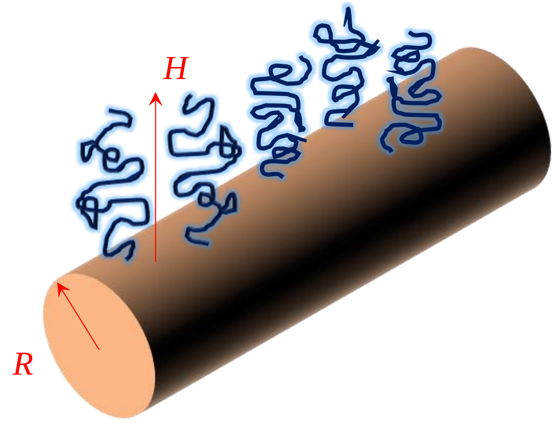
Polymer brushes on cylinders

The first models for polymer brushes assumed a perfectly planar surface, which reduces the problem to one dimension. However, one often wants to modify surfaces of nanostructured materials with polymers brushes. Surface curvature then comes into play. In this problem you will investigate a polymer brush on a *cylinder* (a nanowire) with radius R comparable to the contour length of the polymer. The cylinder is considered to be long enough so that the coils in the middle do not sense any edge effects.

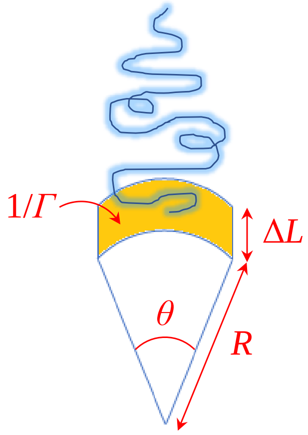


(A) Derive an expression for the free energy G as a function of brush extension h, which besides a, N and Γ now also should be a function of R. You can use the same conformational and excluded volume entropy arguments as in the lectures. (The solvent does not have to be considered and the segment volume is a^3.)

Hint: To see if your answer is reasonable, check what happens when $R \rightarrow \infty$.

(B) Plot $G(h)$ for the case of a = 2 nm, N = 100 and Γ = 0.2 nm^{-2} for some suitable values of R such that the influence from surface curvature becomes clear. (Use MATLAB or similar software.) Describe qualitatively how the equilibrium brush height and free energy change when comparing with a planar surface!

The conformational entropy is treated as for a planar surface. The difference comes in the excluded volume term where we now need to use another expression for the volume that each coil occupies. A unit area on the cylinder that corresponds to one coil will give to a certain angle θ to the center of the cylinder and a certain length ΔL along its axis:



Thus we see that the area is:

$$\frac{\theta}{2\pi} \times 2\pi R \Delta L = \frac{1}{\Gamma}$$

The volume that the coil occupies is given by considering the two "cake slices" represented by cylinder plus brush and cylinder only:

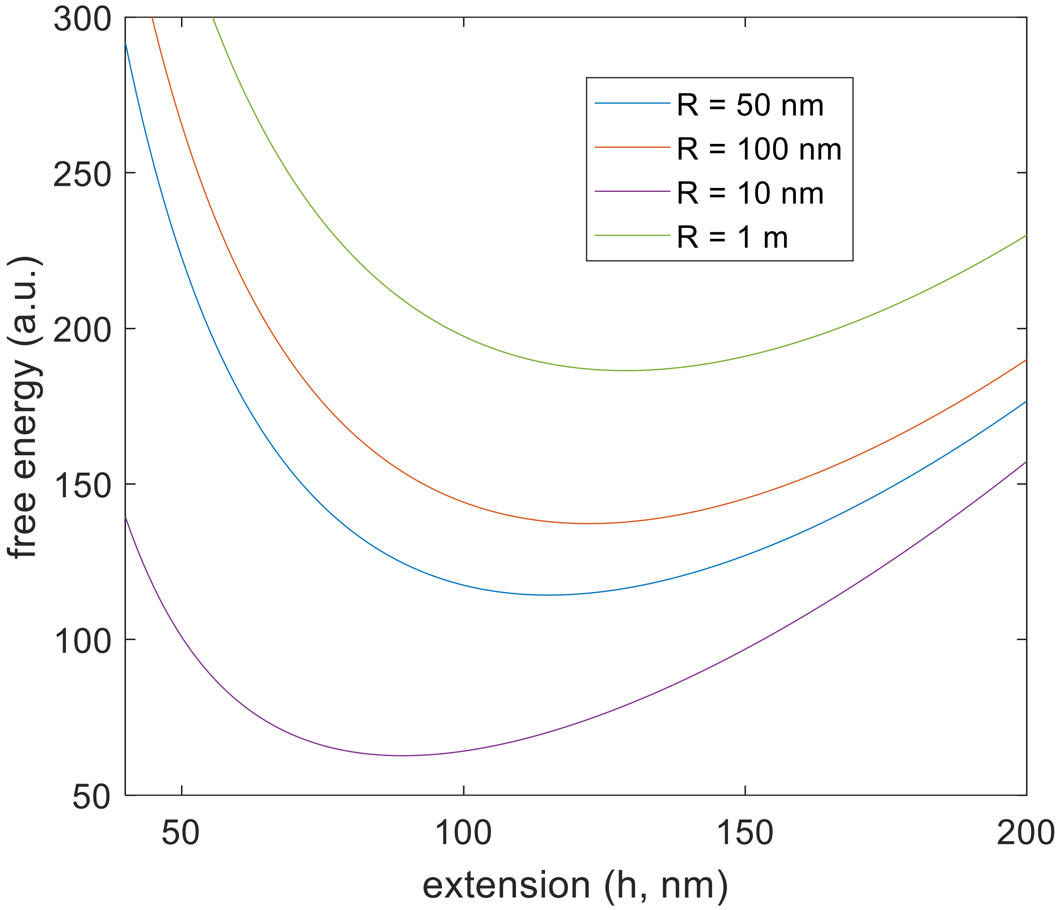
$$V = \frac{\theta}{2\pi} \times \pi [R+h]^2 \Delta L - \frac{\theta}{2\pi} \times \pi R^2 \Delta L = \frac{\theta \Delta L}{2}\left[2Rh + h^2\right] = \frac{h}{\Gamma} + \frac{h^2}{2\Gamma R}$$

Using this value for the excluded volume term the total free energy becomes:

$$\frac{G(h)}{k_B T} = \frac{3h^2}{2Na^2} + \frac{\Gamma N^2 a^3}{h + \frac{h^2}{2R}} + \text{constant}$$

For $R \to \infty$ we get a planar surface and indeed the second term in the denominator disappears so that the usual expression is recovered.

Plots of $G(h)$ show that the brush extends *shorter* as R decreases and that the free energy *decreases* due to the surface curvature. (Follow the position of the energy minimum.) In the cylindrical geometry the coils do not need to stretch out so much to get the extra volume they want and the free energy is reduced due to the extra space available.



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