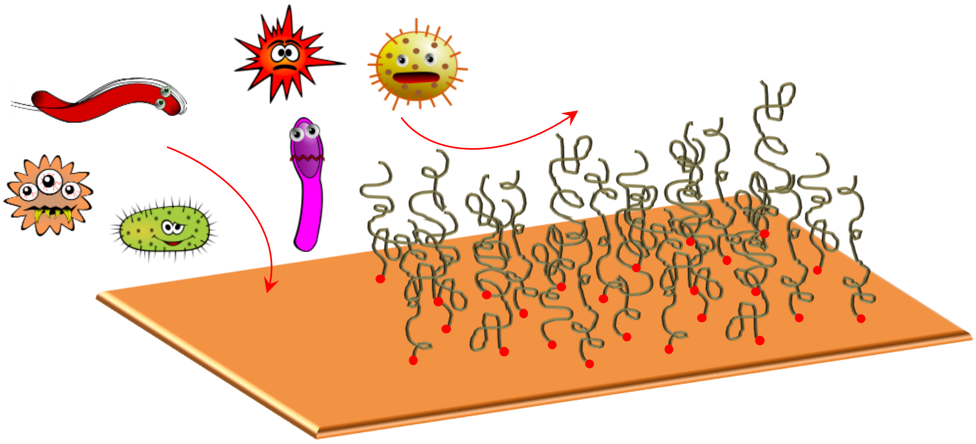
Polymer Brushes as Inert Surface Coatings

In many applications such as implants and biosensors, it is important to have a surface onto which molecules from a biological sample cannot adsorb. This is often referred to as "non-fouling" surfaces. More specifically, one wants to prevent cells and proteins from attaching to the surface. This can be achieved with hydrophilic polymer brushes. It is not straightforward to fully understand why the brush prevents for instance a protein to adsorb on the underlying surface (which is what happens otherwise for most proteins on most surfaces). However, one clear contribution to the non-fouling properties of polymer brushes is that any molecule stuck to the surface will reduce the entropy of the coils. The purpose of this task is to develop a model describing how the entropic effects of the brush can prevent molecular adsorption.



(A) Assume an initial state corresponds to a brush in equilibrium and no molecules adsorbed on the surface. If protein molecules, each with a volume v_p = 100 nm^3 would adsorb on the surface to a coverage Γ_p = 0.05 nm^{-2} what is the change in height of the brush only due to excluded volume entropy loss? The polymer coverage is Γ = 0.1 nm^{-2}, the monomer length a = 1 nm (can be treated as Kuhn steps) and the degree of polymerization N = 100. The temperature is T = 300 K and χ = 0. (Assume a strongly stretched brush analogous to the Alexander - de Gennes model described in the course.)

(B) If some proteins still adsorb, this must be mediated by a free energy decrease of attachment. Assume this contribution is enthalpic with $\Delta H_{ads} = -10k_BT$ per protein (at 300 K). If the polymer brush from above establishes equilibrium with the protein solution, what is the surface coverage of protein molecules? (Assume the same v_p but calculate a new Γ_p.)

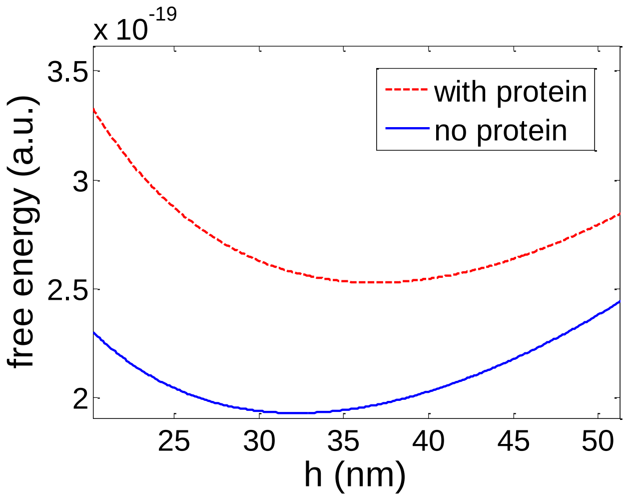
(A) If $\chi = 0$ the solvent can be ignored. If there are proteins attached to the surface, there is an additional excluded volume entropy loss for the polymer. The initial volume is h/Γ and with proteins and the polymer itself $h/\Gamma - Nv - \Gamma_{\mathrm{p}} \times 1/\Gamma \times v_{\mathrm{p}}$. This means that the entropy loss per segment is:

$$\Delta S_{\mathrm{vol}} = k_{\mathrm{B}} \log\left(\frac{\frac{h}{\Gamma} - Nv - \frac{\Gamma_{\mathrm{p}}}{\Gamma}v_{\mathrm{p}}}{\frac{h}{\Gamma}}\right) = k_{\mathrm{B}} \log\left(1 - \frac{Nv\Gamma}{h} - \frac{\Gamma_{\mathrm{p}}v_{\mathrm{p}}}{h}\right) \approx -k_{\mathrm{B}}\left[\frac{Nv\Gamma}{h} + \frac{\Gamma_{\mathrm{p}}v_{\mathrm{p}}}{h}\right]$$

Here we assume the volume fraction of proteins is also small. Next we need to multiply with T, change sign, replace v with a^3 and multiply with N as in the regular derivation. The conformational entropy of stretching is be the same so the new free energy of the brush is:

$$G_{\mathrm{tot}}(h) = \frac{3k_{\mathrm{B}}Th^2}{2Na^2} + \frac{\Gamma k_{\mathrm{B}}TN^2a^3}{h} + \frac{k_{\mathrm{B}}TN\Gamma_{\mathrm{p}}v_{\mathrm{p}}}{h} + \mathrm{constant}$$

If $\Gamma_{\mathrm{p}} = 0$ we recover the previous expression. The brush height can be solved for numerically by a plot with the given values. The constant can be set to zero as it has no influence on the minimum.



Comparing the minima gives an increase in brush height of approximately 4.6 nm and an increase in free energy overall.

Note: The expression for $G(h)$ could look slightly different depending on assumptions made, but it must be based on an excluded volume calculation that introduces the volume of the proteins. To be reasonable the model should give an increased height and energy. Also, the regular brush model should be recovered if $\Gamma_{\mathrm{p}} = 0$.

(B) There will be a free energy decrease of $\Gamma_\mathrm{p}\times 1/\Gamma\times\Delta H_\mathrm{ads}$ due to adsorption at each coil. This modifies the expression for $G(h)$ to:

$$G_\mathrm{tot}(h)=\frac{3k_\mathrm{B}Th^2}{2Na^2}+\frac{\Gamma k_\mathrm{B}TN^2a^3}{h}+\frac{k_\mathrm{B}TN\Gamma_\mathrm{p}v_\mathrm{p}}{h}-\frac{\Gamma_\mathrm{p}}{\Gamma}\Delta H_\mathrm{ads}+\text{constant}$$

If we use ΔH_ads = -10$k_\mathrm{B}T$ and let Γ_p vary we can see that the h which minimizes G varies, but also the value of G at the minimum. In principle we need to minimize G with respect to two variables. However, testing out some values shows that the minimum value of G always increases with Γ_p, which means that no adsorption should happen even at equilibrium.

Note: This part was not so well designed. It was supposed to give a more interesting result with a minimum in G for some value of Γ_p (and an associated value of h) but I made a mistake when I tested the model. A better question would be e.g. what enthalpy value that would result in adsorption. However, if a slightly different excluded volume expression is used one can get a result which does show a minimum in G.