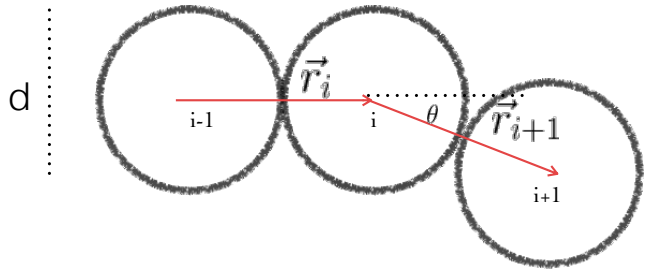
Homework 6

Flexural Rigidity induced by Excluded Volume Interaction

In this exercise, we will consider a "hybrid" chain, where excluded volume interactions are considered only between monomers which are close along the chain. More specifically, let us consider a chain embedded in a two-dimensional space (e.g. deposited on a surface), where each monomer is a hard sphere of diameter d.
In the simplest case, the chain is obtained by attaching one after the other such spheres, which are put in contact with each other, i.e. the distance between the centers of two consecutive monomers is d (see figure). Let $\vec{r}_i$ be the vector connecting the centers of monomers $i-1, i$. When choosing the orientation of $\vec{r}_{i+1}$, only the excluded volume interaction between monomers $i-1, i, i+1$ is taken into account. Namely, the angle θ is taken with uniform probability distribution in the range where no overlaps between two of such monomers are seen. Anyway, for simplicity we neglect the possibility of excluded volume interaction with further monomers along the chain.



1. Show that the excluded volume imposes to take $\theta \in [-\theta_{max}, \theta_{max}]$ and calculate the value of θ_{max}.

2. Show that the excluded volume interaction induces a stiffness in the polymer chain (i.e. that $< \vec{r}_i \cdot \vec{r}_j > \neq 0$ even for $i \neq j$) and calculate its persistence length.

Now imagine that in constructing the chain, two consecutive monomers are placed at a distance $l \geq d$. In other words, the spheres do not touch anymore each other. Go again through points 1 and 2 within this generalized model. What happens for $l/d \to \infty$?

Ideal Chain with Constraints[1]

Let us consider a Freely-Jointed Chain, and let us denote by $\vec{R}_1$ the position vector of one end of the chain. The probability distribution for the other end to be found at position $\vec{R}$ is

$$P\left(\vec{R}\right) = \left(\frac{3}{2\pi N b^2}\right)^{\frac{3}{2}} e^{-\frac{3(\vec{R}-\vec{R}_1)^2}{2Nb^2}} \tag{1}$$

where N is the number of monomers composing the chain, and b is the bond length. Now, suppose to fix once and for all the two ends of the chain at positions $\vec{R}_1$ and $\vec{R}_2$ respectively. Under the assumption $s, N - s \gg 1$, show that the probability for the s^{th} monomer (starting to count from the first end) to be found at position $\vec{R}$ is given by

$$P_s\left(\vec{R}\right) = \left(\frac{3}{2\pi K_s b^2}\right)^{\frac{3}{2}} e^{-\frac{3(\vec{R}-\vec{R}_s)^2}{2K_s b^2}} \tag{2}$$

where

$$K_s \equiv \frac{s(N-s)}{N} \tag{3}$$

and

$$\vec{R}_s \equiv \frac{N-s}{N}\vec{R}_1 + \frac{s}{N}\vec{R}_2 \tag{4}$$

Equation (2) tells essentially that the position vector of a monomer in the middle of the chain still follows a gaussian distribution, but with "renormalized" mean position and variance. Use this result to compute the probability to find the $(N/2)^{th}$ monomer at distance D from the 0^{th} monomer of an ideal ring polymer. For short distances, is it lower or larger than the probability of a linear polymer of length $N/2$ to have the same value of D? When are the two probabilities equal?

[1] Adapted from M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.