Point force manipulation and activated dynamics of polymers adsorbed on structured substrates

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Abstract. – We study the activated motion of adsorbed polymers which are driven over a structured substrate by a localized *point* force. Our theory applies to experiments with single polymers using, for example, tips of scanning force microscopes to drag the polymer. We consider both flexible and semiflexible polymers, and the lateral surface structure is represented by double-well or periodic potentials. The dynamics is governed by kink-like excitations for which we calculate shapes, energies, and critical point forces. Thermally activated motion proceeds by the nucleation of a kink-antikink pair at the point where the force is applied and subsequent diffusive separation of kink and antikink. In the stationary state of the driven polymer, the collective kink dynamics can be described by a one-dimensional symmetric simple exclusion process.

Introduction. – The thermally activated escape over potential barriers under the influence of an external force has been first solved by Kramers for a point particle [1]. Since then this process has been extensively studied not only for point particles [2] but also for extended objects such as elastic strings. Examples are provided by condensed-matter systems: dislocation motion in crystals [3,4], motion of flux lines in type-II superconductors [5], or charge-density waves [6]. An analogous problem is the activated motion of polymers over a potential barrier, which has been considered both for flexible [7] and semiflexible polymers [8,9].

In all of these previous studies, the thermally activated motion is induced by spatially *uniform* forces which are applied to the whole polymer or elastic line. In contrast, in the present article, we will address the thermally activated motion of polymers over potential barriers in the presence of a *point* force which acts only locally on the polymer. We will consider both flexible and semiflexible polymers.

Our theoretical study is motivated by experimental advances in the manipulation and visualization of single polymers using optical [10] and magnetic [11] tweezers, or scanning force microscopy [12]. In ref. [12], it has been demonstrated that these techniques allow to experimentally apply localized point forces to a polymer adsorbed on a substrate. Polymers that are strongly adsorbed onto crystalline substrates such as graphite or mica experience a spatially modulated adsorption potential reflecting the underlying crystal lattice structure and giving rise to preferred orientations of the adsorbed polymer. For such systems, the dynamics of the adsorbed polymer is governed by thermal activation over the potential barriers of the surface potential.
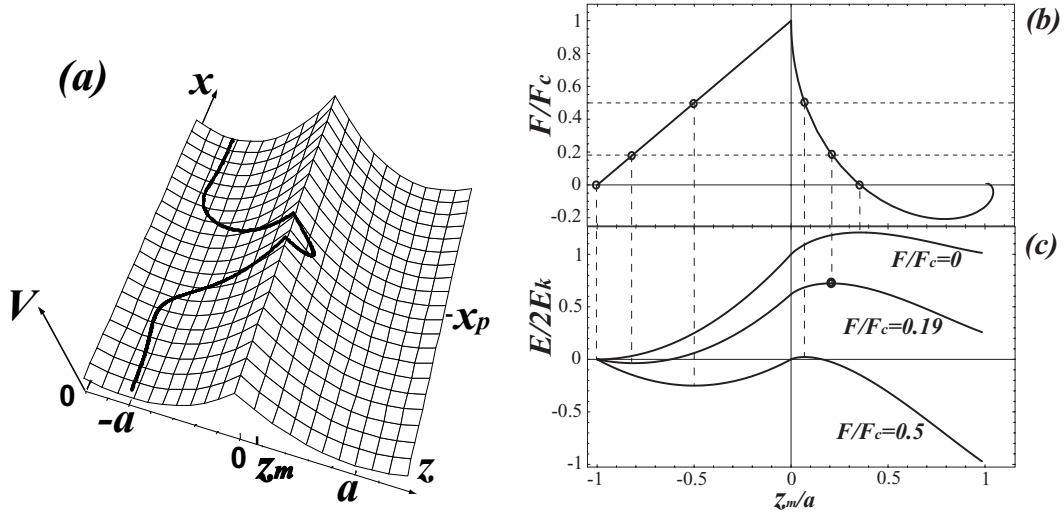
Fig. 1 – (a) Kink-antikink configuration of a semiflexible polymer in a double-well potential V under the action of a point force F_p displacing the midpoint in the z-direction to a value z_m. The configuration $z_k(x)$ is calculated for $F_p/F_c = 0.19$, $z_m/a = 0.21$ ($L_2/w_k = 1.1$, $L_1/w_k = 15$) and has an energy $E/2E_k = 0.72$. (b) The midpoint z_m (in units of a) as a function of the external force (in units of critical force $4E_k/a$). (c) Energy $E(z_m)$ (in units of $2E_k$) of a kink-antikink pair as a function of the midpoint z_m (in units of a) for different forces $F_p/F_c = 0, 0.19, 0.5$.

One example of polymers adsorbed on a structured surface are self-assembling polymer chains consisting of long-chain alkanes and alkylated small molecules on crystalline substrates such as the basal plane of graphite [13]. The alkyl chains orient along the substrate axes thereby providing an effective periodic adsorption potential. Also biopolymers such as DNA or polyelectrolytes can be oriented on the basal plane of graphite by using long-chain alkanes as an oriented template layer [12, 14]. It has been demonstrated experimentally that these polymers can be manipulated individually on the structured surface by applying point forces using the tip of a scanning force microscope [12].

Our main results are as follows. At low forces, the dynamics of the polymer is governed by thermal activation and nucleation of localized kink-like excitations as shown in fig. 1. We calculate the critical point force below which the polymer moves by thermal activation over the barriers of the adsorption potential. The steady state of this activated motion determines the profile and velocity of the moving polymer and is governed by the (collective) driven motion of the kink excitations which can be described as a one-dimensional symmetric simple exclusion process of these excitations. Our results for the critical point force, the velocity, and the profile of the moving polymer are accessible in manipulation experiments on adsorbed polymers and allow to extract material parameters of the polymer and the substrate structure from such experiments. We will first present detailed calculations for stiff, semiflexible polymers. Results for flexible polymers are discussed in the end.

Model. – We consider the dynamics of a semiflexible polymer adsorbed to a planar two-dimensional structured substrate under the influence of an external point force F_p pulling the polymer. A generic model of the substrate structure is a double-well potential that is translationally invariant in one direction, say the x-axis as in fig. 1. The semiflexible polymer

has a bending rigidity κ and persistence length $L_p = 2\kappa/T$, where T is the temperature in energy units. We focus on the regime where the potential wells are sufficiently deep and narrow so that the adsorbed polymer is oriented along the x-axis and can be parameterized by displacements $z(x)$ perpendicular to the x-axis with $-L/2 < x < L/2$, where L is the projected length of polymer, see fig. 1. The Hamiltonian of an oriented polymer is given by

$$\mathcal{H}\{z(x)\} = \int_{-L/2}^{L/2} \mathrm{d}x \left[\frac{\kappa}{2} \left(\partial_x^2 z \right)^2 + V(z) \right],\tag{1}$$

i.e., the sum of bending and potential energy [8,9]. We consider a piecewise harmonic double-well potential

$$V_p(x, z) \equiv V_0(z) - F_p \delta(x - x_p)z\tag{2}$$

with $V_0(z) \equiv \frac{1}{2} V_0(|z| - a)^2$, where V_0 is the depth of the potential. The potential (2) contains the action of a point force pulling the polymer at the point $x = x_p$ with a force F_p in the z-direction. For zero point force $F_p = 0$, the potential is symmetric, translationally invariant in the x-direction, has a barrier height $V_0 a^2/2$, and the distance between minima is $2a$. For $F_p > 0$, the point force in (2) breaks the translational invariance of the system.

Our assumption of an oriented polymer is valid if U-turns of the polymer within a single potential well are suppressed by the bending energy. This is the case if the size $2a$ of each potential well in the z-direction is smaller than the persistence length L_p. This condition is typically fulfilled for adsorbing substrates structured on the nm scale [13]. Furthermore, the polymer should be strongly adsorbed, which corresponds to a small density of thermally induced kink excitations, *i.e.*, $E_k \gg T$, where E_k is the kink energy, see eq. (4) below and ref. [8].

The overdamped motion of the polymer is described by [8,9]

$$\gamma \partial_t z = -\frac{\delta \mathcal{H}}{\delta z} + \zeta(x, t) = -\kappa \partial_x^4 z - V_0'(z) + F_p \delta(x - x_p) + \zeta(x, t),\tag{3}$$

where γ is the damping constant and $\zeta(x, t)$ is a Gaussian distributed thermal random force with $\langle \zeta \rangle = 0$ and correlations $\langle \zeta(x, t)\zeta(x', t') \rangle = 2\gamma T \delta(x - x')\delta(t - t')$. We neglect longitudinal motion of polymer segments (see ref. [9] for a discussion) and do not study the effects of an external tension or compression. For $V_p = 0$, tension and compression have been considered in [15] and [16], respectively.

Static kinks. – First, we calculate the stationary shape of the semiflexible polymer that is deformed by a point force acting at its midpoint into a kink-antikink configuration $z_k(x)$ as shown in fig. 1a. This configuration is obtained by displacing the polymer at the midpoint where the point force acts to a prescribed position z_m and letting the rest of the polymer equilibrate. Therefore, we have to solve the saddle-point equation $\delta \mathcal{H}/\delta z = 0$ for the energy (1), *i.e.*, eq. (3) for the time-independent case and in the absence of noise ($\zeta = 0$), with appropriate boundary conditions *and* a prescribed position $z_k(x_p) = z_m$. For $z_m > 0$ the kink configuration crosses the barrier at two points, see fig. 1a; we choose the origin $x = 0$ and the length L_2 such that these points are $z_k(0) = 0$ and $z_k(L_2) = 0$. The polymer has a total length $L = L_1 + L_2$ and extends from $x = -L_1/2$ to $x = L_1/2 + L_2$, and the force acts at the midpoint $x_p = L_2/2$. The kink-like configuration has to fulfill four boundary conditions, $z_k(-L_1/2) = z_k(-L_1/2 + L_2) = -a$ and $z_k'|_{-L_1/2} = z_k'|_{-L_1/2+L_2} = 0$. At the midpoint $x_p = L_2/2$, we fix the displacement z_m of the polymer $z_k(x_p) = z_m$, and the point force causes a discontinuity in the third derivative, $z_k'''(x_p+) - z_k'''(x_p-) = F_p/\kappa$. In addition, $z_k(x)$ and its first two derivatives have to be continuous at the midpoint, and $z_k(x)$ and its first three derivatives have to be continuous at each crossing point $x_0 = 0, L_2$.

Away from the point force, *i.e.*, for $x \neq x_p$ the saddle point solutions are linear combinations of the four functions $\exp[\pm x/w_k]\exp[\pm ix/w_k]$, where $w_k \equiv \sqrt{2}(\kappa/V_0)^{1/4}$ is the kink width. Construction of the solution through the four regions separated by the crossing points and the midpoint then requires to determine 16 linear expansion coefficients and the two parameters L_2 and z_m as a function of the system size L and the remaining model parameters including the point force from the boundary and matching conditions. The resulting shapes of the kink-like polymer configurations are shown in fig. 1a. Figure 1c shows the energies $E(z_m)$ of the kink-like configuration as a function of z_m for different point forces F_p. For low forces the energies $E(z_m)$ in fig. 1c have two stationary points, a stable minimum at $z_m = z_{m,min} < 0$ (the midpoint does not cross the barrier) and an unstable maximum at $z_m = z_{m,nuc} > 0$. This maximum is unstable with respect to further displacement of the midpoint and represents the critical nucleus configuration. For $F_p = 0$, we obtain another stable minimum at $z_m = a$ (the midpoint reaches the next potential well) which is the static kink-antikink solution [8]. The width w_k of a static kink and its characteristic energy E_k are given by

$$w_k = \sqrt{2}(\kappa/V_0)^{1/4}, \qquad E_k = a^2 \kappa^{1/4} V_0^{3/4}/\sqrt{2}. \tag{4}$$

In the limit of large L, we can find analytic expressions for the resulting stationary positions $z_{m,min}$ and $z_{m,nuc}$ as a function of the applied force F_p, see fig. 1b. We find that there are no stationary positions if the point force F_p exceeds a critical value F_c given by

$$F_c = 4E_k/a = 2\sqrt{2}a\kappa^{1/4}V_0^{3/4}. \tag{5}$$

The midpoint displacement $z_{m,min} < 0$ in the stationary minimum is a linear function of the external force, $z_{m,min} = -a(1 - F_p/F_c)$ and reaches the barrier at $z_{m,min} = 0$ for $F_p = F_c$, see fig. 1b. This force-displacement relation describes the linear response of the polymer before crossing the barrier. For the midpoint displacement in the unstable nucleus configuration $z_{m,nuc} > 0$, on the other hand, we obtain the following set of two equations for $z_{m,nuc}$ and L_2:

$$F_p/F_c = (\cos x - \sin x)e^{-x}\big|_{x=L_2/2w_k}, \qquad z_{m,nuc}/a = 1 - (\sin x + \cos x)e^{-x}\big|_{x=L_2/2w_k}. \tag{6}$$

As shown in fig. 1b, F_p is decreasing for increasing $z_{m,nuc}$ as the critical nucleus configuration widens for small point forces. The negative values of F_p for large $z_{m,nuc}$ indicate that for a semiflexible polymer the kink-antikink configuration reached for $z_m = a$ is stabilized by an energy barrier. Only below a negative threshold force $F_c^- \equiv -F_c e^{-\pi/2} < 0$ the kink-antikink configuration becomes unstable.

Kink nucleation. – Now we turn to the activated kink nucleation in the presence of a point force pushing the polymer over the potential barrier. The point force breaks the translational invariance in x-direction and kink-antikink pairs are only nucleated at $x = x_p$ with a rate J per unit time. This thermally activated process is governed by an energy barrier which is given by the excess energy ΔE_n of the critical nucleus configuration. The energy of the critical nucleus can be obtained from the energy profiles $E(z_m)$ shown in fig. 1c as the difference $\Delta E_n \equiv E(z_{m,nuc}) - E(z_{m,min})$ between minimum and maximum values of the energy $E(z_m)$ of the kink-like configuration. We find $\Delta E_n \sim 2E_k(1 - F_p/F_c)^2$, which vanishes as the force approaches the critical value F_c. The activation energy enters the nucleation current

$$J = (Q_n/2\pi)\exp\left[-\Delta E_n/T\right] \quad \text{with} \quad Q_n^2 \equiv |\omega_{n,0}|\omega_{s,0}\prod_{p>0}(\omega_{s,p}/\omega_{n,p}), \tag{7}$$

which shows Arrhenius-type behaviour. The prefactor Q_n includes the spectrum of attempt frequencies $\omega_{n,p}$ and $\omega_{s,p}$ $(p = 0, 1, \ldots)$ for phononic fluctuations around the critical nucleus
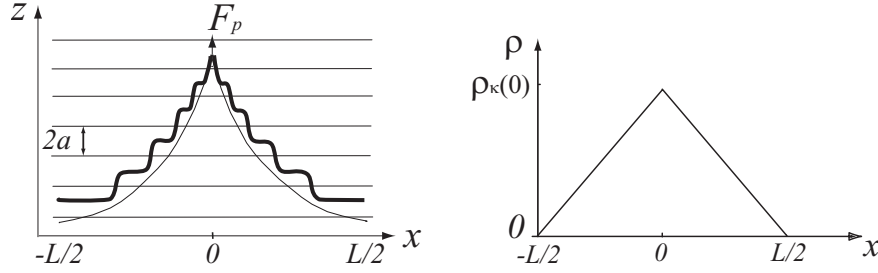
Fig. 2 – (Left) The shape of a semiflexible polymer pulled over a periodically structured surface by a point force acting at the midpoint. The horizontal lines indicate the position of potential barriers. The thick solid line shows a typical polymer configuration $z(x)$, the thin line the average shape $\langle z(x) \rangle$. (Right) The stationary kink density $\rho_k(x)$ as a function of the distance from the point x_p where the force is acting on the polymer.

configuration and the straight configuration $z_m = -a$, respectively. We find one unstable negative mode $\omega_{n,0} \leq 0$, which diverges as $\omega_{n,0} = (V_0/\gamma)[1 - 2^{4/3}(1 - F_p/F_{c,\kappa})^{-4/3}]$ upon approaching the critical force $F_p \approx F_c$, a bound state with $0 < \omega_{n,1} \leq V_0/\gamma$, and a set of positive modes $\omega_{n,p} > V_0/\gamma$ with the same level spacing as the modes of the straight configuration. It is important to note that two translational modes (for kink and antikink) only exist if the point force is zero because the point force breaks the translation invariance. Close to the critical force $F_p \simeq F_c$, we obtain $Q_n^2 \approx (V_0/\gamma)^2[1 - 2^{4/3}(1 - F_p/F_c)^{-4/3}]$.

Collective kink dynamics. – After nucleation of a kink-antikink pair at $x = x_p$ by thermal activation, kink and antikink are driven apart by a small force $\sim E_k/w_k e^{-L_2/w_k}$, which decays exponentially with the distance $L_2 > w_k$ between kink and antikink. This exponential decay is characteristic for a point driving force which interacts only over a distance $\sim w_k$ with the kink and very different from the case of a spatially uniform force, where kinks experience a spatially uniform driving force [8, 17]. For separations $L_2 > w_k$ the kink diffuses essentially freely with a diffusion constant $D_k = 2Tw_k/3\gamma a^2$ [8].

A spatially localized driving force also leads to a distinct steady-state motion of the polymer in a periodically continued potential, see fig. 2. This motion can be described in terms of the collective dynamics of an ensemble of kinks and antikinks which are generated at the *single* point $x = x_p$ by the point force and subsequently separated by the exponentially decaying force. For the following discussion we choose coordinates such that $x_p = 0$, and the polymer extends from $-L/2 < x < L/2$. Because a point force creates kink-antikink pairs only at $x = 0$, we find an ensemble consisting only of kinks in the region $x > 0$ and an ensemble consisting only of antikinks in $x < 0$. As two (anti-)kinks have a mutual short-range repulsion of range w_k, we have an ensemble of diffusing kinks (antikinks) with a hard-core repulsion on the interval $L/2 > x > 0$ ($-L/2 < x < 0$). In order to treat the non-equilibrium dynamics of these ensembles, we introduce a discrete one-dimensional lattice of possible kink positions with spacing $\Delta x = w_k$ which allows to map the dynamics of each ensemble onto the *symmetric simple exclusion process* (SSEP) with open boundaries [18,19]. In the following we consider the kink ensemble ($x > 0$); the antikink ensemble ($x < 0$) can be treated analogously. In the kink ensemble, the kink particles are freely diffusing, *i.e.*, they have *symmetric* rates $D \equiv D_k/w_k^2$ for hopping to the right and left on the lattice $x_i = iw_k$ ($i = 1, \ldots, N$ with $N = L/2w_k$); they interact through their hard-core repulsion. In the SSEP, boundary conditions are specified by

rates α and δ for particles to enter the system at the left ($i = 1$) and right ($i = N$), respectively, if that site is empty. For the kink ensemble we have $\alpha = J$, as kinks are nucleated at $i = 1$ with the Kramers rate (7), and $\delta = 0$ as no kinks enter the system at $i = N$. Furthermore, kinks leave the system diffusively, at $i = 1$ by annihilation with an antikink and at $i = N$ by relaxation of the free polymer end.

Despite the hard-core interaction, the stationary density profile $\rho_k(x)$ of kinks in the SSEP fulfills the stationary diffusion equation, $\partial_x^2 \rho_k = 0$ [18, 19]. Furthermore, our boundary conditions are equivalent to boundary conditions $\rho_k(0) = w_k^{-1} \min(\alpha/D, 1)$ and $\rho_k(L/2) = 0$ for the stationary kink density at the ends of the system. For $\alpha > D$ the system reaches its maximal kink density w_k^{-1} at $x = 0$. The resulting linear density profile $\rho_k(x)$ is

$$\rho_k(x) = \rho_k(0)(1 - 2|x|/L) \quad \text{with} \quad \rho_k(0) = w_k^{-1} \min(\alpha/D, 1) = \min(Jw_k/D_k, 1/w_k) \quad (8)$$

as shown in fig. 2 (right). The average distance between kinks is $1/\rho_k(x)$ and at each kink the polymer position changes by $\Delta z = -2a$ leading to a characteristic *parabolic* polymer shape $\langle z(x) \rangle - z_m = -2a \int_0^{|x|} \mathrm{d}\tilde{x} \rho_k(\tilde{x}) = -2(a/w_k) \min(Jw_k^2/D_k, 1)|x|(1 - |x|/L)$ in the stationary state as shown in fig. 2 (left). The average velocity $v_z \equiv \langle \partial_t z \rangle$ of the polymer in the z-direction is determined by the stationary current $J_{\text{SSEP}} = -D_k \partial_x \rho_k = \min(J, D_k/w_k^2) w_k/L$ of the SSEP. Only for small nucleation rates $J \ll D_k/w_k^2$ the kink interaction can be neglected and the current is directly given by the Kramers rate (7), $J_{\text{SSEP}} \approx Jw_k/L$. During the time $1/J_{\text{SSEP}}$ the polymer advances by a distance $2a$ leading to $v_z = 2aJ_{\text{SSEP}} \approx 2a \min(J, D_k/w_k^2) w_k/L$.

Flexible polymers. – So far we considered semiflexible polymers dominated by their bending energy. In this section we want to outline the main results for flexible Gaussian polymers governed by entropic elasticity with a tension $\sigma = T/2b$, where b is the Kuhn length. The Hamiltonian of a flexible Gaussian polymer on a planar two-dimensional substrate is given by

$$\mathcal{H} = \int_{-L_c/2}^{L_c/2} \mathrm{d}s \left[\frac{\sigma}{2} \left[(\partial_s x)^2 + (\partial_s z)^2 \right] + V(z) \right], \quad (9)$$

where we integrate over the arc length s with $-L_c/2 < s < L_c$, and L_c is the contour length of the polymer. The translationally invariant potential $V(z)$ is a function of z only. Therefore fluctuations in the x-coordinate decouple and are Gaussian with moments $\langle (x(L_c) - x(0)) \rangle = 0$ and $\langle (x(L_c) - x(0))^2 \rangle \approx L_c b/2$. The Rouse dynamics of the z-coordinate of the polymer is given by

$$\gamma \partial_t z = \sigma \partial_s^2 z - V_0'(z) + F_p \delta(s - s_p) + \zeta(s, t), \quad (10)$$

where γ is the damping constant and $\zeta(x, t)$ is a Gaussian-distributed thermal random force. The point force is on the monomer $s = s_p$. For a flexible polymer the kink width is $w_{k,\sigma} = (\sigma/V_0)^{1/2}$ and the kink energy $E_{k,\sigma} = a^2(\sigma V_0)^{1/2}$ [7, 17]. As for the semiflexible polymer, we can calculate the energy $E(z_m)$ of a kink-antikink configuration with prescribed midpoint $z_k(s_p) = z_m$. For a flexible polymer the displacements in the stationary minimum at $z_m = z_{m,min}$ and the maximum representing the nucleus with $z_m = z_{m,nuc}$ are both *linear* functions of the external force, $z_{m,min} = -a(1 - F_p/F_{c,\sigma})$ and $z_{m,nuc} = a(1 - F_p/F_{c,\sigma})$, where the critical force for the flexible polymer is given by $F_{c,\sigma} = 2E_{k,\sigma}/a = 2a(\sigma V_0)^{1/2}$. The nucleation current J_σ for the flexible polymer is given by the same expression (7) as for a semiflexible polymer with the excess energy $\Delta E_n \sim 2E_{k,\sigma}(1 - F_p/F_{c,\sigma})^2$. The spectrum of attempt frequencies $\omega_{n,p}$ for the critical nucleus shows slightly different behaviour for the flexible polymer as the unstable negative mode $\omega_{n,0} \approx -3V_0/\gamma$ does not diverge for $F_p \approx F_{c,\sigma}$, and we

finally obtain $Q_n \approx \sqrt{3}V_0/\gamma$. The collective kink dynamics for a flexible polymer can also be mapped onto a one-dimensional SSEP. As a function of the arc length s, we find a linear stationary kink density profile $\rho_k(s) = \rho_k(0)(1-2|s|/L_c)$ with $\rho_k(0) = \min(J_\sigma w_{k,\sigma}/D_{k,\sigma}, 1/w_{k,\sigma})$ and a parabolic shape $\langle z(s) \rangle = -2(a/w_{k,\sigma}) \min(J_\sigma w_{k,\sigma}^2/D_{k,\sigma}, 1)|s|(1 - |s|/L_c)$ analogously to the semiflexible polymer, cf. eq. (8), where $D_{k,\sigma} = T w_{k,\sigma}/\gamma a^2$ [17] is the kink diffusion constant of the flexible polymer. In the real space coordinates of the substrate, however, the resulting shape is $(\langle x(s) \rangle, \langle z(s) \rangle) = (0, \langle z(s) \rangle)$ and thus, the parabolic shape is lost due to the decoupled Gaussian fluctuations in the x-direction. The result for the velocity $v_z = 2aJ_{\mathrm{SSEP}} \approx 2a \min(J_\sigma, D_{k,\sigma}/w_{k,\sigma}^2)w_{k,\sigma}/L_c$ is analogous to the semiflexible polymer.

Conclusion. – In summary, we described the activated motion of single adsorbed polymers on a structured substrate displaced by localized *point* forces, which can be realized experimentally using, *e.g.*, scanning force microscopy tips. The dynamics is governed by kink-like excitations for which we have calculated shapes, energies, and critical point forces. Kink and antikink pairs are *locally* nucleated by the point force and then undergo a separation which is diffusive on separations larger than the kink width w_k. We have calculated the nucleation rate (7) using Kramers theory. The collective kink dynamics can be mapped onto a one-dimensional symmetric simple exclusion process (SSEP). Using this mapping, we find the average polymer velocity and a characteristic average parabolic shape for a driven semiflexible polymer.

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