Solution 6

Flexural Rigidity induced by Excluded Volume Interaction

1. By construction, the centers of two consecutive monomers lie at a distance d, so that no overlap is possible. Within our "local" approximation of the excluded volume, the only overlap can thus come from monomers which are at distance 2 along the chain, i.e. the ones labeled $i-1$ and $i+1$ in the picture. By connecting the centers of these two monomers with a line, an isosceles triangle is formed with the bonds $\vec{r}_i$, $\vec{r}_{i+1}$. The distance b between the centers of $i-1$ and $i+1$ can thus be easily shown to be

$$b = 2d\cos\frac{\theta}{2}$$

The condition of non-overlapping monomers can be stated by imposing $b \geq d$, from which one easily obtains that $\theta \in \left[-\frac{2}{3}\pi, \frac{2}{3}\pi\right]$.

2. The probability distribution of θ is given by

$$P(\theta) = \begin{cases} \frac{3}{4\pi} & \text{if } \theta \in \left[-\frac{2}{3}\pi, \frac{2}{3}\pi\right] \\ 0 & \text{otherwise} \end{cases}$$

Now, by using the same approach as we did in Homework 2, we first calculate $< \vec{r}_i \cdot \vec{r}_{i+1} >$:

$$< \vec{r}_i \cdot \vec{r}_{i+1} >= d^2 \int_{-\pi}^{\pi} P(\theta)\cos\theta d\theta = d^2 \frac{3}{4\pi}\int_{-\frac{2}{3}\pi}^{\frac{2}{3}\pi} \cos\theta d\theta = \frac{3\sqrt{3}}{4\pi}d^2$$

The correlation will then be "propagated" along the chain, giving the general result

$$< \vec{r}_i \cdot \vec{r}_j >= \left(\frac{3\sqrt{3}}{4\pi}\right)^{|i-j|} d^2$$

Now, by definition

$$< \vec{r}_i \cdot \vec{r}_j >= d^2 e^{-\frac{d|i-j|}{l_p}}$$

from which we finally derive for the persistence length

$$l_p = \frac{d}{\ln\frac{4\pi}{3\sqrt{3}}} \simeq 1.13d$$

In other words, the chain is very flexible, since the persistence length is only a bit larger than the bond length.

Now, in the more general case, by making the same geometric construction as before, we get for the distance between the monomers $i-1$ and $i+1$

$$b = 2l\cos\frac{\theta}{2}$$

By imposing the condition $b \geq d$, we find that $\theta \in [-\theta_{max}, \theta_{max}]$, with

$$\theta_{max} = 2 \arccos \frac{d}{2l}$$

Note that for $l = d$, we have $\theta_{max} = \frac{2}{3}\pi$, as it should be. The correlation between consecutive monomers is

$$\begin{aligned} < \vec{r}_i \cdot \vec{r}_{i+1} > &= l^2 \frac{1}{2\theta_{max}} \int_{2\theta_{max}}^{2\theta_{max}} \cos\theta d\theta = \frac{\sin\theta_{max}}{\theta_{max}} l^2 \\ &= \frac{l^2}{\theta_{max}} \sqrt{1 - \cos^2(\theta_{max})} = \frac{d}{2l} \frac{\sqrt{1 - \frac{d^2}{4l^2}}}{\arccos \frac{d}{2l}} l^2 \end{aligned}$$

where we used the fact that $\cos(\theta_{max}) = 2\cos^2(\theta_{max}/2) - 1 = 2\left(\frac{d}{2l}\right)^2 - 1$. Finally the persistence length is easily computed:

$$l_p = \frac{l}{\ln \frac{\arccos \frac{d}{2l}}{\frac{d}{2l}\sqrt{1-\frac{d^2}{4l^2}}}}.$$

In the limit $l/d \to \infty$, the size of the spheres becomes smaller and smaller with respect to the bond length, so that we intuitively expect the excluded volume effect to become more and more negligible. Mathematically, the denominator of the previous formula diverges, so that one finds $l_p \to 0$, as expected for a chain with uncorrelated vectors.

Ideal Chain with Constraints

Let us divide the chain into two parts: one attached to the end in $\vec{R}_1$ and made of s monomers, the other one attached to the end in $\vec{R}_2$ and made of $N - s$ monomers. If we let free the second end of each chain, since $s, N - s \gg 1$ Gaussian statistics can be used, so that the probabilities of such end to be found at position $\vec{R}$ are

$$P_1(\vec{R}) = \left(\frac{3}{2\pi s b^2}\right)^{\frac{3}{2}} e^{-\frac{3(\vec{R}-\vec{R}_1)^2}{2sb^2}}, \qquad P_2(\vec{R}) = \left(\frac{3}{2\pi(N-s)b^2}\right)^{\frac{3}{2}} e^{-\frac{3(\vec{R}-\vec{R}_2)^2}{2(N-s)b^2}}$$

The probability density of finding both the free ends at position $\vec{R}$ is proportional to their product, which after some algebraic manipulations can be written as

$$P_1(\vec{R})P_2(\vec{R}) = \left(\frac{9}{4\pi^2 N K_s b^4}\right)^{\frac{3}{2}} e^{-\frac{3(\vec{R}-\vec{R}_s)^2}{2K_s b^2}} e^{-\frac{3(\vec{R}_1-\vec{R}_2)^2}{2Nb^2}}$$

However, such a probability density has to be properly normalized over all the two-chains states compatible with the single constrained one (i.e. all the states such that the two ends of the chains are located at the same point). In order to calculate such a normalization factor, we can simply compute the integral

$$\begin{aligned} \int d\vec{R} P_1(\vec{R})P_2(\vec{R}) &= \left(\frac{9}{4\pi^2 N K_s b^4}\right)^{\frac{3}{2}} e^{-\frac{3(\vec{R}_1-\vec{R}_2)^2}{2Nb^2}} \int d\vec{R} e^{-\frac{3(\vec{R}-\vec{R}_s)^2}{2K_s b^2}} = \\ &= \left(\frac{9}{4\pi^2 N K_s b^4}\right)^{\frac{3}{2}} e^{-\frac{3(\vec{R}_1-\vec{R}_2)^2}{2Nb^2}} \left(\frac{2K_s b^2 \pi}{3}\right)^{\frac{3}{2}} = \\ &= \left(\frac{3}{2\pi N b^2}\right)^{\frac{3}{2}} e^{-\frac{3(\vec{R}_1-\vec{R}_2)^2}{2Nb^2}} \end{aligned}$$

We note *en passant* that the normalization factor is nothing but the probability density of having a random walk of length N connecting positions $\vec{R}_1$ and $\vec{R}_2$. This is expected, since our constrained

problem can be seen as the conditioned probability of our two chains to meet at $\vec{R}$, provided we already know that their ends meet somewhere in space. By normalizing, we finally obtain

$$P_s\left(\vec{R}\right) = \frac{P_1(\vec{R})P_2(\vec{R})}{\int d\vec{R}' P_1(\vec{R}')P_2(\vec{R}')} = \left(\frac{3}{2\pi K_s b^2}\right)^{\frac{3}{2}} e^{-\frac{3\left(\vec{R}-\vec{R}_s\right)^2}{2K_s b^2}}$$

which is the formula given in the text.
Now, in the case of a ring polymer, one has $\vec{R}_1 = \vec{R}_2 = \vec{R}_s$. Moreover, note that $K_{N/2} = N/4$. The probability distribution of having distance D is thus

$$P_{ring}(D) = P_{\frac{N}{2}}(D) = 4\pi D^2 \left(\frac{3}{2\pi\frac{N}{4}b^2}\right)^{\frac{3}{2}} e^{-\frac{3D^2}{2\frac{N}{4}b^2}} = 4\pi D^2 \left(\frac{6}{\pi N b^2}\right)^{\frac{3}{2}} e^{-\frac{6D^2}{Nb^2}}$$

On the other hand, the probability of a linear $N/2$-polymer to have end to end distance D is given by

$$P_{linear}(D) = 4\pi D^2 \left(\frac{3}{2\pi\frac{N}{2}b^2}\right)^{\frac{3}{2}} e^{-\frac{3D^2}{2\frac{N}{2}b^2}} = 4\pi D^2 \left(\frac{3}{\pi N b^2}\right)^{\frac{3}{2}} e^{-\frac{3D^2}{Nb^2}}$$

The ratio of the two densities is thus

$$q(D) \equiv \frac{P_{ring}(D)}{P_{linear}(D)} = 2^{\frac{3}{2}} e^{-\frac{3D^2}{Nb^2}}$$

By noting that $q(0) = 2^{3/2} > 1$, we argue that the probability density for low distances is larger in the case of the ring, which is what one could have intuitively expected. Naturally, for larger distances the linear polymer will be favored[1] with respect to the ring one. The switching of roles happens for D^* such that $q(D^*) = 1$. Some simple manipulations immediately show that

$$D^{*2} = \frac{\log 2}{2} N b^2$$

[1] Maybe the locution "less unfavoured" would give in this case a better catch of the actual picture.