Statistics of a flexible polymer

Consider a flexible polymer chain in three dimensions. The chain is composed of consecutive straight segments, all of equal length l, each denoted by the vector $\vec{R}_i, i = 1, \ldots, N$. At segment joints, the two segments are free to equally rotate in any orientation, however, there is a correlation on the plane defined by the two segments

$$\langle \vec{R}_{i+1} \cdot \vec{R}_i \rangle = l^2 \cos\alpha,$$

where the constant α is the average angle between two consecutive segments.

1. Show that
$$\langle \vec{R}_{i+2} \cdot \vec{R}_i \rangle = l^2 \cos^2\alpha.$$

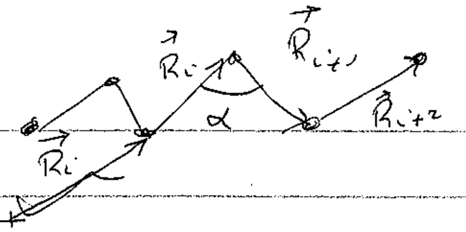
2. Given that the end to end distance on the chain can be written as $\vec{R} = \sum_{i=1}^{N-1} \vec{R}_i$, show that,
$$\langle R^2 \rangle = (N-1)l^2 \left[\frac{1+\cos\alpha}{1-\cos\alpha} - \frac{2\cos\alpha}{N-1} \frac{1-(\cos\alpha)^N}{(1-\cos\alpha)^2} \right]$$

3. In the long chain limit, $N \gg 1$ and for small α, show that the average square end to end distance reduces to
$$\langle R^2 \rangle = 2Nll_p = (Nl/2l_p)(2l_p)^2,$$
by defining $l_p \approx 2l/\alpha^2$. This is precisely the result for a freely jointed chain of $Nl/2l_p$ segments of length $2l_p$. Provide an interpretation of this result.

08-NOV-2019

Imagine now steps are correlated : ~~$\langle u_{i+1}\cdot u_i\rangle = l^2\cos\alpha$~~

$$\langle \vec{R}_{i+1}\cdot\vec{R}_i\rangle = l^2\cos\alpha$$



Angle between to successive segments is α ~~on~~ average. BUT: this is on the $(\vec{R}_i, \vec{R}_{i+1})$ plane. The next segment is free to rotate around any angle.

We now compute the end to end distance:

$$\vec{R} = \sum_{i=1}^{N-1}\vec{R}_i \quad \text{so that} \quad \langle R^2\rangle = \left\langle \left(\sum_{i=1}^{N-1}\vec{R}_i\right)^2\right\rangle =$$

$$= \sum_{i=1}^{N-1}\langle R_i^2\rangle + \sum_{i,j\neq i}^{N-1}\langle \vec{R}_i\cdot\vec{R}_j\rangle$$

fixed length segments

$$= (N-1)l^2 + \sum_{i,j\neq i}^{N-1}\langle \vec{R}_i\cdot\vec{R}_j\rangle$$

We need to evaluate the correlation between distant segments.

$$\langle \vec{R}_{i+2}\cdot\vec{R}_i\rangle = \langle \vec{R}_{i+2}\cdot\underbrace{\vec{R}_{i+1}\cdot\vec{R}_{i+1}}_{l^2}\cdot\vec{R}_i\rangle\frac{1}{l^2} =$$

no orientation correlation between $(i+2)$ and i (freely jointed)

$$= \langle \vec{R}_{i+2}\cdot\vec{R}_{i+1}\rangle\langle\vec{R}_{i+1}\cdot\vec{R}_i\rangle\frac{1}{l^2} =$$

$$= l^2\cos\theta\, l^2\cos\theta\frac{1}{l^2} = l^2(\cos\theta)^2$$

$$\Rightarrow \quad \langle \vec{R}_i\cdot\vec{R}_j\rangle = l^2(\cos\theta)^{|j-i|}$$

$$\Rightarrow \quad \boxed{\langle R^2\rangle = (N-1)l^2 + l^2\sum_{i,j\neq i}^{N-1}(\cos\theta)^{|j-i|}}$$

Sum the geometric series. $\displaystyle\sum_{k=0}^{n-1} ar^k = a\left(\frac{1-r^n}{1-r}\right)$

$$\langle R^2\rangle = (N-1)\ell^2 + \ell^2\left[\sum_{i=1}^{N-1}\left(\sum_{j=1}^{i-1}(\cos\theta)^{i-j} + \sum_{j=i+1}^{N-1}(\cos\theta)^{j-i}\right)\right]$$

See next page

$$\overset{?}{=} (N-1)\ell^2 + \ell^2\left[\sum_{i=1}^{N-1}\left(\frac{1-(\cos\theta)^i}{1-\cos\theta} - 1 + (\cos\theta)^i\,\frac{1-(\cos\theta)^{N-i-1}}{1-\cos\theta}\right)\right]$$

$$= (N-1)\ell^2 + \ell^2\left\{\sum_{i=1}^{N-1}\left[\frac{\cancel{1}-(\cos\theta)^i-\cancel{1}+\cos\theta}{1-\cos\theta} + \frac{(\cos\theta)^i-(\cos\theta)^{N-1}}{1-\cos\theta}\right]\right\}$$

$$= (N-1)\ell^2 + \frac{\ell^2}{1-\cos\theta}\sum_{i=1}^{N-1}\left[\cancel{1} - \cancel{(\cos\theta)^i} + \cos\theta + \cancel{(\cos\theta)^i} - (\cos\theta)^{N-1}\right]$$

$$\boxed{\langle R^2\rangle = (N-1)\ell^2 + \frac{\ell^2}{1-\cos\theta}(N-1)\left(\cos\theta - (\cos\theta)^{N-1}\right)}$$

Formula given does not quite agree. ??

$$\langle R^2\rangle = (N-1)\ell^2\left\{1 + \frac{(N-1)}{1-\cos\theta}\left(\cos\theta - (\cos\theta)^{N-1}\right)\right\}$$

$$\cancel{\langle R^2\rangle = (N-1)l^2 + \frac{l^2}{1-\cos\theta}\left\{2(N-1) - \frac{1-(\cos\theta)}{1-\cos\theta}\right.}$$

$$\sum_{j=1}^{i-1} (\cos\theta)^{i-j} \underset{k=i-j}{=} \sum_{k=i-1}^{1} (\cos\theta)^{k} = \sum_{k=0}^{i-1} (\cos\theta)^{k} - 1$$

$$= \frac{1-(\cos\theta)^{i}}{1-\cos\theta} - 1$$

$$\sum_{j=i+1}^{N-1} (\cos\theta)^{j-i} \underset{k=j-1}{=} \sum_{k=i}^{N-2} (\cos\theta)^{k} = (\cos\theta)^{i} \sum_{k=0}^{N-i-2} (\cos\theta)^{k}$$

$$= (\cos\theta)^{i} \frac{1-(\cos\theta)^{N-i-1}}{1-\cos\theta}$$