

Supplemental Material for “Controlling adsorption of semiflexible polymers on planar and curved substrates”

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(i) Discussion of different interpolation functions $I(x)$. (ii) Analytical transfer matrix calculation for planar substrate in the stiff limit, which gives the critical potential strength for a square-well potential in the limit of small potential range. (iii) Details of the cumulant method and finite size scaling procedure used to obtain the critical potential strength in Monte-Carlo simulations. (iv) Results for the critical correlation length exponent ν of the adsorption transition for a planar substrate. (v) Additional simulation snapshots in the desorbed state.

I. ADSORPTION TO A PLANAR SUBSTRATE

A. Interpolation function of Deng *et al.*

In Ref. 1, Deng *et al.* also use an interpolation function to describe the crossover of the critical potential strength g_c for adsorption between the stiff and flexible limit. They measure the critical potential strength in units of $k_B T/2L_p$ rather than $k_B T/\ell$ as in (11); the critical potential strength does not exhibit a maximum if measured in these units. In Ref. 1, an interpolation $g_c(2L_p/k_B T) = \tilde{I}(2L_p/\ell)$ with a scaling function

$$\tilde{I}_{\text{Deng}}(x) = \frac{(c_F/2)x^2}{[C_2 x^2 + C_1 x + 1]^{2/3}}$$

is used with two fit parameters $C_1 \simeq 0.94$ and $C_2 \simeq 0.38$, which are determined from numerical transfer matrix calculations.

Comparing the two scaling forms, we find the relation

$$\tilde{I}(x) = xI(x/2), \quad I(x) = \tilde{I}(2x)/2x$$

Consequently the scaling function proposed in Ref. 1 corresponds to

$$I_{\text{Deng}}(x) = \frac{c_F x}{[4C_2 x^2 + 2C_1 x + 1]^{2/3}} \quad (\text{S1})$$

This scaling function does not obey the constraints (13) and (14) listed in the main text:

- (i) The numerical prefactor c_{SF} has been treated as a fit parameter because an analytical result was not available. Using their fit results, we find $c_{SF} = 2^{-4/3} c_F C_2^{-2/3} \simeq 0.619$, which is close but smaller

than our analytical result $c_{SF} \simeq 0.929$. The reason is a different determination of the critical potential strength from simulations. Deng *et al.* use an extrapolation of adsorbed fraction, which is the first cumulant of the adsorption energy, to zero, whereas we mainly use the third cumulant.

- (ii) The constraint (14) regarding the correct next to leading order asymptotics in the stiff limit has not been applied. The scaling function (S1) has the asymptotics $I_{\text{Deng}}(x) = (c_F/2C_2^{2/3})x^{-1/3} + \mathcal{O}(x^{-4/3})$ for $x \gg 1$, which differs from the analytical prediction (14).

B. Alternative interpolation function $I(x)$.

In this appendix, we use the scaling argument for the deflection length λ and $g_c \sim k_B T/\lambda$ to motivate a functional form of the interpolation function $I(x)$. The argument is based on a result for the thermal displacement $\langle z^2 \rangle(L) \equiv \langle (z(L) - z(0))^2 \rangle$ of a free worm-like chain in the direction perpendicular to the average preferred orientation in x -direction.

For a free worm-like chain in two dimensions ($D = 2$), the thermal displacement $\langle z^2 \rangle(L)$ can be calculated analytically. In $D = 2$, we can parametrize the configuration by a single angle $\theta(s)$ by $\mathbf{t}(s) = \partial_s \mathbf{r}(s) = (\cos \theta(s), \sin \theta(s))$. The angular correlations are

$$\langle (\theta(s) - \theta(s'))^2 \rangle = \frac{k_B T}{\kappa} |s - s'| = \frac{2|s - s'|}{L_{p,D}}$$

and

$$\langle \theta(s)^2 \rangle = d_1 L/L_{p,D}$$

with a numerical constant d_1 .

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The angular correlations can be used to calculate

$$\begin{aligned}
\langle (z(L) - z(0))^2 \rangle &= \int_0^L ds_1 \int_0^L ds_2 \langle \sin \theta(s_1) \sin \theta(s_2) \rangle \\
&= \int_0^L ds_1 \int_0^L ds_2 \frac{1}{2} \left(e^{-\frac{1}{2} \langle (\theta(s_1) - \theta(s_2))^2 \rangle} - e^{-\frac{1}{2} \langle (\theta(s_1) + \theta(s_2))^2 \rangle} \right) \\
&= \int_0^L ds_1 \int_0^L ds_2 \frac{1}{2} \left(e^{-\frac{1}{2} \langle (\theta(s_1) - \theta(s_2))^2 \rangle} - e^{-\langle \theta^2(s_1) \rangle - \langle \theta^2(s_2) \rangle + \frac{1}{2} \langle (\theta(s_1) - \theta(s_2))^2 \rangle} \right) \\
&= \int_0^L ds_1 \int_0^{s_1} ds_2 \left(e^{-(s_1 - s_2)/L_{p,D}} - e^{-2d_1 L/L_{p,D}} e^{(s_1 - s_2)/L_{p,D}} \right) \\
&= L_{p,D}^2 \left(\frac{L}{L_{p,D}} - 1 + e^{-L/L_{p,D}} \right) - e^{-2d_1 L/L_{p,D}} L_{p,D}^2 \left(-\frac{L}{L_{p,D}} - 1 + e^{L/L_{p,D}} \right) \\
&\equiv L_{p,D}^2 f_{d_1}(L/L_{p,D})
\end{aligned}$$

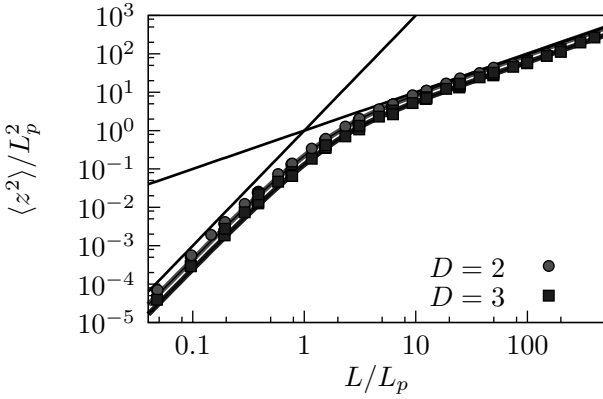


FIG. S1. MC data for $\langle z^2 \rangle(L)/L_p^2$ as a function of L/L_p for a free worm-like chain in $D = 3$ and $D = 2$ dimensions confirms the scaling form $\langle z^2 \rangle(L)/L_p^2 = c f_{d_1}(L/L_p)$, see eq. (S2), with $d_1 = 0.76 \pm 0.08$ and a prefactor $d_2 = 0.61 \pm 0.01$ in three and $d_2 = 0.94 \pm 0.01$, $d_1 = 0.84 \pm 0.09$ in two dimensions (for $L/b_0 = 50, 100, 200, 300, 400$ and $L_p/b_0 = 2, 4, 8, \dots, 1024$). We fix the first tangent to have a well-defined z -direction.

Although this calculation is difficult to adapt to three spatial dimensions, we expect a similar behavior for $D = 3$ with an eventually different numerical prefactor d_2 :

$$\frac{\langle z^2 \rangle(L)}{L_{p,D}^2} = d_2 f_{d_1}(L/L_{p,D}). \quad (\text{S2})$$

Because of $\langle z^2 \rangle(L) = \langle (\mathbf{r}(L) - \mathbf{r}(0))^2 \rangle / D$ for a free worm-like chain in the flexible limit $L \gg L_{p,D}$, we expect $d_2 = 2/D$. Simulation results for a free SHC in $D = 3$, which we present in Fig. S1, confirm the scaling form (S2) with $d_1 = 0.76 \pm 0.08$ and a prefactor $d_2 = 0.61 \pm 0.01$ close to the expectation $d_2 = 2/3$. For the results in $D = 2$ we get $d_2 = 0.94 \pm 0.01$, which is close to $d_2 = 1$, and $d_1 = 0.84 \pm 0.09$. Because the scaling form is very insensitive to variation of d_2 for $L/L_{p,D} \gg 1$, we determine the parameters d_1 and d_2 only with values $L/L_{p,D} \leq 10$.

Therefore, the inverse function $f_{d_1}^{-1}(x)$ can be used

to solve the condition $\langle z^2 \rangle(\lambda)/L_{p,D}^2 = d_2 f_{d_1}(\lambda/L_{p,D}) = \ell^2/L_{p,D}^2$ for the deflection length λ . This suggests a critical potential strength $g_c = (k_B T/\ell) I(L_{p,D}/\ell)$ with a scaling function

$$I(x) = \frac{1}{x f_{d_1}^{-1}(x^{-2}/d_2)} \quad (\text{S3})$$

with only two free parameters d_1 and d_2 . In the flexible limit $x = \lambda/L_{p,D} \gg 1$, we use $f_{d_1}(x) \approx x$, in the stiff limit $x = \lambda/L_{p,D} \ll 1$, we have $f_{d_1}(x) \approx (d_1 - 1/3)x^3$. The choices $d_2 = c_F$ and $d_1 = (c_{SF}/c_F)^3 + 1/3$ will reproduce the known flexible and stiff limits. In contrast to the interpolation function from eq. (15), the function $I(x)$ in eq. (S3) contains only two free parameters. Therefore, the maximum of interpolation function $I(x)$ is already determined by d_1 and d_2 .

We have determined the fit parameters d_1 and d_2 from the MC simulation results for the critical potential strength both by the cumulant method and finite size scaling and both in $D = 2$ and $D = 3$. The theoretical expectation $d_2/c_F = 1$ and $\frac{d_2}{c_{SF}^3} (d_1 - \frac{1}{3}) = 1$ for the parameters d_1 and d_2 agrees reasonably well with the simulation results.

In addition, the scaling argument leading to eq. (S3) strongly suggests a constraint on the functional form of the scaling function $I(x)$ for the critical potential strength g_c : The asymptotics for the stiff limit shows that the scaling function $f_{d_1}(x)$ has a series expansion $f_{d_1}(x) = x^3 g(x)$ with some analytical function $g(x)$ with $g(0) \neq 0$. Therefore, the inverse function should have a functional form $f_{d_1}^{-1}(y) = y^{1/3} \tilde{g}(y^{1/3})$ with another analytical function $\tilde{g}(x)$ with $\tilde{g}(0) \neq 0$. It follows from eq. (S3) that the scaling function $I(x)$ should have an asymptotic form

$$I(x) \sim \frac{x^{-1/3}}{\tilde{g}(\text{const } x^{-2/3})} \quad \text{for } x \gg 1. \quad (\text{S4})$$

Our first choice $I(x) \sim c_1 x^{-1/3} (c_2 + c_3 x^{-2/3} + x^{-4/3})^{-1}$,

data set	$\frac{d_2}{c_{SF}}(d_1 - \frac{1}{3})$	d_2/c_F	$\max(I)$
theory(D=3)	1	1	1.84
cumulant	1.21±0.04	0.82±0.01	2.47
finite size	1.0±0.1	0.54±0.02	3.36
theory(D=2)	1	1	1.26
cumulant	1.5±0.1	0.60±0.02	1.24
finite size	1.19±0.07	0.35±0.01	1.92

TABLE I. Simulation results for the fit parameters d_1 and d_2 for the interpolation function $I(x)$ from eq. (S3) in comparison with theoretical expectations. The maximum value of the resulting interpolation function is given for comparison. All fits for the cumulant method are performed for MC data from simulations with $N = 200$, $\ell = 2b_0$, $k = 1000 k_B T/b_0^2$. For the analysis of simulation data we use the cumulant method or finite size scaling as explained in the text.

see eq. (15), also fulfills this constraint, whereas the scaling function used in Ref. 1 does not meet this constraint.

C. Analytical transfer matrix calculation in the semiflexible limit

Using the transfer matrix method in the weakly bent or stiff limit $L_p \gg \ell$ we will give an analytical derivation of the critical adsorption strength for weakly bent semiflexible polymers for a planar surface and a short-range adsorption potential, i.e., determine the numerical prefactor c_{SF} in (8) analytically.

In the following we measure all length scales in Kuhn lengths $2L_p = 2\kappa/k_B T$ and all energies in $k_B T$, i.e., we replace

$$z \rightarrow \frac{z}{2L_p}, \ell \rightarrow \frac{\ell}{2L_p}, L \rightarrow \frac{L}{2L_p}, g \rightarrow \frac{2L_p}{k_B T} g. \quad (\text{S5})$$

In the stiff limit we have $\ell \ll 1$ in rescaled units. We consider the restricted partition sum $Z(z, v, z_0, v_0, L)$ of a semiflexible polymer of length L with initial point $z(0) = z_0$, initial tangent $\partial_x z(0) = v_0$, end point $z(L) = z$, and end tangent $\partial_x z(L) = v$ in the Monge representation (4) appropriate for a weakly bent polymer. The restricted partition sum $Z(z, v, z_0, v_0, L)$ fulfills a transfer matrix equation of the Klein-Kramers type²

$$\partial_L Z = (-v\partial_z + \partial_v^2 - V(z)) Z \quad (\text{S6})$$

with boundary condition $Z(z, v, z_0, v_0, 0) = \delta(z - z_0)\delta(v - v_0)$ at $L = 0$.

For an adsorbed polymer we make the Ansatz $Z(x, v, z_0, v_0, L) \sim Z_E(z, v)e^{-EL}$ where $E = \Delta f < 0$ is the adsorption free energy per length of the polymer, i.e., the free energy difference of the adsorbed state as compared to the free state ($V = 0$). We approach the desorption transition for $E \nearrow 0$. The “stationary” restricted partition function $Z_E(z, v)$ (which we normalize according to $\int dz \int dv Z_E(z, v) Z_E(z, -v) = 1$) fulfills^{3,4}

$$-EZ_E = (-v\partial_z + \partial_v^2 - V(z)) Z_E. \quad (\text{S7})$$

In general we obtain a complete spectrum of solutions for energy eigenvalues E_n with a ground state energy E_0 . The solution $Z(z, v, z_0, v_0, L)$ satisfying the boundary conditions at $L = 0$ is obtained by summing over all solutions, $Z(z, v, z_0, v_0, L) = \sum_n Z_{E_n}(z, v) Z_{E_n}(z_0, -v_0) e^{-E_n L}$. On length scales $L \gg \xi = 1/|E_0|$ exceeding the correlation length ξ of the adsorption transition, the ground state dominates and

$$Z(z, v, z_0, v_0, L) \approx Z_{E_0}(z, v) Z_{E_0}(z_0, -v_0) e^{-E_0 L}. \quad (\text{S8})$$

The ground state partition function $Z_{E_0}(z, v)$ contains the information about the segment distribution $c(z, v) \sim Z_{E_0}(z, v) Z_{E_0}(z, -v)$ of a polymer segment in the adsorbed state. The ground state energy E_0 determines the free energy of adsorption $\Delta f = E_0 < 0$ and the correlation length of the adsorption transition via $\xi = 1/|E_0|$. The condition $E_0 = 0$ determines the critical potential strength g_c for adsorption. The partition function $Z_0(z, v)$ at $E_0 = 0$ gives the critical segment distribution. Our main aim will be to determine g_c from the condition $E_0 = 0$ in the following. Scaling properties of $Z_{E_0}(z, v)$ and $Z(z, v, z_0, v_0, L)$ have already been discussed in Refs.^{5,6}.

In order to calculate the ground state energy E (we leave out to subscript “0” in the following) and the corresponding “stationary” restricted partition function $Z_E(z, v)$, we first consider the region $z > \ell$ outside the potential range, where $V(z) = 0$ and we can separate the z -dependence for the adsorbed state using $Z_E = e^{-\alpha z} \Psi_{\alpha, E}(v)$, because the operators ∂_z and $v\alpha + \partial_v^2$ commute. The function $\Psi_{\alpha, E}(v)$ satisfies

$$(\alpha v + \partial_v^2) \Psi_{\alpha, E} = -E \Psi_{\alpha, E},$$

(analogous to the Schrödinger equation of a quantum particle in an electric field α), which gives

$$\Psi_{\alpha, E}(v) = \alpha^{-1/6} \text{Ai} \left(- \left(v\alpha^{1/3} + E\alpha^{-2/3} \right) \right),$$

where $\text{Ai}(x)$ is the Airy function⁷. The ground state solution for $z > \ell$ has to be a linear combination of the eigenfunctions of ∂_z and $\alpha v + \partial_v^2$

$$Z_E(z, v) = \int_0^\infty d\alpha A_E(\alpha) e^{-\alpha z} \Psi_{\alpha, E}(v). \quad (\text{S9})$$

with a coefficient function $A_E(\alpha)$.

The coefficient function has to be determined by a family of matching and boundary conditions at the potential well and the wall, that is at $z = \ell$ and $z = 0$. In the limit of a small potential depth we approximate the square-well adsorbing potential $V_a(z)$ by a delta-function in the middle of the square-well, $V_a(z) = -gl\delta(z - \ell/2)$, with the same integrated potential strength $\int_0^\ell V_a(z) = -gl$ (shaded area in Fig. 2). This approximation is valid in the stiff limit $\ell \rightarrow 0$. Integrating the stationary transfer matrix equation (S7) over z from 0 to ℓ and neglecting the terms of higher order in ℓ we get matching conditions

$$v(Z_E(\ell, v) - Z_E(0, v)) = gl Z_E(\ell/2, v) \quad (\text{S10})$$

for each v . We also have to obey boundary conditions $Z_E(0, v) = 0$ for all $v > 0$: It is not possible that the last tangent is starting at the wall at $z = 0$ and pointing away ($v > 0$) because continuity of tangents would lead to configurations crossing the wall.

1. Critical potential strength

In order to determine the coefficient function $A_E(\tilde{\alpha})$ we make use of a set⁸ of functions $\Phi_{\alpha, E}$, which are biorthogonal to $\Psi_{\alpha, E}(z, v)$

$$\int_0^\infty dv v \Psi_{\alpha, E}(v) \Phi_{\tilde{\alpha}, E}(v) = \delta(\alpha - \tilde{\alpha}). \quad (\text{S11})$$

on the half-space $v > 0$. We use the representation (S9) in the matching condition (S10) and apply $\int_0^\infty dv \dots \Phi_{\tilde{\alpha}, E}(v)$ on both sides of the matching condition to make use of the biorthogonality (S11). Assuming a small potential width we approximate $\exp(\tilde{\alpha}\ell) \approx 1$ and obtain a self-consistent integral equation for the coefficient function $A_E(\tilde{\alpha})$

$$A_E(\tilde{\alpha}) = g\ell \int_0^\infty dv \int_0^\infty d\alpha A_E(\alpha) e^{-\ell\alpha/2} \times \Psi_{\alpha, E}(v) \Phi_{\tilde{\alpha}, E}(v).$$

Investigating this integral equation for $E \approx 0$ in the vicinity of the adsorption transition will allow us to (i) determine $A_E(\alpha)$ and thus the polymer segment distribution and (ii) to find the critical potential strength g_c at the transition $E = 0$.

We substitute $\alpha = 2\beta/\ell$ and $v = w(\ell/2)^{1/3}$, which implies $\Psi_{\alpha, E}(v) = (\ell/2)^{1/6} \Psi_{\beta, E(\ell/2)^{2/3}}(w)$, and obtain

$$A_E(\tilde{\alpha}) = g\ell \left(\frac{\ell}{2}\right)^{-\frac{1}{2}} \int_0^\infty dw \int_0^\beta d\beta e^{-\beta} \times \Psi_{\beta, E(\ell/2)^{2/3}}(w) \Phi_{\tilde{\alpha}, E} \left(w(\ell/2)^{1/3}\right) A_E(2\beta/\ell). \quad (\text{S12})$$

In principle, this integral equation can be solved by iteration. We start with $A_E(\alpha) \approx A_E$, which is assumed to be *independent* of α . Iterating this equation once for $E \approx 0$ close to the transition and in the stiff limit $\ell \ll 1$, we find that the resulting first iteration for $A_E(\alpha)$ is indeed only weakly dependent on α for $E \approx 0$ and remains *independent* of α exactly at the transition $E = 0$. Therefore, the first iteration already gives the correct scaling behavior of $A_E(\alpha)$ and allows to determine the critical potential strength g_c exactly for $E = 0$. For constant A_E and $E(\ell/2)^{2/3} \approx 0$, we can perform the β -integration to

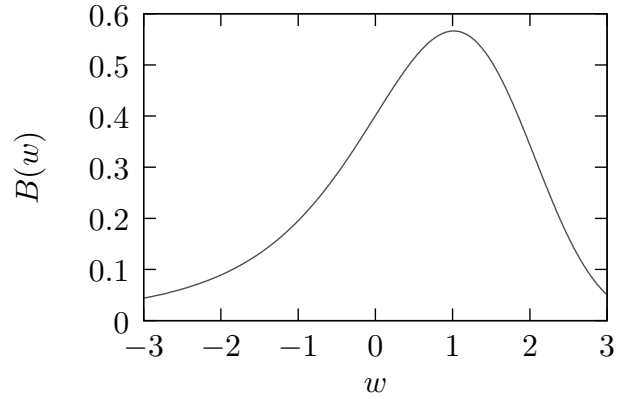


FIG. S2. Function $B(w)$, see eq. (S13) with a maximum at $w \simeq 1.01$.

obtain

$$B(w) \equiv \int_0^\beta d\beta e^{-\beta} \Psi_{\beta, 0}(w) = 2^{1/3} 3^{-2/3} \frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{1}{3})} M_{\frac{5}{6}, \frac{2}{3}} \left(-\frac{w^3}{9}\right) + 2^{-4/3} 3^{-5/6} \frac{\Gamma(\frac{1}{3})}{\Gamma(\frac{1}{2})} w M_{\frac{7}{6}, \frac{4}{3}} \left(-\frac{w^3}{9}\right), \quad (\text{S13})$$

where $M_{a,b}(x)$ is Kummer's confluent hypergeometric function of the first kind⁷, and eq. (S12) becomes

$$A_E(\tilde{\alpha}) = g\ell \left(\frac{\ell}{2}\right)^{-1/2} \int_0^\infty dw B(w) \times \Phi_{\tilde{\alpha}, E} \left(w(\ell/2)^{1/3}\right) A_E \quad (\text{S14})$$

The α -dependence of the coefficient function A_E in eq. (S14) stems from the biorthogonal function, and we find

$$A_E(\alpha) = \tilde{\mathcal{N}}_{E, \ell} \int_0^\infty dw B(w) \Phi_{\alpha, E} \left(w(\ell/2)^{1/3}\right) \quad (\text{S15})$$

with a normalization factor $\tilde{\mathcal{N}}_{E, \ell}$, which is independent of α but can depend on E and ℓ in general.

Because $B(w)$ decreases exponentially for $w \gg 1$, see Fig. S2, and $\ell \ll 1$ in the stiff limit, we can use an approximation for small arguments,

$$\Phi_{\alpha, E} \left(w(\ell/2)^{1/3}\right) \approx \frac{\sqrt{3w}}{\pi} \left(\frac{\ell}{2}\right)^{1/6} e^{-\frac{2}{3}(-E)^{3/2}/\alpha}. \quad (\text{S16})$$

This leads to

$$A_E(\alpha) \approx \mathcal{N}_\ell \exp \left(-\frac{2}{3} \frac{(-E)^{3/2}}{\alpha}\right) \quad (\text{S17})$$

in the stiff limit $\ell \ll 1$ with a modified normalization factor \mathcal{N}_ℓ . Using this result for $A_E(\alpha)$, we find that the normalization factor $\mathcal{N}_\ell \propto \ell^{-1/3}$ is independent on E . The

coefficient function $A_E(\alpha)$ becomes indeed independent of α for $E \approx 0$, i.e., close to the transition. This justifies our initial assumption of a *constant* coefficient function $A_E(\alpha) \approx A_E(0)$. Therefore, the first iteration already provides a self-consistent solution of equation (S12) in the limits of interest.

In order to obtain the critical potential strength g_c we set $E = 0$ in (S14) and use $\int_0^\infty dw B(w)w^{1/2} = 2^{1/3}3^{-1/6}\pi/\Gamma(1/3)$ to find

$$\begin{aligned} \frac{1}{g_c \ell} &= \frac{\sqrt{3}}{\pi} \left(\frac{\ell}{2}\right)^{-1/3} \left(\int_0^\infty dw B(w)w^{1/2}\right) \\ &= \frac{2^{2/3}3^{1/3}}{\Gamma(1/3)} \ell^{-1/3} \end{aligned} \quad (\text{S18})$$

In original unrescaled units, see eq. (S5), this corresponds to a critical potential strength

$$g_c = 2^{-1}3^{-1/3}\Gamma(1/3) \frac{k_B T}{\ell} \left(\frac{L_p}{\ell}\right)^{-1/3} \quad (\text{S19})$$

The scaling behavior of g_c agrees with the result (8) from the scaling argument and we quantify the numerical prefactor in (8) to be $c_{SF} = 2^{-1}3^{-1/3}\Gamma(1/3) \simeq 0.929$.

2. Critical exponent ν

The exponent ν characterizes the critical behavior of the ground state energy $|E| \sim |g - g_c|^\nu$ as a function of $g - g_c$ close to the adsorption transition at $E = 0$. Because of the relations $|\Delta f| = |E| = 1/\xi$, the exponent ν characterizes both the critical behavior of the correlation length ξ and of the free energy of adsorption Δf (i.e., hyperscaling holds). For $g > g_c$, the correlation length ξ of the adsorption transition is defined by the distribution of loops lengths, which decays exponentially for large loop lengths with a characteristic decay length given by the correlation length ξ .

Because the exponent ν characterizes the critical free energy behavior, it also determines the order of the adsorption transition: For $\nu > 1$ the transition is continuous, whereas it is a first order transition for $\nu < 1$. It is a remarkable feature of the polymer adsorption transition that a correlation length $\xi = 1/|E|$, which describes the typical length scale of loops, can always be defined and diverges at the transition, even if the transition is of first order.

Using the result (S15) for $A_E(\alpha)$ in the self-consistent equation (S12), we obtain the relation $g = g(E)$ in the form

$$\frac{1}{g\ell} \approx \frac{1}{\tilde{N}_\ell} \int dv Z_E(\ell, v) \quad (\text{S20})$$

Expanding about $E \approx 0$ gives the exponent ν . A leading $|E|$ -dependence $Z_E(\ell, v) - Z_0(\ell, v) \sim |E|^{3/2}$ has been obtained in Ref. 8 and suggests $\int dv (Z_E(\ell, v) - Z_0(\ell, v)) \sim$

$|E|$, corresponding to $\nu = 1$. Thus, the transfer matrix approach in the approximation of a weakly bent semiflexible polymer gives⁵ $\nu = \nu_{SF} = 1$ for purely position-dependent adsorption potentials as we use here. This suggests that the adsorption transition is first order or second order with a weak logarithmic correction^{5,6}.

3. Corrections from Crossover to an effective flexible polymer model

The transfer matrix calculation in the approximation of a weakly bent polymer is, strictly speaking, only valid in the stiff limit $L_p \rightarrow \infty$. Corrections start to arise if the unrescaled correlation length ξ exceeds the persistence length⁹ L_p : Because ξ specifies the typical length of an unbound desorbed loop of the polymer, loops start to loose orientation and to develop overhangs if $\xi > L_p$ or $\xi = 1/|E| > 2$ in rescaled units (S5). This happens for potential strengths close to the critical value $g_c = g_{c,SF} = c_{SF}(k_B T/\ell)(L_p/\ell)^{-1/3}$ in the semiflexible limit as given by eq. (S19) or eq. (8) in the main text (in unrescaled units), where the correlations length ξ starts to increase and the transfer matrix ground state energy E becomes small according to $|E| \sim |g - g_c|^\nu$ with $\nu = \nu_{SF} = 1$. The condition $|E| < 1/2$ corresponds to $|g - g_c| < 1/2$ (or $|g - g_c| < k_B T/L_p$ in unrescaled units).

Because $g_c \sim \ell^{-2/3}$ (or $g_c \sim (k_B T/L_p)(L_p/\ell)^{2/3}$ in unrescaled units, see eq. (S19)), corrections will always dominate if $\ell \gg 1$ such that $|g - g_c| < g_c \ll 1/2$ for all $g < g_c$. In this regime the weak bending approximation breaks down completely. The regime $\ell \gg 1$ corresponds to $\ell \gg L_p$ in unrescaled units, which is the flexible limit.

Corrections to the weak bending results also arise in the stiff limit $\ell \ll 1$ or $\ell \ll L_p$ in unrescaled units. In the stiff limit corrections arise only in a small interval $|g - g_{c,SF}| < k_B T/L_p \ll g_{c,SF}$ around $g_{c,SF}$. If $|g - g_{c,SF}| < k_B T/L_p$ we have to use an effective flexible polymer model with a Kuhn length $b_K = 2L_p$ and an effective adsorption potential per length $g_{\text{eff}} \sim |\Delta f| = |E| \sim g - g_{c,SF}$, which derives from the free energy exponent $\nu = \nu_{SF} = 1$ in the weak bending approximation, and an effective potential range $\ell_{\text{eff}} \sim \langle z^2 \rangle^{1/2}(\xi) \sim \xi^3/L_p \sim L_p$.

This effective flexible model determines the actual free energy exponent⁶ $\nu_F = 2$. Close to the transition, where $\xi > L_p$ or $|g - g_{c,SF}| < k_B T/L_p$, we expect a crossover from an apparent exponent $\nu_{SF} = 1$ to the actual exponent $\nu = \nu_F = 2$ for a flexible polymer, and the adsorption transition becomes continuous. However, in a system of finite size L , this crossover should only become apparent if $L > L_p$ such that a hierarchy of length scales $L > \xi > L_p$ is possible. Otherwise, $\xi > L_p$ also implies $\xi > L$, and finite size effects mask the crossover.

The crossover to an effective flexible behavior also leads to a shift of the critical potential strength. For the effective flexible polymer the critical potential strength for adsorption is given by $g_{c,\text{eff}} = c_F \frac{k_B T L_p}{\ell_{\text{eff}}^2}$, cf. eq. (10) in

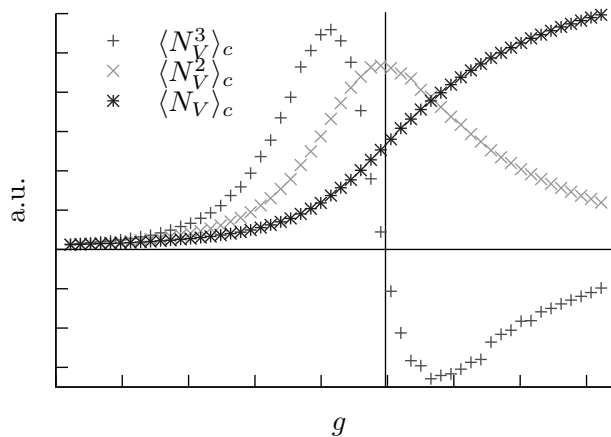


FIG. S3. Typical shape of the first three cumulants of the order parameter N_V , the number of beads of the SHC within the potential range. We locate the adsorption transition by the criterion $\langle N_V^3 \rangle_c = 0$ in simulations.

the main text. The actual critical potential strength g_c is given by the condition $g_c - g_{c,SF} = g_{c,\text{eff}}$ or

$$g_c = g_{c,SF} + c_F \frac{k_B T}{L_p}, \quad (\text{S21})$$

which is slightly higher than the stiff limit result $g_c = g_{c,SF}$. Equation (S21) shows that the leading corrections to the critical potential strength (11) in the stiff limit are of the form $I(x) \approx c_{SF} x^{-1/3} + \mathcal{O}(x^{-1})$, which is exactly the third constraint (14).

II. DETERMINATION OF CRITICAL POTENTIAL STRENGTH IN SIMULATIONS

In order to determine the critical potential strength in simulations we use two methods – a cumulant method and finite size scaling – both of which are explained in detail in this section.

A. Third cumulant method

An effective method to determine the critical potential strength uses the fact that the derivative of the free energy density with respect to the potential strength g gives the mean fraction of polymer length in the square-well potential, which provides an order parameter for the adsorption transition. For the discrete SHC, we have $\partial_g f = \langle N_V \rangle / N$, where N_V is the number of beads of the SHC within the potential range $0 < z < \ell$. Because of the crossover to an effective flexible behavior close to the adsorption transition, we expect a continuous adsorption transition and the second cumulant of the order parameter, i.e., the second derivative $\partial_g^2 f = \langle (N_V - \langle N_V \rangle)^2 \rangle = \langle N_V^2 \rangle_c$ of the free energy should diverge. Because of finite

size effects we find a maximum rather than a divergence in the simulations, which results in a vanishing third cumulant $\partial_g^3 f = \langle N_V^3 \rangle_c = 0$ at the transition, as shown in Fig. S3. Therefore, we can use the vanishing third cumulant to locate the adsorption transition in simulations. In order to find the zero of the third cumulant we interpolate between the first negative and last positive value to determine the critical potential strength. We use this criterion both for the planar and for curved geometries to locate the adsorption transition.

B. Finite size scaling procedure

Finite size scaling of the specific heat allows to determine the critical potential strength g_c and to calculate the critical exponent ν for the correlation length and the free energy. We apply this method to analyze the simulation data for the planar substrate.

To systematically find the best parameter set (ν, g_c) , we calculate a quantity $S(\nu, g_c)$ which measures the squared differences from one specific heat data set f to the interpolated curves \tilde{f} of another set for different length¹⁰ L , as shown in Fig. S4. As contour lengths we use $L/b_0 = 50, 100, 150, 200, 300, 400, 600$ and 800 . To be able to compare different parameter sets (ν, g_c) we take only the relative differences.

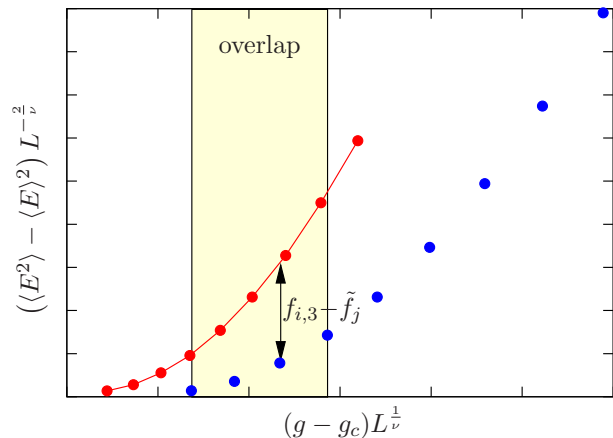


FIG. S4. Example for the overlap region of two data sets for $L_p = 2b_0$ and $\ell = b_0$ for two different lengths $L = 800 b_0$ and $L = 400 b_0$. In this example we have $N_{\text{over}} = 4$ and use $g_c \ell / k_B T = 0.3$ and $\nu = 1.4$.

For this analysis only a limited number N_{over} of data points in the overlapping region can be used. Our best estimate for (ν, g_c) is the parameter set that minimizes the overall error

$$S(\nu, g_c) = \frac{1}{N_{\text{over}}} \sum_i \sum_{j \neq i} \sum_{k=1}^{N_{\text{over}}} \left(1 - \frac{\tilde{f}_j}{f_{i,k}} \right)^2$$

The determination of ν is quite difficult because the minimum is often rather shallow as shown in the example in

Fig. S5.

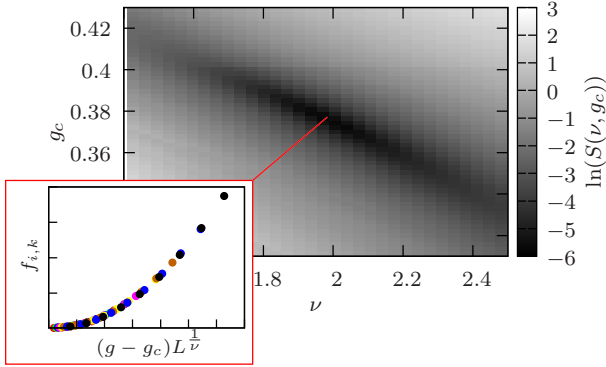


FIG. S5. Logarithmic overall error $\ln(S(\nu, g_c))$ as a function of parameters $g_c/k_B T$ and ν . Inset: Scaling function $f_{i,k}$ for the optimal choices $\nu_{\min} = 1.99$ and $g_{c,\min}/k_B T = 0.37$. Analysis for MC data for parameters $L_p = 2b_0$, $k = 100k_B T/b_0^2$ and $\ell = b_0$.

A simple approach to estimate the error in this procedure is given by¹⁰

$$\Delta g_c = \eta g_{c,\min} \left(2 \ln \frac{S(\nu_{\min}, g_{c,\min}(1 \pm \eta))}{S(\nu_{\min}, g_{c,\min})} \right)^{1/2}$$

$$\Delta \nu = \eta \nu_{\min} \left(2 \ln \frac{S(\nu_{\min}(1 \pm \eta), g_{c,\min})}{S(\nu_{\min}, g_{c,\min})} \right)^{1/2},$$

where $\eta \equiv 0.01$ gives the relative distance to the minimum. We note that this method of error estimation might be flawed, because the determination of g_c is much more precise than the determination of ν . While changes in g_c mainly shift data points in Fig. S4 horizontally and influence the overlap region, variation of ν affects mostly the rescaled specific heat values $f_{i,k}$ themselves and, thus, shift data points vertically in Fig. S4. If the overlap region becomes smaller the overall error $S(\nu, g_c)$ increases fast. This explains why the variation of g_c influences $S(\nu, g_c)$ much more than ν such that the determination of ν is more difficult. To take this into account, we compute the minimal and maximal value of g_c and ν , where $S(\nu, g_c) < (1 + \eta_2)S(\nu_{\min,\max}, g_{c,\min,\max})$, where η_2 is an arbitrary parameter. These minimal and maximal values for g_c and ν should be a valid estimation of the error.

III. SIMULATION RESULTS FOR CRITICAL EXPONENT ν FOR PLANAR SUBSTRATE

The finite size scaling procedure also allows us to determine the critical exponent ν for adsorption to a planar substrate. Results for the exponent ν are shown in Fig. S6 as a function of the stiffness parameter L_p/ℓ .

The exponent ν is around $\nu = 2$ for small bending rigidity and lowers towards $\nu = 1$ with increasing stiffness. This is in agreement with the theoretical expectation that adsorption of flexible polymers is a continuous transition with $\nu_F = 2$. A semiflexible polymer should exhibit a critical behavior corresponding to $\nu_{SF} = 1$ with a crossover to a flexible behavior with $\nu = \nu_F = 2$ in the small regime $|g - g_{c,SF}| < k_B T/L_p$ around the transition, where the correlation length ξ exceeds L_p as explained in section IC 2. This crossover might be the reason that we obtain values $\nu \approx 1.4$ significantly larger than $\nu = 1$ for stiff polymers using the finite size scaling.

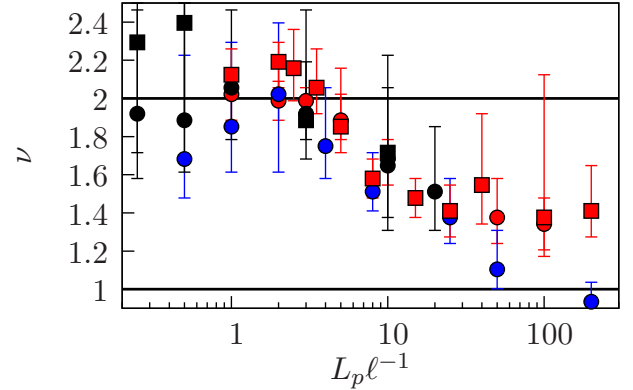


FIG. S6. Finite size scaling results for the critical exponent ν in $D = 3$ dimensions (circles) and $D = 2$ dimensions (squares) as a function of the dimensionless stiffness parameter L_p/ℓ for $\ell = 1$ (red), $\ell = 2$ (blue) and $\ell = 4$ (black). Simulation parameters are as in Fig. 4.

IV. ADDITIONAL SIMULATION SNAPSHOTS

In Fig. S7 we present additional simulation snapshots in the desorbed phase for all three adsorption geometries.

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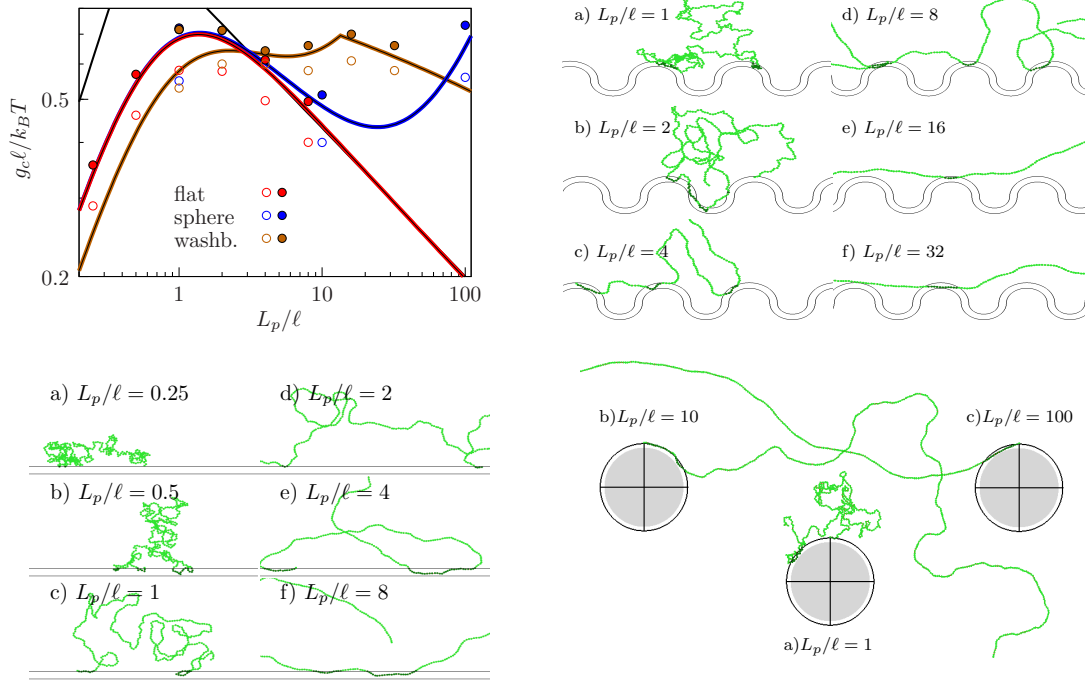


FIG. S7. Phase diagrams for a planar substrate (red line), an adsorbing sphere (blue line) and an adsorbing washboard in $D = 2$ (brown line) and simulation snapshots in the desorbed phases corresponding to the open circles in the phase diagram. Solid circles correspond to the simulation snapshots in the adsorbed phase presented in the main text.