

Supporting Information

A: Calculation of radial distribution functions

To get an effective propagator in one dimension, we first transform (1) into spherical coordinates:

$$x - a = \rho \sin \theta \cos \phi, \quad y = \rho \sin \theta \sin \phi, \quad z = \rho \cos \theta. \quad (14)$$

The two scalar products in the combined exponents of Eq.(1) become:

$$(\mathbf{r} \pm b\hat{\mathbf{z}})^2 = a^2 + b^2 + \rho^2 + 2a\rho \sin \theta \cos \phi \pm 2b\rho \cos \theta. \quad (15)$$

The next step of integration over the solid angle on the unit hemisphere is not easy. We need to evaluate

$$I = \int_0^{\pi/2} d\theta \sin \theta \int_0^{2\pi} d\phi e^{-\alpha \cos \phi \sin \theta \pm \beta \cos \theta}, \quad (16)$$

where parameters α and β involve N, b, a and ρ . This is solved by realizing that the integrand has a non-trivial axial symmetry. We transform back into Cartesian coordinates about the target: $x' = \cos \phi \sin \theta$, $z' = \cos \theta$, and rotate these new coordinates by an angle $\varphi = \tan^{-1}(\beta/\alpha) = \tan^{-1}(b/a)$ around the y -axis. The direction of this rotation depends on the sign of the z -term in the exponent (i.e. whether we are dealing with the ‘real’ or ‘image’ Gaussian term). This rotation means we are essentially integrating $\exp(-\sqrt{a^2 + b^2}x)$. However, we must be careful when we define the surface we are integrating over. Since we aren’t integrating over a line in the plane of the surface, the hemisphere appears tilted with respect to the variable of integration x , as in Figure. The surface element is given by $\psi(x)\sqrt{1 - x^2}ds$. On the unit sphere $y = \pm\sqrt{1 - x^2}$, and the element ds is given by

$$ds = \sqrt{1 + \left(\frac{\partial y}{\partial x}\right)^2} dx = \frac{dx}{\sqrt{1 - x^2}}. \quad (17)$$

The opening angle of the surface element has the exact expression

$$\psi(x) = \begin{cases} 2\pi, & -1 \leq x < -\cos \varphi \\ \pi - 2 \sin^{-1} \left(\frac{x \tan \varphi}{\sqrt{1-x^2}} \right), & -\cos \varphi \leq x \leq \cos \varphi \\ 0, & \cos \varphi < x \leq 1 \end{cases} \quad (18)$$

The radial probability density is defined with the normalisation over only the allowed half-space:

$$\int_0^\infty d\rho \rho^2 P_{eq}(\rho) = 1 \quad (19)$$

where a factor of 2π accounting for the area of a hemispherical shell, $2\pi\rho^2$, has been absorbed into $P_{eq}(\rho)$ for simplicity. Using this, we find that the radial probability density takes the form

$$\begin{aligned} P_{eq}(\rho) = & 2\pi \sqrt{\frac{N\pi}{6}} \left(\frac{3}{2\pi N b^2} \right)^{3/2} e^{-\frac{3(a^2+b^2+\rho^2)}{2Nb^2}} \times \\ & \left[\frac{2Nb^2}{3\rho\sqrt{a^2+b^2}} \left[\cosh \left(\frac{3\sqrt{a^2+b^2}}{2Nb^2} \rho \right) - \cosh \left(\frac{3\rho a}{2Nb^2} \right) \right] \right. \\ & \left. + \frac{2b}{a} I_1 \left(\frac{3\sqrt{a^2+b^2}}{Nb^2} \rho \right) - \frac{4b^2}{\pi a^2} \sinh \left(\frac{3\sqrt{a^2+b^2}}{Nb^2} \rho \right) \right]. \end{aligned} \quad (20)$$

Comparing the magnitudes of different terms in the square brackets, we discover that the modified Bessel function I_1 term is by far the dominant, which leads to the approximated expression Eq. (5) in the main text.

B: Calculation of looping time

Here we show that the mean looping time of a polymer, as calculated from our method, coincides with the expression derived by Szabo et al.⁹ If we consider first the more general problem of a chain with one end tethered in place (in reality, since we can change our frame

of reference of the polymer, we may do this for the free chain). Then, the distribution of the free end of an ideal polymer chain is given by

$$P(\mathbf{r}) = \left(\frac{3}{2\pi Nb^2} \right)^{3/2} \exp \left(-\frac{3\mathbf{r}^2}{2Nb^2} \right) \quad (21)$$

We want to calculate the time for the free end to hit a sphere of radius ε centered a distance a from the first monomer. As in Part A, we may transform into spherical polar coordinates and then integrate over the polar angles to obtain a probability distribution over r . This integral is very similar in form to Eq. (16), but with the integration limits extended over the entire unit sphere, and $\beta = 0$:

$$I = \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi e^{-\alpha \cos \phi \sin \theta} \quad (22)$$

Transforming back into Cartesian coordinates, we have

$$I = 2\pi \int_{-1}^1 dx e^{-\alpha x} = \frac{2\pi}{\alpha} (e^\alpha - e^{-\alpha}). \quad (23)$$

As such, the resulting radial probability distribution about the target is

$$P_{eq}(\rho) = \frac{1}{a\rho} \sqrt{\frac{3}{2\pi Nb^2}} \left(e^{-\frac{3(\rho-a)^2}{2Nb^2}} - e^{-\frac{3(\rho+a)^2}{2Nb^2}} \right). \quad (24)$$

When we use this probability distribution in the expression for mean first passage time

$$\tau = \int_\varepsilon^\infty d\rho [D\rho^2 P_{eq}(\rho)]^{-1} \left[\int_\rho^\infty d\rho' \rho'^2 P_{eq}(\rho') \right]^2, \quad (25)$$

we find that the integral, though not analytically solvable, is dominated by the value of the integrand at small ρ . As $\rho \rightarrow 0$, the probability distribution tends to a non-zero constant,

and so we can make the approximation

$$\begin{aligned}\tau_{\text{on}} &\approx \sqrt{\frac{\pi}{54}} \frac{(Nb^2)^{3/2}}{D} e^{\frac{3a^2}{2Nb^2}} \int_{\varepsilon}^{\infty} \frac{d\rho}{\rho^2} \\ &= \sqrt{\frac{\pi}{54}} \frac{(Nb^2)^{3/2}}{D\varepsilon} e^{\frac{3a^2}{2R_g^2}}.\end{aligned}\tag{26}$$

From here, it is a matter of setting $a = 0$ to recover the Szabo result for the looping time of a polymer in three dimensions, shown in (11).

C: Parallel walls at large separation

One way of writing the solution to the Edwards equation in the case of two walls is given in (8), but we may also write the solution as an infinite sum of Gaussian images:

$$\begin{aligned}G(x, y, z) = \sum_{j=-\infty}^{\infty} \left(\frac{3}{2\pi Nb^2} \right)^{3/2} e^{-\frac{3(x^2+y^2)}{2Nb^2}} &\left(e^{-\frac{3(z-2jd-b)^2}{2Nb^2}} \right. \\ &\left. - e^{-\frac{3(z-2jd+b)^2}{2Nb^2}} \right)\end{aligned}\tag{27}$$

In fact, (8) is just the Fourier series expansion of this expression. If we take the receptor to be aligned directly opposite the tether (i.e. the displacement perpendicular to the parallel plates between the tether and receptor, $a = 0$), then we may exploit the azimuthal symmetry of this expression, and use the same hemispherical integral construction as in Section , only with $\psi = 2\pi$. Instead of integrating over the whole sphere, we just integrate over the hemisphere.

We make the coordinate transformation so that we are centred on the target, with the positive z-direction pointing into the space, $z' = d - z$, and introduce the radial coordinate $r^2 = x^2 + y^2 + z'^2$. The radial probability distribution is given formally by

$$r^2 P_{eq}(r) = 2\pi r \sqrt{\frac{\pi N}{6}} \int_0^r dz' G(r, z'),\tag{28}$$

where the factor $\sqrt{\pi N/6}$ is the partition function. Although algebraically convoluted, this turns out to be integration of an exponential.

At first sight, the small- r expansion actually has an r^2 , rather than r^3 dependence, but these terms actually cancel once the sum is performed. Exploiting the exponential decay with increasing j for large d , we are able to neglect all terms apart from $j = 0$ and $j = 1$ in the sum. We are left, to leading order, with the expression:

$$r^2 P_{eq}(r)_{r \rightarrow 0} \approx \frac{9dr^3}{2N^2b^5} \left[(1 - b/d) e^{-\frac{3d^2(1-b/d)^2}{2Nb^2}} - (1 + b/d) e^{-\frac{3d^2(1+b/d)^2}{2Nb^2}} \right] \quad (29)$$

Finally, we expand in the small parameter b/d (since d is much larger than the radius of gyration, this is sensible), to obtain the final expression

$$r^2 P_{eq}(r)_{r \rightarrow 0} = \frac{27d^2r^3}{N^3b^6} e^{-\frac{3d^2}{2Nb^2}}. \quad (30)$$

This represents the limit of wide gap, or strong chain stretching $d \gg R_g$, opposite to the Eq. (9). The expression for an arbitrary gap is possible, but the more practical approach is to form an interpolation between the short- d and the long- d expressions. This interpolation is given in the Eq. (10); we have tested it and found it approximating the numerical exact expression very well.