Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information for: "Segregation of polymers under cylindrical confinement: Effects of polymer topology and crowding"

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I. SCALING OF THE FREE ENERGY BARRIER WITH N FOR INFINITELY LONG CHANNELS

As noted in Section 4.1.2 of the article, the free energy barrier height for polymers confined to an infinite-length cylinder is proportional to polymer length N for both linear and ring polymers for all cylinder diameters considered. To illustrate, Fig. 1 shows the barrier height, $\Delta F \equiv F(0) - F(\infty)$ vs N for polymers of length N=200 for both linear and ring polymers. For D=4, fits to the data yield values of the barrier height per monomer of $\Delta F/N$=0.799 for ring polymers and 0.378 for linear polymers. For D=7, we find $\Delta F/N$=0.263 for ring polymers and 0.132 for linear polymers.

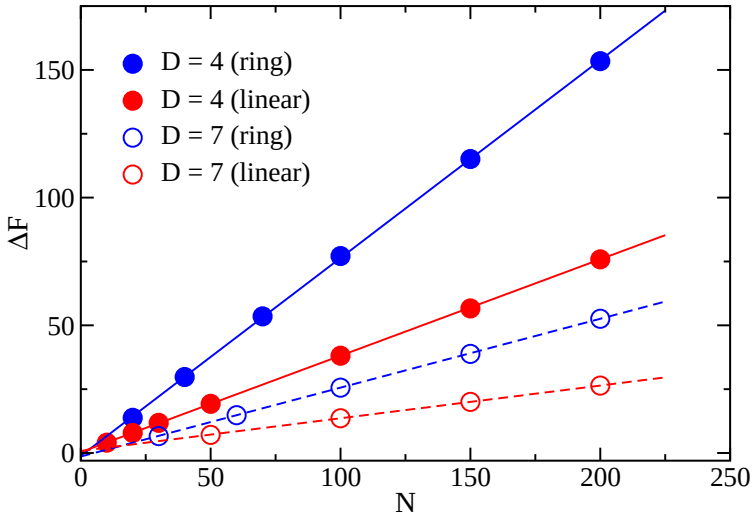

FIG. 1. Comparison of the variation of the free energy barrier height ΔF with polymer length N for ring polymers and linear polymers, each for D=4 and D=7.

II. RELATIONSHIP BETWEEN OVERLAP FREE ENERGY FUNCTIONS FOR LINEAR AND RING POLYMERS

In section 4.1.2 of the article, we consider the relationship between the free energy functions for linear and rings polymers. Results presented in Fig. 5 compared the free energy functions for the two polymer topologies in the case of a tube diameter of D=7 and for polymers of length N=200. In particular, it was noted that the scaling $F \to 2F$ and $\lambda \to 0.582\lambda$ for linear polymers caused the curve to collapse onto that of the ring polymer. The results were rationalized in terms of a theoretical model that predicted scaling factors reasonably close to, but still distinct from those that gave the best collapse of the data, i.e. $F \to 1.803F$ and $\lambda \to 0.637\lambda$. It is worth examining the variation of this scaling with changes to the confinement channel diameter, D. Figure 2 shows results for D=4 and D=11. As in the case of D=7, data collapse is achieved by a simple scaling of F and λ for the linear polymer. The scaling factors for the D=4 case are identical to those for D=7. However, the optimal scaling for D=11 is now $F \to 1.795F$ and $\lambda \to 0.610\lambda$. The change in the scaling factors upon increasing D is likely due to two separate effects. The first is related to finite-size effects associated with the de Gennes blob model, which was employed in the theoretical model. As the diameter increases, the size of the blob (i.e. the number of monomers per blob, g) increases as well. A previous study has shown that the scaling predicted by the blob model is expected to become accurate for $D \gtrsim 10$ for single freely-jointed chains, provided the polymer is sufficiently long.[1] On the other hand, for the fixed N=200 employed here, the number of blobs, n_{b}, will *decrease* as D increases, which could give rise to an increase in finite-size discrepancies. A second issue concerns the approximation suggested in Ref. 2 for estimating the overlap free energy for polymers confined to channels. The simplest form of the model suggests that the free energy cost for overlapping linear polymers can be estimated from using the free energy difference for a single polymer for the cases of tubes of diameter D and $D/\sqrt{2} = 0.707D$. A similar result holds for estimating the overlap free energy of overlapping rings. However, as noted in Ref. 2, as well in in the present article (see Fig. 6), this scaling is leads to quantitative discrepancies. To estimate the free energy, our results (presented in Section III of the SI) show that a scaling of $D \to rD$ works for scaling coefficients that are in the range $r > 0.707$. In particular, r increases from 0.748 to 0.843 as D is varied from D=4 to D=11 for linear polymers. In the case of rings, r increases from 0.724 to 0.788 as D is varied over the same range. The value of r appears to be asymptotically approaching a fixed value as

D increasing, but for the range of D considered here, the finite-size discrepancies are evident from this change in r. The finite-size effects arising from both of these sources (i.e. the blob model and the scaling factor r used to estimate the overlap free energy) lead to the variation in scaling factors that best provides the data collapse for the linear and ring polymer free energy functions. Only calculations using much longer polymer chains together with large D will fully resolve this matter.

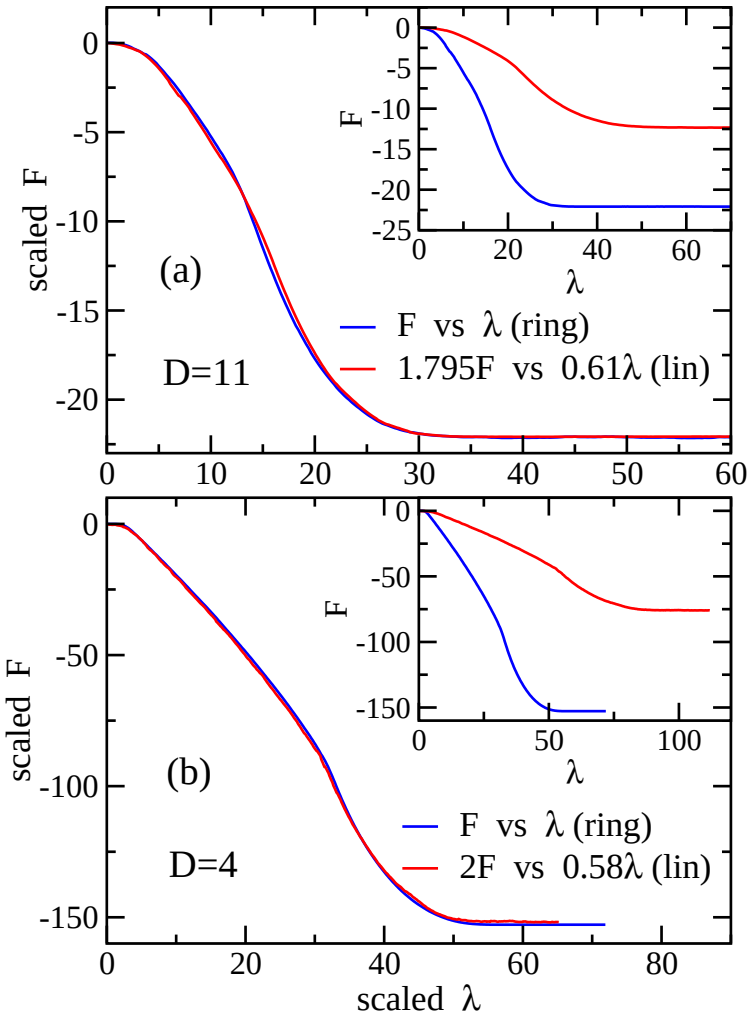

FIG. 2. (a) The blue curve shows the overlap free energy vs λ for polymer rings of length $N = 200$ in a confining cylindrical tube of diameter $D = 11$. The overlaid red curve shows the scaled overlap free energy function of two cylindrically confined $N = 200$ linear polymers. The latter curve has been scaled along F and λ, as indicated in the legend. The inset shows unscaled free energy functions for the ring and linear polymer systems. (b) As in (a), except for a confining cylinder diameter of $D = 4$.

III. FURTHER DETAILS AND COMMENTS ON THE RESULTS PRESENTED IN FIG. 6 OF THE ARTICLE

In the main part of Fig. 6 of the article, the free energy barrier per polymer is calculated for two overlapping polymers (ΔF_2) and for the case of a single polymer that transitions between a tube of diameter D and another with diameter $D/\sqrt{2}$ (ΔF_1). In the case of both ring and linear polymers, the absolute difference between ΔF_1 and ΔF_2 grows with increasing D. As shown in Fig. 3, the relative difference, $\sigma_F \equiv (\Delta F_1 - \Delta F_2)/\Delta F_2$ increases with D as well.

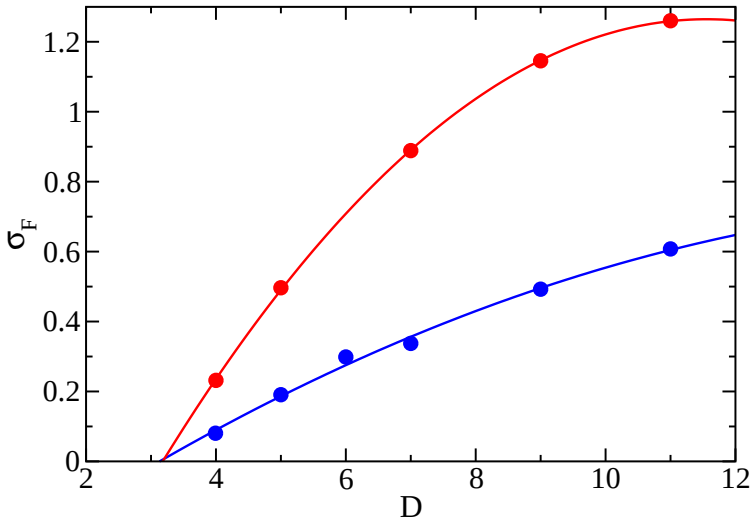

FIG. 3. Variation of the relative difference of the barrier heights, $\sigma_F \equiv (\Delta F_1 - \Delta F_2)/\Delta F_2$, vs tube diameter D. Here, ΔF_2 is the free energy barrier per polymer for two overlapping polymers and ΔF_1 is the barrier height for a single polymer that transitions between a tube of diameter D and another with diameter $D/\sqrt{2}$. Results are shown for both linear and ring polymers of length N=200.

The inset of Fig. 6 of the article shows the variation of the ratio $r \equiv D'/D$ with tube diameter D, where D' is the diameter of the tube required so that $\Delta F_1 = \Delta F_2$ for the cases of both ring and linear polymers. Here, we elaborate on the procedure used to determine the values of r. As an illustration, Fig. 4(a) shows the variation of the free energy F_1 of a single linear polymer of length N=200 with position z of its centre of mass along a channel. The channel initially has a constant cross sectional area with diameter D=7 and transitions through a tapered section of length $L_{\rm tap}$=10 into a region with a constant diameter D'. Results for several values of D' ($< D$) are shown. Figure 4(b) shows the variation of the barrier height ΔF_1 (calculated using

the curves of Fig. 4(a)) vs $r \equiv D'/D$. The red curve is a polynomial fit to the data. The green curve marks the value of ΔF_2, the overlap free energy calculated for two linear chains confined to a tube of D=7. The value of r for which $\Delta F_1 = \Delta F_2$ is determined simply from the location of the intersection of the red and green lines.

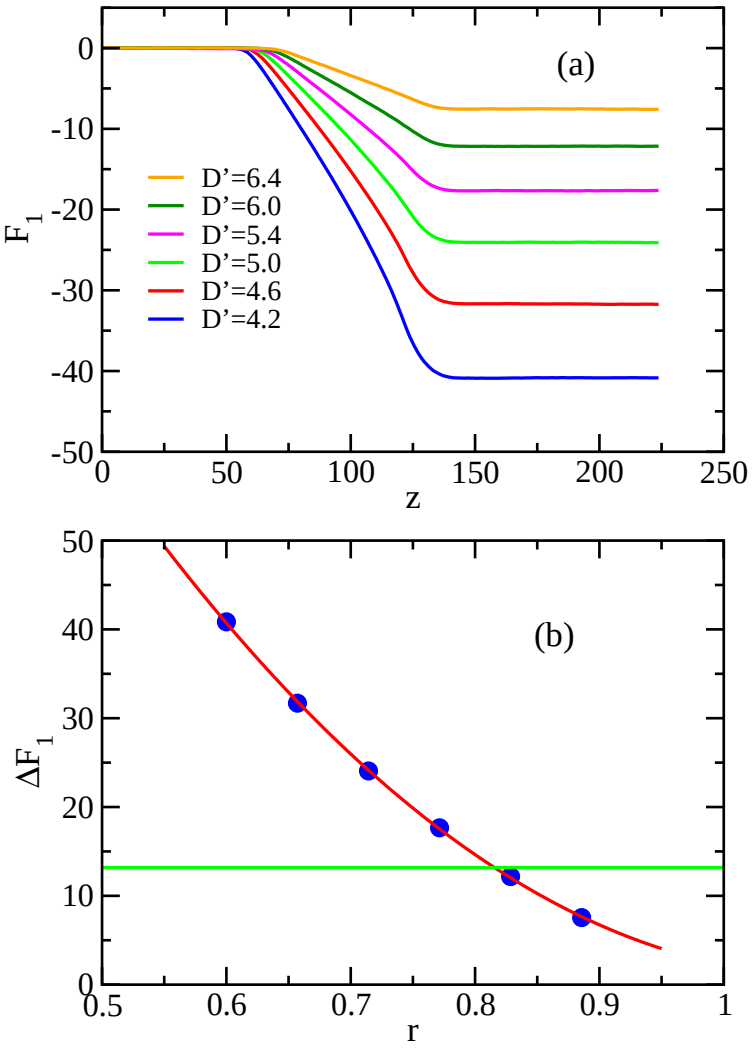

FIG. 4. (a) Variation of the free energy of a single linear polymer F_1 with position z along the channel as the channel narrows from diameter D=7 to a reduced diameter D' through a tapered region of length $L_{\rm tap}$=10. Results for various D' are shown. (b) Variation of the free energy difference ΔF_1 (calculated from the functions in (a)) vs r, where $r \equiv D'/D$. The red curve is a polynomial (degree=2) fit to the data. The green line indicates the value of ΔF_2, the overlap free energy per chain of two linear polymers in a channel of diameter D=7. The intersection point of the red and green curves marks the estimated ratio r at which $\Delta F_1 = \Delta F_2$.

IV. LOCATION OF THE FREE ENERGY MINIMUM FOR POLYMERS IN FINITE-LENGTH CHANNELS

As noted in Section 4.2 of the article for the case of polymers confined to cylinders of finite length L, the free energy functions exhibit a minimum value at a location $\lambda_{\min}$ corresponding to the most probable separation distance between the polymers' centres of mass. A simple argument presented in that section suggested that $\lambda_{\min} \approx (L+D)/2$ for both linear and ring polymers. As shown in Fig. 5 below, this scaling is approximately satisfied for polymers of both topologies for various tube diameters and lengths. The likely origin of the slight overestimate is the combined effect of a somewhat stronger lateral confinement at the hemispheric end-cap as well as a small degree of chain overlap at the interface of the polymers, as noted in the article.

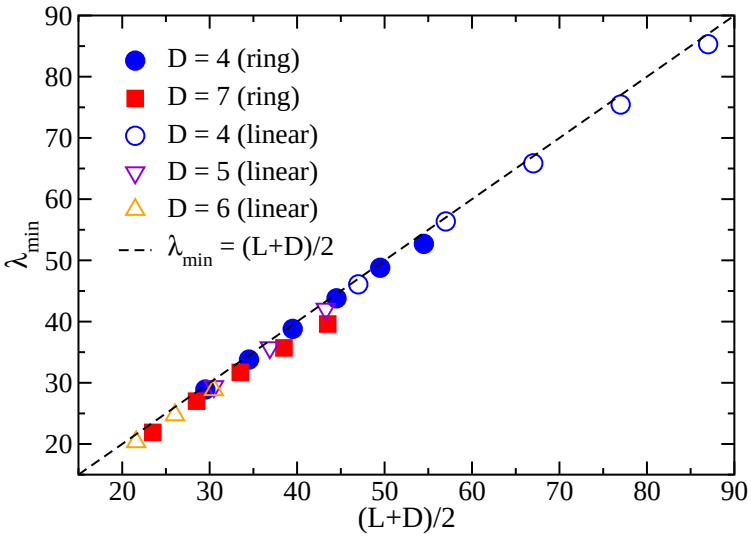

FIG. 5. Free energy minimum centre-of-mass separation $\lambda_{\min}$ vs $(L+D)/2$ for polymers confined to cylinders of finite length. Results are shown for ring and linear polymers of length N=200 for various values of the confinement diameter D.

V. ADDITIONAL RESULTS FOR CONFINED POLYMERS IN THE PRESENCE OF CROWDING

In this section we present additional results for the case of polymers in the presence of crowding that complement the results shown in Section 4.3 of the paper.

Figure 6 shows results for the extension length $L_{\rm ext}$ and the overlap distance, $L_{\rm ov}$ for polymers of length N=80 confined to a tube of diameter D=4 and length L=8. These results were acquired during the same simulations that were used to calculate the free energy curves shown in Fig. 10(b) of the article. The most notable trend is the fact that both the extension length and overlap distance decrease with increasing crowder density.

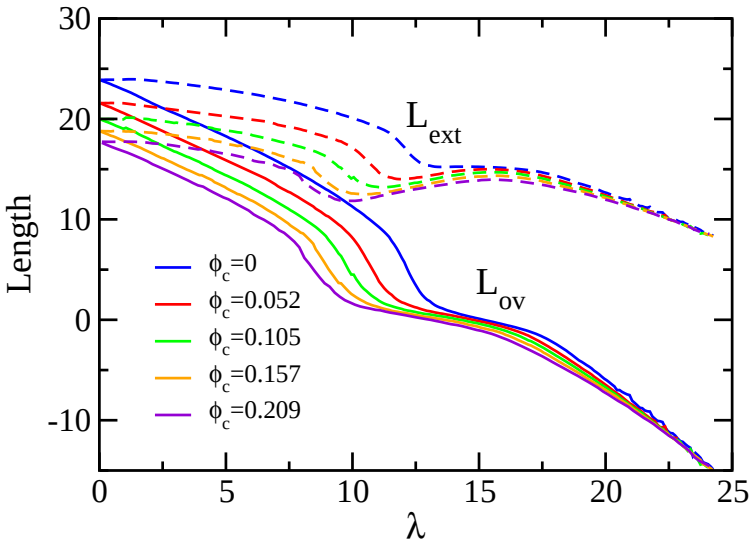

FIG. 6. Variation of extension and overlap lengths for segregating ring polymers in the presence of crowding agents. Results are shown for polymers of length N=80 in a capped tube with D=4 and length L=28. Results for several crowder packing fractions are shown. The crowders each have size $\sigma_{\rm c}$=1.0.

Figure 7 shows the effects of varying the confinement tube length on the segregation free energy function for polymers confined to a tube with a fixed diameter of D=4 and for several lengths. In most cases, an the presence of crowders decreases the free energy barrier ΔF ($\equiv F(0) - F(\lambda_{\rm min})$, where $\lambda_{\rm min}$ is the value of λ at the location of the free energy minimum). However, for sufficiently short tubes (in this case the result for L=14), crowding in fact increases slightly the height of the barrier. These trends are discussed in Section 4.3 of the article.

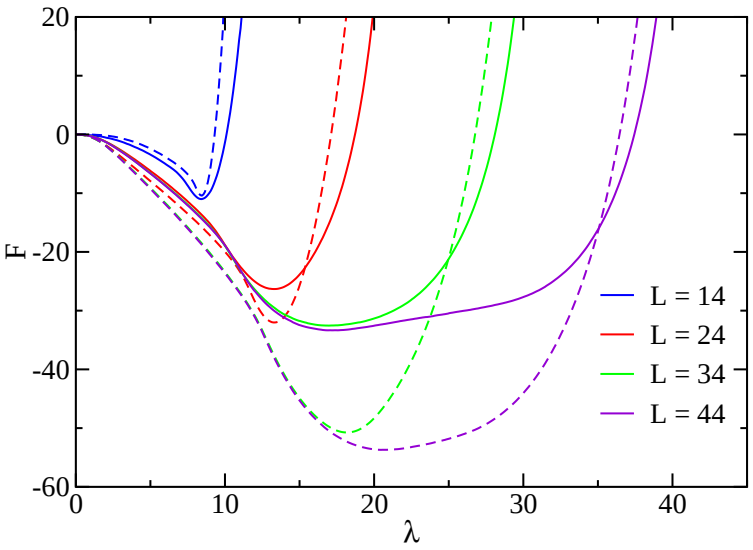

FIG. 7. Free energy vs λ for ring polymers confined in a tube of finite length in the presence of crowding agents. Calculations were carried out for polymers of length N=80 in a confining cylindrical tube of diameter D=4 and with crowders of diameter σ_c=1. Results are shown for crowder packing fraction ϕ_c=0.105 (solid curves) and ϕ_c=0 (dashed curves) for several values of confinement tube length, L.

Figure 8 shows the variation of the extension length with λ for polymers of length N=40 in the presence of crowders of two different sizes. These results were acquired in the same simulations used to calculate the free energy functions shown in Fig. 12 of the article. It is noteworthy that for any given crowder density the extension length *increases* as the crowder size decreases. This effect is related to the increase in the free energy barrier height with decreasing crowder size evident in Fig. 12 of the article, as discussed in Section 4.3.

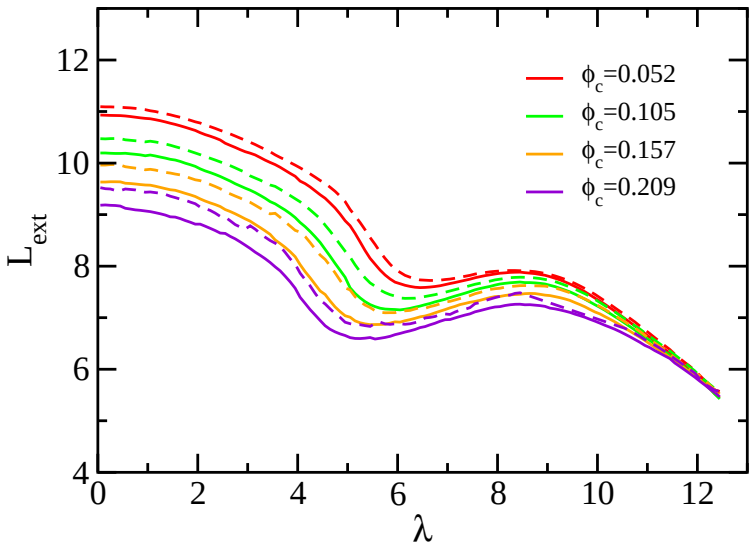

FIG. 8. Variation of extension lengths with λ for segregating ring polymers in the presence of crowding agents. Results are shown for polymers of length N=40 in a capped tube with D=4 and length L=14. Results are shown for several crowder packing fractions are shown with crowders of size σ_c=1.0 (solid curves) and σ_c=0.5 (dashed curves).

REFERENCES

[1]J. Kim, C. Jeon, H. Jeong, Y. Jung and B.-Y. Ha, *Soft Matter*, 2013, **9**, 6142–6150.

[2]Y. Jung, C. Jeon, J. Kim, H. Jeong, S. Jun and B.-Y. Ha, *Soft Matter*, 2012, **8**, 2095–2102.