Supporting Text: Alexander–de Gennes (AdG) Theory

Microscopic detail of polymer brushes is obtained by fitting force data to the AdG theory (1). Based on the AdG theory, the force per unit area (*f*) (i.e., pressure) between two surfaces with adsorbed or grafted polymer brushes is given by (2)

$$f = P(D) = \frac{k_B T}{s^3}\left[\left(\frac{2L}{D}\right)^{9/4} - \left(\frac{D}{2L}\right)^{3/4}\right] \quad \text{for } D < 2L$$

where k_B is Boltzmann's constant, T is temperature, s is the mean spacing between grafting points, D is the distance between two surfaces, and L is the equilibrium thickness of the polymer brush. The first term comes from the osmotic pressure, which increases as the two surfaces approach each other, and the polymer concentration increases. The second term accounts for the decrease in elastic energy as the chains are compressed.

For $D/2L$ in the range of 0.2–0.9 the above pressure is roughly exponential and is adequately given by

$$P(D) \approx \frac{100 k_B T}{s^3} e^{-\pi D/L}.$$

In the case where only one surface is covered, the AdG equation can then be rewritten by substituting $2D$ for D and dividing the right-hand side by 2 (3, 4). Over the restricted range of $0.2 < D/L < 0.9$,

$$P(D) \approx \frac{k_B T}{2s^3}\left[\left(\frac{L}{D}\right)^{9/4} - \left(\frac{D}{L}\right)^{3/4}\right] \approx \frac{50 k_B T}{s^3} e^{-2\pi D/L}.$$

This approximation essentially ignores the strong osmotic repulsive forces resulting from the compression of the polymer chains at $D < 0.2$.

To find an expression for the force F, the geometry of the AFM tip can be assumed to be spherical (with a radius of curvature R_{tip}) with an effective interaction area A_{eff} given by $A_{eff} = 2\pi R_{tip} D$ (2). By replacing P by F/A, one obtains

$$F = \frac{100\pi R_{tip} D}{s^3} k_B T e^{-2\pi D/L}.$$

To further account for the geometry of the tip–Au nanodot interaction, R_{tip} is replaced by $R_{eff} = (R_1 R_2)/(R_1 + R_2)$, where R_1 and R_2 represent the radius of the tip and nanodot, respectively (2).

1. De Gennes, P. G. (1987) *Adv. Colloid Interface Sci.* **27,** 189–209.
2. Israelachvili, J. N. (1995) *Intermolecular and Surface Forces* (Academic, London).
3. O'Shea, S. J., Welland, M. E. & Rayment, T. (1993) *Langmuir* **9,** 1826–1835.
4. Butt, H. J., Kappl, M., Mueller, H., Raiteri, R., Meyer, W. & Ruhe, J. (1999) *Langmuir* **15,** 2559–2565.