Repulsion Exerted on a Spherical Particle by a Polymer Brush

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the polymer from 0 at the free end to 1 at the grafted end. This allows the total polymer concentration to be specified as

where 0^{-1} is the volume occupied by each segment. The

The first term integrates the single-chain free energy, $-k_{\rm B}T \ln q_{\rm f}({\bf r}, 1)$, over the grafting distribution, $\sigma\delta(z-\epsilon)$, while the second term subtracts half of the field energy to correct for the usual double counting of the internal energy that occurs in mean-field theory.

To solve the diffusion eq 9, we implement a Crank-Nicholson algorithm in cylindrical coordinates, (

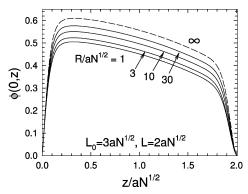


Figure 4. Polymer concentration, $\phi(0, z)$, directly beneath (i.e., $r_{\perp} = 0$) particles of various radii, R, each compressing the brush from a thickness of $L_0 = 3aN^{1/2}$ down to $L = 2aN^{1/3}$. The dashed curve denotes the limit of uniform compression.

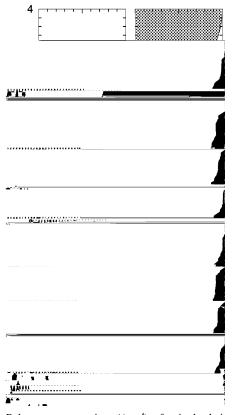


Figure 5. Polymer concentration, $\phi(\mathbf{r}; \mathbf{r}')$, of a single chain grafted at $r'_{\perp} = 0$ and $z' = \epsilon$ in a brush of thickness L_0

that $l(r_{\perp})$ remains nearly constant over lateral distances of $aN^{1/2}$.

The slow convergence does not bode well for the utility of the Derjaguin approximation. However, it is the force that concerns us most, and fortunately the Derjaguin approximation will prove to be far more successful in this regard. Its estimate of the force, eq 32, only requires the free energy penalty of a uniformly compressed brush, which is plotted in Figure 6 for SCFT and SST. As expected, the SCFT predictions approach the SST result (dashed curve) in the limit of $L_0 \rightarrow \infty$, but this convergence is again rather slow. For the realistic brush thicknesses considered in Figure 6, the SCFT interaction begins well before $L=L_0$ due to significant fluctuations about the classical trajectories.^{17,31} The resulting underestimation by SST never really improves even for relatively high compressions.

The compression by finite-sized particles is examined in Figure 7a, by plotting the free energy penalty vs particle radius at a separation of $L = 1.5aN^{1/2}$ and a typical brush thickness of $L_0 = 2aN^{1/2}$. This plot tests the linear dependence on R predicted by the Derjaguin approximation in eq 29, which gives a straight line passing from the origin through the open circle. This and the more accurate Derjaguin approximation in eq 27 both agree nicely with the SCFT prediction using the full 2-dimensional calculation. Furthermore, the agreement extends down to particle sizes of $R \gtrsim 2aN^{1/2}$, which is remarkably better than the previous performance regarding the segment concentrations. If we, however, use the Derjaguin approximation with SST, eq 27 gives the dashed curve while eq 29 predicts a straight line through the filled circle. Although these SST results are consistent with each other, they are more than an order of magnitude too small. Figure 7b shows analogous results for a brush of twice the thickness, $L_0 = 4aN^{1/2}$, at the same relative compression. As expected, the SST-based predictions become more accurate, but they still underestimate the interaction by a factor of \sim 3 even though the brush thickness is beyond typical experimental conditions.

Now that the linear dependence, $\Delta F \propto R$, has been established, Figure 8 examines the energy penalty, ΔF , as a function of compression, L, for particles of a fixed radius, $R=10aN^{1/2}$. Again the full 2-dimensional SCFT predictions (symbols) are well estimated by the Derjaguin approximation in eq 29 when $\Delta f(l)$ is supplied by SCFT (solid curves); even for this modest particle size, the difference is only a few percent. On the other hand, the SST-based prediction in eq 30 (dashed curve) seriously underestimates the interaction energy for brushes of realistic thickness.

IV. Discussion

Our full 2-dimensional SCFT calculation removes the requirement of large particle radius, R, by the Derjaguin approximation and large brush thickness, L_0 , by the SST. Nevertheless, there still remain a few conditions that any application must adhere to. For instance, the spacing between grafting points must be small enough (i.e., $\sigma^{-1/2} \ll aN^{1/2}$) to ensure sufficient overlap among the chains to justify our meanfield treatment, and the brush must be semidilute (i.e., ≤30% concentration) for the self-consistent field condition in eq 5 to be valid. The polymers should also be flexible (i.e., many persistent lengths long) and not overly extended (i.e., much longer than L_0) for the Gaussian chain model to apply. We have also assumed a neutral particle, but an affinity for the solvent is unlikely to have any significant effect other than to slightly widen the depletion zone. On the other hand, a significant tendency to adsorb polymer will modify the interaction.⁵

Experimental brushes generally have unperturbed heights in the range, $L_0/aN^{1/2}\approx 1-3.^{5-8}$ Under such conditions, the SST is the dominant source of inaccuracy in the analytical prediction, eq 30, for the repulsive interaction. Of course, this is inevitable given how the SST seriously underestimates the range and strength of $\Delta f(l)$ in Figure 6. Whitmore and Baranowski

reduce the free energy. Thus, the Derjaguin approximation provides an upper bound for ΔF , and so the true 2-dimensional SST prediction would be even smaller than the dashed curves in Figures 7 and 8. This argument does not strictly extend to the SCFT, because of the finite width of the individual polymer profiles, $\phi(\mathbf{r}; \mathbf{r}')$, as shown in Figure 5. Nevertheless, the full SCFT calculation does predict a softer repulsion than the SCFTbased Derjaguin approximation, except for very small particles with $R \leq aN^{1/2}$. However, the reduction in ΔF is very slight, despite the considerable lateral displacement of segments that occurs in the full SCFT (compare Figures 2 and 3). This is analogous to what happened in an earlier SST calculation for the interaction between two brush-coated spheres.²⁹ Evidently, there is a weak sensitivity to the details of the polymer trajectories that allows the Derjaguin approximation to accurately predict the interaction force for much smaller particles than one should realistically expect.

V. Summary

The steric repulsion on a spherical particle by a planar polymer brush has been predicted using the standard Gaussian chain model for high-molecular-weight polymers with a mean-field treatment appropriate to semidilute brushes. It has been common practice to estimate such forces analytically by adapting the strong-stretching theory (SST) of Milner, Witten, and Cates 12 for uniform compression to curved geometries using the Derjaguin approximation. 10 The SST requires the brush thickness, L_0 , to be large relative to the characteristic polymer size, $aN^{1/2}$