

**Supplemental Material for: “Equilibrium behaviour of two cavity-confined polymers:
Effects of polymer width and system asymmetries”**

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I. CLARIFICATION OF THE CALCULATION EMPLOYING A 2D GENERALIZATION OF KRAMERS THEORY

In Section 4.3 of the article, we examined the dynamics of two polymers confined to a cavity with a rectangular cross-section. We found that the polymers swap positions on either end of the box with a dwell-time distribution that is characterized by a time constant, τ_d . The time constant varies with the changes in the dimensions of the cavity as a result in concomitant changes in the underlying free-energy landscape. To understand the relationship between τ_d and the free energy, we employed a multidimensional generalization of Kramers theory.¹ Here, we clarify some details of the calculation used in that analysis.

As noted in Section 4.3 of the article, the theory predicts that

$$e^{\beta\Delta F} = D\tau_d^*, \quad (1)$$

where

$$\tau_d^* \equiv \frac{Q_B\omega_B\omega_W}{2\pi Q_W}\tau_d. \quad (2)$$

Here, D is the Rouse diffusion coefficient, ΔF is the free energy barrier height, and ω_B and ω_W represent the effective frequencies of the well and barrier, respectively. In addition, Q_B and Q_W are the partition functions associated with the non-reactive modes at the free energy barrier and well, respectively. The quantities ω_W and ω_B are obtained from the free energy function, $F(x, y)/k_B T \equiv -\ln \mathcal{P}(x, y)$, as follows. First, a cross section of the free energy function in the y direction at $x=0$ is fit to a function of the form $F(y) = A + B(y - y_{\min})^2 + C(y - y_{\min})^3 + D(y - y_{\min})^4$, where y_{\min} is the position of the free energy minimum. From this fit, we choose $B = \omega_W^2/2$. Next, we fit a cross section of the free energy along the minimum free energy path in the vicinity of the saddle point at $y = 0$ to the function $F(y) = A + By^2 + Dy^4$, from which we choose $-B = \omega_B^2/2$. The quantity Q_W is obtained via a numerical approximation to the the following integral over the nonreactive mode: $\int_{-L_x/2}^{L_x/2} dx \exp[-(F(x, y_{\min}) - F_{\min})/k_B T]$, where F_{\min} is the free energy at the minimum ($x = 0, y = y_{\min}$). Likewise, the partition function for the nonreactive mode at the barrier, Q_B , located at $y = 0$, is given by $\int_{-L_x/2}^{L_x/2} dx \exp[-(F(x, 0) - F_{\text{bar}})/k_B T]$, where F_{bar} is the free energy at the barrier. Note that the free energy barrier height is of course $\Delta F = F_{\text{bar}} - F_{\min}$.

II. EFFECT OF TOPOLOGICAL ASYMMETRY FOR POLYMERS CONFINED TO AN ELLIPTICAL CAVITY

In Section 4.4 of the article, we examined the behaviour of a long linear semiflexible polymer and a short ring polymer, both confined to a cavity with an elliptical cross section. The linear polymer had a length of $N_1 = 1000$ monomers and a bending rigidity of $\kappa = 6.36$, and the ring polymer had a length of $N_2 = 25$ monomers. In addition, the elliptical cross section of the cavity had an area of $A = 3000$ and a height of $h = 15$. (All quantities are given in the reduced units defined in the article.) Various values of the eccentricity of the ellipse were considered.

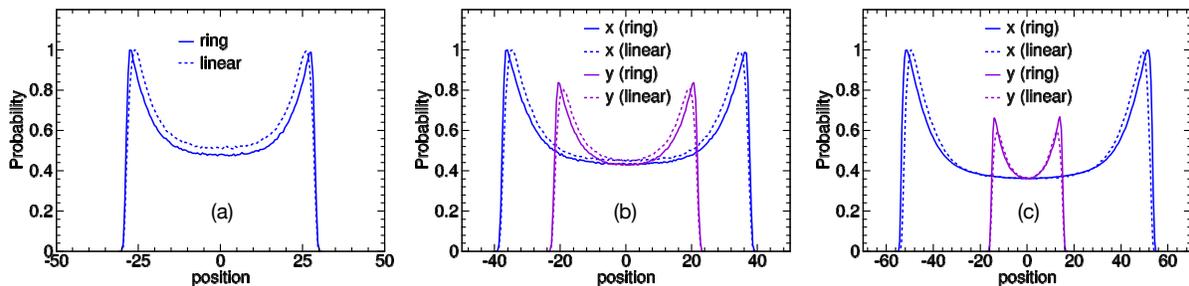


FIG. 1. Cross sections along the x and y axes (defined in the article) of the centre-of-mass probability distributions for a short polymer of length $N_2 = 25$ trapped with a long, linear, semiflexible polymer of length $N_1 = 1000$ and bending rigidity $\kappa = 6.36$ in a cavity. The cavity has an elliptical cross section of area $A = 3000$ and height $h = 15$. Results are shown for eccentricities of (a) $e = 0$, (b) $e = 0.8$, and (c) $e = 0.95$. Each graph shows results for cases where the short polymer has linear and ring topologies. For convenience, distributions have been scaled so that the maximum of the underlying 2D distribution for $\mathcal{P}(x, y)$ is equal to one. Note the cross sections for x and y are identical for $e = 0$.

The distribution of the ring polymer is largely determined by the fact that it is so much shorter than the linear polymer. Here, we examine the effects of the topological difference between the two polymers. To do this, we carry out the same calculations that were described in Section 4.4 with the single change that the topology short polymer is linear rather than ring type. Figure 1 shows cross sections of the 2D probability distributions for the short polymer along the x and y axes (defined in the article) for cavity eccentricities of $e = 0, 0.8$ and 0.95 . The results clearly

show that the topology of the short polymer has a minimal effect on the distributions. The single notable effect is the slightly greater degree of repulsion from the lateral walls for the linear polymer. This is evident in the fact that the probability peaks are displaced slightly inward for the linear polymer relative to that for the ring polymer. This feature most likely arises because of the slightly larger average size of the linear polymer.

REFERENCES

¹B. J. Matkowsky, A. Nitzan, and Z. Schuss, *J. Chem. Phys* **88**, 4765 (1988).