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Notes

Compression of Polymer Brushes: Quantitative Comparison of Self-Consistent Field Theory with Experiment

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Polymeric brushes, formed by densely grafting polymer chains to a surface, have become a convenient means of modifying surface properties.[1] Of particular interest is the steric repulsion created between opposing brushes, which can, for example, be used to stabilize colloidal particles against flocculation caused by attractive van der Waals forces. Taunton et al.[2] were the first to measure the repulsion on a sufficiently well characterized system to allow quantitative comparison with theory. Their experiment measured the force as a function of separation, D, between two crossed cylindrical surfaces of radius, $R \approx 1$ cm, covered by 3.0 ± 0.5 mg/m^2 of tethered polystyrene chains of molecular weight, 141 kg/mol, immersed in toluene solvent.

Taunton at el. initially compared their experimental force to the well-known scaling theory of Alexander and de Gennes,[3] producing good quantitative agreement over several decades using just two fitting parameters. Shortly after, Milner[4] compared the experiment with the strong-stretching theory (SST) that he developed with Witten and Cates.[5] The monodisperse version of SST predicted a somewhat weaker force than what the experiment measured, even when Milner used the upper limit of the surface coverage, 3.5 mg/m^2. He realized, however, that the brush height and thus the force would increase with polydispersity. When Milner accounted for the reported polydispersity index of PDI $\equiv M_w/M_n = 1.02$, the SST provided similar agreement to that of the scaling theory, but without the use of any fitting parameters.

The SST itself is an analytical approximation of the numerical self-consistent field theory (SCFT) of Edwards,[6] obtained by ignoring fluctuations about the most probable chain trajectories (often referred to as classical paths). Milner argued that these fluctuation effects should be less important than the polydispersity effects, suggesting that they could be safely ignored. However, our recent comparisons[7] of SST and SCFT have shown that fluctuations are important for typical experimental conditions. Here we repeat the theoretical comparison to the experiment of Taunton et al., but this time accounting for chain fluctuations with a SCFT calculation as described in ref 7.

To ensure a completely unbiased comparison, we stick with the same parameter values used in the original Letter of Milner,[4] except that we now use the polymer coverage of 3.0 rather than 3.5 mg/m^2. The degree of polymerization is again taken as $N = 1356$, the statistical segment length is set to $a = 7.547$Å, the grafting density is $\sigma = 0.0001281$Å^{-2}, and the excluded volume parameter is $v = 33.66$Å$^3\rho_0$,[8] where ρ_0^{-1} is the segment volume. (Note that we work with 4 significant digits simply to avoid any significant accumulation of rounding errors.)

We begin by examining the dimensionless concentration profile, $\phi(z)$, of an uncompressed monodisperse brush. In SST, it is given by the parabolic shape,

$$\phi(z) = \frac{3aN^{1/2}}{2L^3}(L^2 - z^2) \tag{1}$$

which extends up to the classical brush height of

$$L = N\left(\frac{4a^2 v\sigma}{\pi^2 \rho_0}\right)^{1/3} \tag{2}$$

beyond which $\phi(z \geq L) = 0$. For the given parameters, we obtain $L = 628$ Å, which is about 5% smaller than the value, $L = 662$ Å, used by Milner assuming the upper limit of the experimentally determined surface coverage. Figure 1 compares this SST profile (dotted curve) to the equivalent SCFT profile (dashed curve) calculated with identical parameter values. The fluctuations about the classical paths have two significant consequences. First, they cause a narrow depletion zone of width, $\mu \equiv a^2N/4L \approx 30$Å,[7] next to the substrate, but this is of little relevance to the compression force. Second, they create a tail that extends beyond the classical brush height by a characteristic distance, $\xi \equiv (a^4N^2/L)^{1/3} \approx 200$ Å,[7,9] and this will significantly increase the range of the compression force.

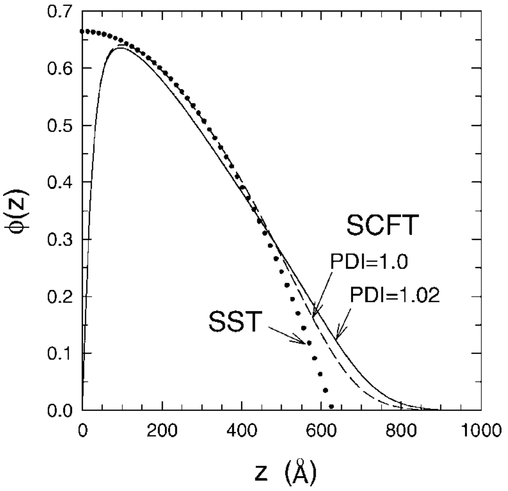

Figure 1. Brush profile, $\phi(z)$, calculated using SST with monodisperse chains (dotted curve) and using SCFT with both monodisperse (dashed curve) and polydisperse (solid curve) chains.

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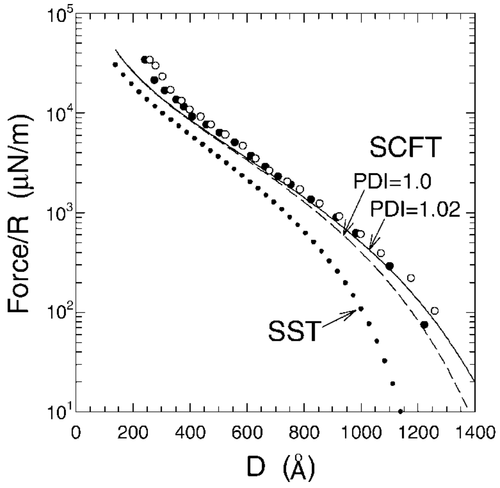

Figure 2. Compression force between two crossed brush-coated cylinders as a function of their separation, D. The curves are calculated for the same three cases in Figure 1, and the symbols denote the experimental measurements by Taunton et al.[2]

To investigate the effect of polydispersity, we employ the method of Cooke and Shi,[10] where the SCFT is expanded in moments of the molecular weight distribution. For such a small polydispersity index of PDI = 1.02, the expansion can be truncated at the second moment (i.e., M_w), avoiding any need to assume a shape for the distribution. The resulting brush profile is shown in Figure 1 with a solid curve. The polydispersity increases the height of the brush by about 30Å or 5%, which is significant but still much smaller than the 10% increase predicted by SST[4] and far smaller than the increase due to chain fluctuations.

Now we evaluate the force between the two crossed brush-coated cylinders of radius, R, as a function of separation, D. For the present case where $R \gg L$, the force can be accurately estimated from the Derjaguin approximation,[11]

$$\text{force} \approx 4\pi\sigma R[f(D/2) - f(\infty)] \tag{3}$$

in terms of the free energy per chain, $f(l)$, of a flat brush compressed to a height of l. In the SST, the free energy per chain is[4]

$$f(l) = \frac{5f_0}{9}\left[\left(\frac{l}{L}\right)^{-1} + \left(\frac{l}{L}\right)^{2} - \frac{1}{5}\left(\frac{l}{L}\right)^{5}\right] \tag{4}$$

for $l < L$ and otherwise

$$f(l \geq L) \equiv f_0 = \frac{9\pi^2 k_B T L^2}{40 a^2 N} \tag{5}$$

Figure 2 compares the resulting SST prediction (dotted curve) for the compression force between monodisperse brushes to the experimental measurements (symbols), assuming a temperature of T = 298 K (25 °C). Now that we are using the best experimental estimate of the surface coverage, the SST seriously underestimates the force. However, this is largely corrected when the chain fluctuations are included using SCFT (dashed curve). The inclusion of polydispersity (solid curve) has a small effect, but nevertheless it does improve the agreement with experiment. With it, the SCFT falls nicely among the experimental data points, except at very high levels of compression. This is likely where the brushes begin to exceed the semidilute concentrations assumed by the theory.

Competing theories such as the Alexander–de Gennes model and the SST for polymer brushes are generally judged by their agreement with experiments. Since experiments have concluded[12] that both theories are similarly capable of quantitatively explaining the compression force, they are sometimes regarded as equally valid. However, there are a number of very good reasons to favor the SST. The Alexander-de Gennes model is based on scaling arguments that start from an assumed profile for the brush, whereas SST actually predicts the shape of the profile from first principles. Furthermore, the SST makes true quantitative predictions whereas the Alexander–de Gennes model requires fitting parameters. Perhaps this strength of the SST was diminished slightly by its need to use the upper limit of the estimated grafting density to achieve a good fit, but this issue has now been resolved with our SCFT calculation.

The only merit that the Alexander–de Gennes model seems to possess over the SST is its treatment of self-avoidance of the polymers using the concept of blobs, defined by the approximate distance between intermolecular contacts. The model assumes that the chain dimensions scale as $N^{0.6}$ (instead of $N^{0.5}$) inside the blobs. Despite this one refinement, there are a number of serious shortcomings. First of all, the model assumes the chains are uniformly stretched with all the chain ends located at the extremity of the brush; the inaccuracy of this approximation is well-known from SST.[4,5] This, in turn, leads to the assumption that all the blobs are of equal size, whereas in fact they should become larger away from the substrate as the polymer concentration decreases. The assumed scaling of $N^{0.6}$ inside the blobs also neglects the fact that the polymer chains are under significant tension. Furthermore, the approach has no obvious way of accounting for chain fluctuations or polydispersity, which we now know are important considerations. Thus the modest correction to the scaling exponent can hardly begin to compensate for the numerous deficiencies in the model. In any case, the SST and SCFT calculations do account for the self-avoidance of chains in an approximate way by the fact that the statistical segment length, a, chosen by Milner[4] was obtained from polymer solutions of a similar concentration to that of the brush.

As for SST and SCFT, there is no judgment to be made regarding which is more accurate, because they are both based on the exact same underlying model and mean-field approximation. Any differences between them are entirely attributable to the mathematical approximations used to simplify the numerical SCFT down to the analytical SST. Still the SST could potentially produce better agreement with experiment for particular quantities due to an accidental cancelation of the various inaccuracies, but even so it would never make any logical sense to suggest that SST is more accurate than SCFT. In any case, the SCFT did produce the better agreement with experiment, as expected.

In summary, we have compared SCFT predictions for the force between semidilute brushes to the benchmark experiments of Taunton et al.[2] The comparison was done with previously established parameters, and without any fitting parameters whatsoever. The SCFT provides a significant quantitative improvement over SST, yielding excellent agreement with the experiment. Contrary to the previous conclusion in ref 4, the effect of polydispersity is relatively small but the effect of chain fluctuations is far too large to ignore. Although the analytical expressions of SST provide invaluable aids to understanding the qualitative behavior of polymeric brushes, the numerical SCFT is necessary in order to provide quantitatively accurate predictions for normal experimental conditions.

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