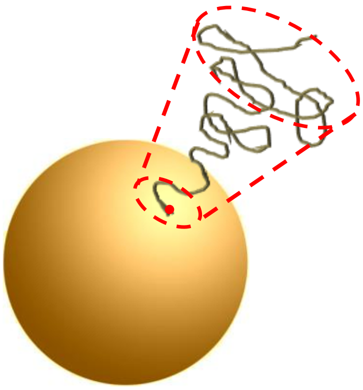
Polymer Brushes on Nanoparticles

One way to modify the properties of suspensions with nanoparticles is to coat them with polymers. This is of interest for instance in drug delivery by nanoparticles and other types of “nanomedicine”, where one wishes to prevent protein adsorption on the particles. Typically, a hydrophilic polymer like poly(ethyleneglycol) is grafted to the nanoparticles. However, when the particle size is similar to the contour length of the polymer, the brush morphology is strongly affected and ordinary theory for planar surfaces breaks down.

The purpose of this task is to develop a model for how thick brush one expects on a nanoparticle with radius R. The model assumes a strongly stretched brush and is analogous to the Alexander - de Gennes model described in the course (for planar surfaces).



(1) Derive an expression for the volume of one individual coil in the brush expressed as brush height h (m), surface coverage Γ (m^{-2}) and nanoparticle radius R (m).

Tip: Spherical symmetry can be utilized with coordinates of radius ($r > 0$), polar angle ($0 < \theta < \pi$) and azimuthal angle ($0 < \varphi < 2\pi$). The infinitesimal area element on a sphere is then $dA = r^2\sin(\theta)d\theta d\varphi$ and the volume element becomes $dV = dAdr$.

(2) Write the total free energy as a function of h, taking into account conformational entropy, excluded volume and solvent interactions. What happens when $R \rightarrow \infty$ in your expression?

Tip: Follow the derivation in polymer lecture 2.

(3) Determine the brush height H that minimizes the free energy graphically or numerically for $a = 1$ nm, $N = 1000$, $\chi = 0$, $\Gamma = 1$ nm^{-2} and $R = 10$ nm at room temperature. Compare with the result for planar surface and discuss the influence from surface curvature qualitatively.

(1) Derive an expression for the volume of one individual coil in the brush expressed as brush height *h* (m), surface coverage Γ (m^{-2}) and the radius *R* (m) of a spherical nanoparticle.

→

The area element for one coil in the spherical coordinate system is:

$$A=\int_{\varphi_1}^{\varphi_2}\int_{\theta_1}^{\theta_2} r^2\sin\theta \mathrm{d}\theta \mathrm{d}\varphi = r^2\int_{\varphi_1}^{\varphi_2}\{-\cos(\theta)\}_{\theta_1}^{\theta_2}\mathrm{d}\varphi = r^2\int_{\varphi_1}^{\varphi_2}\cos(\theta_1)-\cos(\theta_2)\mathrm{d}\varphi = r^2[\varphi_2-\varphi_1][\cos(\theta_1)-\cos(\theta_2)]$$

Here written for some arbitrary angular intervals for θ and φ. On the particle surface $r = R$ and we get:

$$\Gamma=\frac{1}{A(r=R)}=\frac{1}{R^2[\varphi_2-\varphi_1][\cos(\theta_1)-\cos(\theta_2)]}$$

Integrating for the volume:

$$V=\int_R^{R+h}A(r)\mathrm{d}r=\int_R^{R+h}r^2[\varphi_2-\varphi_1][\cos(\theta_1)-\cos(\theta_2)]\mathrm{d}r=[\varphi_2-\varphi_1][\cos(\theta_1)-\cos(\theta_2)]\int_R^{R+h}r^2\mathrm{d}r$$

$$=\frac{1}{\Gamma R^2}\int_R^{R+h}r^2\mathrm{d}r=\frac{1}{\Gamma R^2}\left\{\frac{r^3}{3}\right\}_R^{R+h}=\frac{[R+h]^3-R^3}{3\Gamma R^2}=\frac{3R^2h+3Rh^2+h^3}{3\Gamma R^2}$$

(2) Write the total free energy as a function of *h*, taking into account conformational entropy, excluded volume and solvent interactions. What happens when $R\to\infty$ in your expression?

→

The conformational entropy term is the same as for a regular brush. The height is assumed to be the end to end distance of the coil and thus:

$$E_{\mathrm{con}}=\frac{3k_{\mathrm{B}}Th^2}{2Na^2}$$

For the excluded volume and solvent interactions, the volume (h/Γ) for a planar surface brush is replaced by the volume calculated above. This leads to the total free energy:

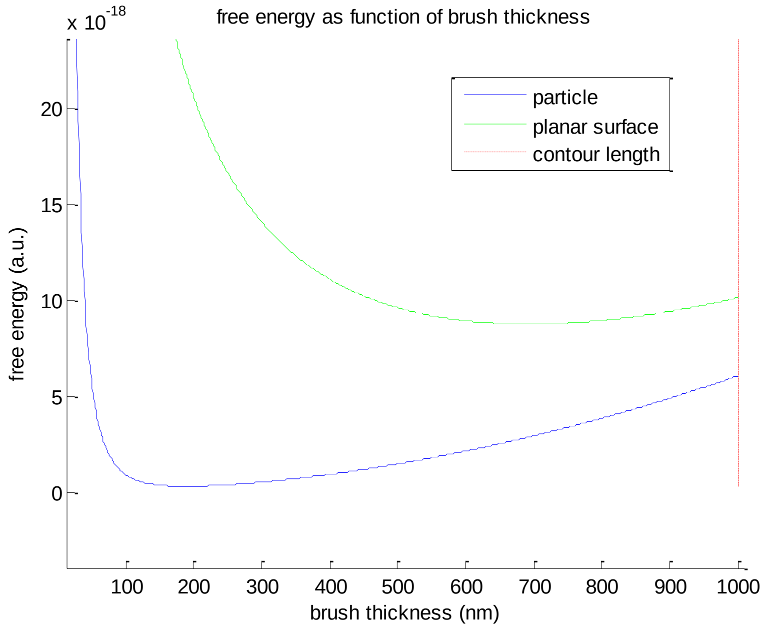
$$E_{\mathrm{tot}}=\frac{3k_{\mathrm{B}}Th^2}{2Na^2}+k_{\mathrm{B}}T[1-2\chi]N^2a^3\frac{3\Gamma R^2}{3R^2h+3Rh^2+h^3}+\mathrm{constant}$$

When $R\to\infty$ it can be seen that only a Γ/h term remains and the expression for a planar surface is recovered.

(3) Determine the brush height *H* that minimizes the free energy graphically or numerically for a = 1 nm, N = 1000, χ = 0, Γ = 1 nm^{-2} and R = 10 nm at room temperature. Compare with the result for a planar surface and discuss the influence from surface curvature qualitatively.

→

Plot of the expression for free energy as a function of *h* (constant set to zero):



H is approximately 190 nm. The brush on the particle is much thinner and has lower energy because of the higher amount of free volume available in the spherical system.

Notes: Part 1 can be actually solved easily without spherical coordinates by considering that the total brush volume is the outer sphere (with brush) minus the inner sphere (particle). This gives the volume per coil when the surface area and grafting density are known. The values in part 3 are a bit extreme in terms of surface coverage and leads to an unreasonable volume fraction of polymer. The fact that one has room temperature does not matter since the absolute energy is anyway unknown.