Homework 3
03/10/2013

(Gaussian) Freely Jointed Chain with Varying Step Length

Consider a freely jointed chain in d dimensions, but let each bond vector $\vec{r}_i$ be drawn from the Gaussian probability distribution

$$p(\vec{r}) = \frac{1}{(2\pi a^2)^{\frac{d}{2}}} e^{-\frac{\vec{r}^2}{2a^2}} \ .$$

Find the probability distribution of the end to end distance $\vec{R}_e = \sum_{i=1}^{N} \vec{r}_i$ and calculate $\langle \vec{R}_e^2 \rangle$.
Hint: remember that the Gaussian integral in d dimensions is $\int d\vec{r}\, e^{-\alpha \vec{r}^2} = (\pi/\alpha)^{d/2}$.

Equivalent Freely Jointed Chain

A common feature of all ideal chains is that the mean square end-to-end distance is proportional to the number of monomers, i.e. $\langle R_{end}^2 \rangle \propto n$.
The simplest ideal chain is the *freely jointed chain model* with constant bond length l; it has $\langle R_{end}^2 \rangle = nl^2$ and its maximum end-to-end distance is $R_{max} = nl$.
Any ideal polymer made of n bonds of length l can be "macroscopically" described by an **equivalent freely jointed chain** made by N freely-jointed bonds of effective length b and with the same $\langle R_{end}^2 \rangle$ and R_{max} of the actual polymer. The length of the effective bond b is called the **Kuhn length** of the polymer.
Calculate the Kuhn length of:

1. the model of the homework 2, i.e.$\langle R_{end}^2 \rangle = nl^2 \frac{1+\epsilon}{1-\epsilon}$, $R_{max} = ?$;
2. the freely rotating chain with fixed bond angle θ, i.e. a chain where the angle θ_i formed by segments $\vec{r}_i$ and $\vec{r}_{i+1}$ is fixed to a certain value θ, while the angle ϕ_i is taken uniformly in $[0, 2\pi]$. In this case, it is easy to show (do it!) that $\langle R_{end}^2 \rangle = nl^2 \frac{1+\cos\theta}{1-\cos\theta}$. Who is $R_{max} = ?$;
3. a polyethylene chain with a fixed bond angle $\theta = 68°$, (actual) bond length $l = 1.54\,\text{Å}$, $\frac{\langle R_{end}^2 \rangle}{nl^2} = 7.4$, and the same R_{max} as for the freely rotating chain.

The double-stranded DNA has a bond length of about $l \approx 3\,\text{Å}$ and a Kuhn length $b \approx 100\,nm$. If we model it as a freely rotating chain, what is the approximate value of the bond angle θ?
Hint: is the double-stranded DNA a stiff polymer? What does this tell us about θ?

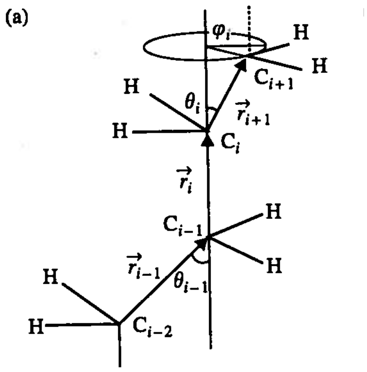

Figure 1: In the freely rotating chain model the angle θ is fixed once and for all (from *Polymer Physics*, M.Rubinstein and R.H.Colby).