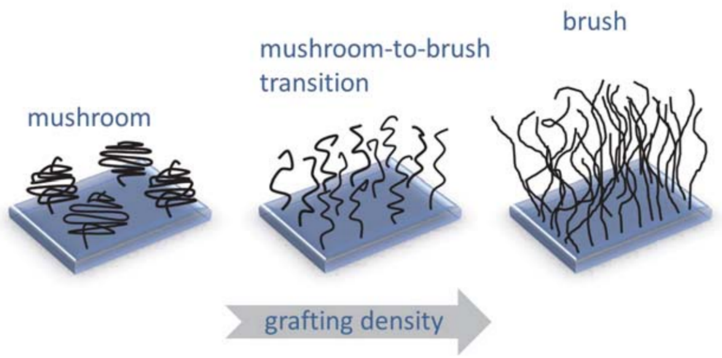
5th Tutorial on MD - Inclusion Free Energy of a Nanoparticle in a Polymer Brush

Using LAMMPS we will calculate the free energy of inclusion $\Delta F_{\text{inclusion}}$ of a nanoparticle entering a polymer brush. You receive a LAMMPS script `in.brush` and a starting configuration of a polymer brush `brush.data`.

Brush Parameters and Basic Properties

1.) Use the provided information to calculate the grafting density σ of the brush. It is defined as the number of grafted chains per unit area, $\sigma = n_{\text{chains}}/A$.

2.) Is this system a polymer brush or not? Hint: One way to judge this is to estimate the overlap grafting density $\sigma^*=1/(\pi R_g^2)$ assuming ideal chain statistics with $R_g^2 = Nb^2/6$.



[1]

3.) After equilibrating the system, calculate a density profile $\rho(z)$ of the polymer brush, i.e. a histogram of all monomers in the brush along z. Also, calculate the probability density of the end monomers of the brush chains. Choose a suitable normalization in each case. Where are the end monomers located in the brush? What insight to we gain about the predominant chain conformations in the brush?

Adding a Nanoparticle (NP) to the System

4.) Edit the provided starting configuration in such a way, that an additional atom, the NP, is located above the brush. Introduce an additional atom type and assign the NP to this type. Set the radius of the particle to $R = 3.0$ in order to simulate a nanoparticle (Hint: `pair_style lj/extend`). Set up the pair potential in such a way that the NP has purely repulsive interactions with the other particles in the system.

The particle does not want to enter the brush due to the repulsive interactions and the maximization of entropy. In order to quantify this effect we want to calculate the force and free energy required for the partice to go into the brush. Since such an event is statistically extremely improbable to happen spontaneously it is difficult to sample it and perform measurements. We will therefore use a technique called **"Umbrella sampling"**, which makes it possible to sample rare phenomena.

[1]Image source: Y.Yu, Switchable Adhesion and Friction By Stimulus Responsive Polymer Brushes (2017), doi: 10.3990/1.9789036542807

Force Profile and Free Energy of Inclusion of the NP

5.) Attach the NP to a harmonic spring along z by using the LAMMPS command `fix spring`. This will expose the NP to a potential of the form $U(z) = \frac{1}{2}k_0(z - z_o)^2$. Therefore the average z-position of the NP is fixed near a value $z_0$of our choice. Start a few separate simulations, where you attach the particle at different z_0 (3 - 5 simulations, but more are better). Measure the average displacement $\langle z - z_0\rangle$from the equilibrium position of the spring and the average vertical force $\langle F_z\rangle(z_0) = \langle k_0(z - z_0)\rangle$ on the particle for each simulation.

6.) Plot the resulting curve $\langle F_z\rangle(z_0)$, i.e. the vertical force as a function of the z-coordinate of the particle. What shape does this force-distance profile have? Where does the NP experience the strongest repulsive force and why?

7.) Integrate the force profile numerically to calculate the free energy of inclusion of a NP, $\Delta F_{\text{inclusion}} = \int_{z_{\text{outside}}}^{z_{\text{inside}}} F_z(z)dz$. This can be done, for example, by using the trapezoidal rule.