, which we want to describe using a model connecting length scales below and above the persistence length $L_p \equiv 2\kappa/T$ ($k_B \equiv 1$). At the desorption transition the correlation length $\xi_\parallel$, which gives the typical length of thermally desorbed segments, diverges. If the length of desorbed segments is comparable or smaller than L_p, i.e., for $\xi_\parallel < L_p$ we apply the theory for the adsorption of a weakly bent *semiflexible* polymer [1], whereas we apply standard results for the adsorption of *flexible* Gaussian polymers [2] in combination with an effective or renormalized adsorption potential for $\xi_\parallel > L_p$. Using this approach we obtain a result for the critical potential strength W_c for thermal desorption and for the free energy of adsorption f_W which describes the full crossover from the semiflexible to the flexible regime.

On length scales comparable or smaller than L_p, the thermally fluctuating semiflexible polymer is only weakly bent and stays oriented, say along the x-axis. The desorption transition can then be described by the one-dimensional distance $z(x)$ of polymer segments from the adsorbing surface $z = 0$, where $0 < x < L$ and $L < L_c$ is the projected polymer length. Bending and adhesion energy of the weakly bent semiflexible polymer give a Hamiltonian

$$\mathcal{H}_{\text{SF}} = \int_0^L dx \left[\frac{\kappa}{2} (\partial_x^2 z)^2 + V(z(x)) \right]. \qquad (1)$$

We consider generic square well adsorption potentials of range ℓ, as they arise from van der Waals forces, screened electrostatic interactions, and crosslinking molecules. In these cases, the potential range ℓ is comparable to the polymer thickness, the Debye-Hückel screening length, and the size of the linker molecule, respectively. For simplicity we neglect a possible orientation dependence in crosslinker–mediated adhesion [1] and consider adhesive square well potentials

$$V(z) = \begin{cases} W & \text{for} \quad z < \ell \\ 0 & \text{for} \quad z > \ell \end{cases} \qquad (2)$$

where $W < 0$ is the bare adhesion strength and $V(z) = \infty$ for $z < 0$ due to the hard wall.

The desorption transition for this Hamiltonian has been studied by transfer matrix techniques in Ref. [1]. The critical potential strength for desorption is

$$W_{c,\text{SF}} = -\frac{\sqrt{3\pi}}{2} \frac{T}{\ell^{2/3} L_p^{1/3}}, \qquad (3)$$

The transfer matrix treatment shows that the free energy difference between adsorbed and free state vanishes as

$$f_{W,\text{SF}} \approx W_{c,\text{SF}} |w_{\text{SF}}| / \ln |w_{\text{SF}}|^{-1} \qquad (4)$$

where $w_{\text{SF}} \equiv (W - W_{c,\text{SF}})/W_{c,\text{SF}}$ is the reduced potential strength. Therefore, the correlation length $\xi_\parallel = T/|f_{W,\text{SF}}| \propto |w_{\text{SF}}|^{-\nu}$ diverges with an exponent $\nu = 1 + \log$.

The weak bending approximation is valid as long as tangent angles are small, i.e., $\langle \phi^2 \rangle \sim \langle (\partial_x z)^2 \rangle \sim \xi_\parallel/L_p \lesssim 1$, which is equivalent to the condition $\xi_\parallel \lesssim L_p$ mentioned above. This condition is fulfilled for $|W - W_{c,\text{SF}}| \gtrsim T/L_p$, i.e., outside a window of adhesion strengths of width T/L_p around the critical value $W_{c,\text{SF}}$.

For $\xi_\parallel \gg L_p$, i.e., for $|W - W_{c,\text{SF}}| \ll T/L_p$, the semiflexible polymer is described as effectively flexible Gaussian polymer with $N = L_c/L_p$ essentially uncorrelated Kuhn segments of length $b = L_p$. Each adsorbed Kuhn segment of length $b \equiv L_p$ is weakly bent and performs small scale fluctuations governed by the Hamiltonian $\mathcal{H}_{\text{SF}}$, which gives rise to an *effective* adsorption potential $V_{\text{eff}}(z)$, which contains entropic contributions from small scale fluctuations. $V_{\text{eff}}(z)$ is also short-ranged and can be assumed to have the same square well form (2) as the bare potential but with the effective binding energy

$$W_{\text{eff}} = f_{W,\text{SF}} \sim W - W_{c,\text{SF}} \qquad (5)$$

given by the free energy of adsorption of each semiflexible Kuhn segment and a potential width $\ell_{\text{eff}} = L_p$ set by the thermal fluctuations $\langle z^2 \rangle \sim b^3/L_p = L_p^2$ of each Kuhn segment. In (5) we neglected the small logarithmic correction in (4).

The critical properties of the actual desorption transition are obtained in the limit of large $\xi_\parallel$ and, thus, given by the critical behaviour of the effective flexible polymer model. The Kuhn segment length $b = L_p$ and the effective adsorption potential $V_{\text{eff}}(z)$ contain all effects from the bending rigidity. The standard transfer matrix approach for Gaussian polymers [2] shows that the critical effective potential for thermal desorption is

$W_{\text{eff},c} = -\frac{\pi^2}{24}\frac{T}{L_p}$. Using (5) this is equivalent to a bare critical potential for desorption

$$
\begin{aligned}
W_c &\approx W_{c,\text{SF}}[1 - \frac{\pi^2}{24}(\ell/L_p)^{2/3}] \\
&\approx -\frac{\sqrt{3\pi}}{2}\frac{T}{\ell^{2/3}L_p^{1/3}}[1 - \frac{\pi^2}{24}(\ell/L_p)^{2/3}]. \quad (6)
\end{aligned}
$$

Because $W_c < W_{c,\text{SF}}$, the polymer indeed desorbs in the flexible regime that describes the large scale behavior. The free energy of adsorption in the effective flexible polymer model is given by

$$
f_W \approx 3W_{\text{eff}}^2 L_p/T \sim 3(W - W_{c,\text{SF}})^2 L_p/2T \quad (7)
$$

The correlation length $\xi_\parallel = T/|f_W| \propto |w|^{-\nu}$, where $w \equiv (W - W_c)/W_c$, diverges with an exponent $\nu = 2$.

The critical properties of the desorption transition at $W = W_c$ are described by the *flexible* polymer model, i.e., thermal desorption is of second order with $\nu = 2$. On the other hand, the transition point $W_c \sim W_{c,\text{SF}}$ and apparent critical properties in the entire region $|W - W_c| \gtrsim T/L_p$ are governed by the *semiflexible* Hamiltonian $\mathcal{H}_{\text{SF}}$ with $\nu = 1 + \log$.

For $\xi_\parallel < L_p$ or $|W - W_c| \gtrsim T/L_p$ the free energy of adsorption $f_W = f_{W,\text{SF}}$ is given by the free energy of adsorption (4) of a semiflexible polymer. For $\xi_\parallel \gg L_p$ or $|W - W_c| \ll T/L_p$, on the other hand, the free energy of adsorption is given by the result (7). Neglecting the small logarithmic corrections in the result (4), we obtain a consistent crossover scenario for the free energy of adsorption, which connecting length scales below and above L_p:

$$
|f_W| \approx \begin{cases} 3(W - W_c)^2 L_p/2T & \text{for } |W - W_c| \ll T/L_p \\ |f_{W,\text{SF}}| \sim |W - W_c| & \text{for } |W - W_c| \gtrsim T/L_p \end{cases}
$$
$$(8)$$

The semiflexible regime is characterized by $|W - W_c| \gtrsim T/L_p$, which is equivalent to $|f_W| \gtrsim T/L_p$ or $\xi_\parallel \lesssim L_p$. The flexible regime is characterized by $|W - W_c| \ll T/L_p$, which is equivalent to $|f_W| \ll T/L_p$ or $\xi_\parallel \gg L_p$.

Constrained free energy for thermal desorption of a semiflexible polymer. The thermal desorption of a weakly bent semiflexible polymer in the regime $|f_W| = T\xi_\parallel \gtrsim T/L_p$ as described by the Hamiltonian $\mathcal{H}_{\text{SF}}$ has been studied by transfer matrix techniques in Ref. [1]. This approach also allows to calculate the restricted partition sum $Z(h)$ over all polymer configurations with a given height h of the end point. In Ref. [1], the scaling form

$$
Z(h) = (h/L_p)^{\theta/2+1/3}\Omega(L_p^{1/2}h/\xi_\parallel^{3/2})e^{L/\xi_\parallel} \quad (9)
$$

for the restricted partition sum with a critical exponent $\theta = -5/3$ characterizing the segment distribution close to the wall has been derived, together with an explicit result for the shape function

$$
\Omega(y) \propto \int_0^\infty d\alpha\, \alpha^{-1/2}e^{-\alpha - 2y/3\alpha} = \sqrt{\pi}e^{-(8y/3)^{1/2}}. \quad (10)
$$

Using (10) in (9) we obtain the constrained free energy

$$
\begin{aligned}
\Delta F(h) &= -T\ln[Z(h)/Z(0)] \\
&= -\frac{T}{2}\ln\left(\frac{h}{L_p}\right) + \frac{2^{7/4}}{3^{1/2}}h^{1/2}\kappa^{1/4}|f_W|^{3/4} \quad (11)
\end{aligned}
$$

of a weakly bent semiflexible polymer.

Desorption kinetics. Here we give more details on the analysis of the thermally activated desorption kinetics in the semiflexible regime $|f_W| \gtrsim T/L_p$. The analysis is based on the time-dependent probability $P(t)$ of finding the polymer still adsorbed at time t. With the Arrhenius-type desorption rate $k_d \sim \tau^{-1}e^{-f_0/f_d}$, where $f_0 \equiv L_p^{1/2}|f_W|^{3/2}/T^{1/2}$, the kinetics of desorption is governed by the differential equation

$$
dP/dt = -k_d P \quad (12)
$$

for the probability $P(t)$. Analogous formulations have been used to describe the rupture of molecular bonds, see [3], where $P(t)$ corresponds to the probability of finding the bond intact at time t.

For a time-constant force $f_d > f_{d,c}$, eq. (12) simply gives $P(t) = e^{-k_d t}$. Also for a time-ramped force $f_d(t) = r_d t$, which increases from the critical force with a constant and slow loading rate $r_d \ll f_0/\tau$ the desorption kinetics is dominated by thermal activation, and we find $P(t) = \exp(-\int_0^t d\tilde{t}k_d(\tilde{t}))$. The most probable desorption time t^* maximizes the probability $P(t)k_d(t)$ of desorption at time t, i.e., $\frac{d}{dt}|_{t^*}(P(t)k_d(t)) = 0$. Using (12) this condition finally leads to the self-consistent equation

$$
\tau e^{f_0/r_d t^*} = r_d t^{*2}/f_0 \quad (13)
$$

for t^*. The desorption process is thermally activated for $r_d < f_0/t^*$. In this regime we find

$$
t^* \sim (f_0/r_d)/\ln(f_0/r_d\tau) \quad (14)
$$

and the condition for thermally activated behavior is indeed fulfilled for a slow loading rate $r_d \ll f_0/\tau$. In the opposite limit of fast loading rates $r_d \gg f_0/\tau$, the barrier becomes smaller than T *before* the polymer starts to desorb and the process is no longer thermally activated.

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[3] E. Evans and K. Ritchie, Biophys. J. **72**, 1541 (1997).