Solution 2
28/09/2017

An "Almost" Freely Jointed Chain

1.

$$\langle \vec{R}_{gyr}^2 \rangle \;=\; \frac{1}{(n+1)^2}\sum_{i=0}^{n}\sum_{j=i}^{n}\langle(\vec{R}_i-\vec{R}_j)^2\rangle \;=\; \frac{1}{(n+1)^2}\sum_{i=0}^{n}\sum_{j=i}^{n}\langle(\sum_{k=i+1}^{j}\vec{r}_k)^2\rangle$$

The last term $\langle(\sum_{k=i+1}^{j}\vec{r}_k)^2\rangle$ corresponds to the average end-to-end distance $\langle R_{end}^2\rangle$ of a freely jointed chain of size $j-i$:

$$\langle(\sum_{k=i+1}^{j}\vec{r}_k)^2\rangle = (j-i)l^2$$

Therefore :

$$\begin{aligned}
\langle \vec{R}_{gyr}^2 \rangle \quad &= \quad \frac{l^2}{(n+1)^2}\sum_{i=0}^{n}\sum_{j=i}^{n}(j-i) \\
&\overset{j-i\to j}{=} \quad \frac{l^2}{(n+1)^2}\sum_{i=0}^{n}\sum_{j=0}^{n-i} j \\
&= \quad \frac{l^2}{(n+1)^2}\sum_{i=0}^{n}\frac{(n-i)\,(n-i+1)}{2}; \\
&\overset{n-i\to i}{=} \quad \frac{l^2}{2\cdot(n+1)^2}\sum_{i=0}^{n} i(i+1) \\
&= \quad \frac{l^2}{6}\frac{n(n+2)}{n+1} \\
&\overset{n\gg 1}{\approx} \quad \frac{l^2\cdot n}{6}
\end{aligned}$$

2.
First note that

$$\langle \vec{r}_{i-1}\cdot\vec{r}_i\rangle \;=\; \langle l^2\cos(\theta_{i-1,i})\rangle \;=\; l^2\langle\cos(\theta_{i-1,i})\rangle\ .$$

Imagine the plane perpendicular to the direction of $\vec{r}_{i-1}$. All positions of $\vec{r}_i$ in the upper half space ($\theta < \frac{\pi}{2}$) are equally distributed so:

$$\langle\cos\theta\rangle_{\theta<\frac{\pi}{2}} = \frac{\int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}}\sin\theta d\theta\cos\theta}{\int_0^{2\pi} d\phi\int_0^{\frac{\pi}{2}}\sin\theta d\theta} = \frac{1}{2}\ ,$$

and similarly $\langle\cos\theta\rangle_{\theta>\frac{\pi}{2}} = -\frac{1}{2}$.
Finally,

$$\langle\cos\theta\rangle = \left(\frac{1}{2}+\epsilon\right)\langle\cos\theta\rangle_{\theta<\frac{\pi}{2}} + \left(\frac{1}{2}-\epsilon\right)\langle\cos\theta\rangle_{\theta>\frac{\pi}{2}} = \epsilon \ .$$

We now calculate

$$\langle\vec{r}_{i-1}\cdot\vec{r}_{i+1}\rangle \ = \ l^2\langle\cos(\theta_{i-1,i+1})\rangle \ .$$

We don't know directly the probability distribution for this, but we can imagine that the existing correlations $\langle\vec{r}_{i-1}\cdot\vec{r}_i\rangle \neq 0$ and $\langle\vec{r}_i\cdot\vec{r}_{i+1}\rangle \neq 0$ will result in a correlation between bonds two steps aside along the chain and in general between all pairs of bonds.
Let's consider bonds of unitary length or define $\vec{n}_i \equiv \frac{\vec{r}_i}{l}$, so $\langle\cos\theta_{i-1,i+1}\rangle = \langle\vec{n}_{i-1}\cdot\vec{n}_{i+1}\rangle$. Now decompose $\vec{n}_{i+1}$ on the orthogonal basis formed by $\vec{n}_i$ and two suitable vectors $\vec{o}_1$,$\vec{o}_2$:

$$\vec{n}_{i+1} = \vec{n}_i\left(\vec{n}_i\cdot\vec{n}_{i+1}\right) + \vec{o}_1\left(\vec{o}_1\cdot\vec{n}_{i+1}\right) + \vec{o}_2\left(\vec{o}_2\cdot\vec{n}_{i+1}\right) \ .$$

By making use of such a basis, we can compute the desired correlation:

$$\begin{aligned}
\langle\vec{n}_{i-1}\cdot\vec{n}_{i+1}\rangle &= \langle(\vec{n}_{i-1}\cdot\vec{n}_i)\left(\vec{n}_i\cdot\vec{n}_{i+1}\right)\rangle + \langle(\vec{n}_{i-1}\cdot\vec{o}_1)\left(\vec{o}_1\cdot\vec{n}_{i+1}\right)\rangle + \langle(\vec{n}_{i-1}\cdot\vec{o}_2)\left(\vec{o}_2\cdot\vec{n}_{i+1}\right)\rangle \\
&= \langle(\vec{n}_{i-1}\cdot\vec{n}_i)\rangle\langle(\vec{n}_i\cdot\vec{n}_{i+1})\rangle + 0 + 0 \\
&= \epsilon^2 \ .
\end{aligned}$$

Two comments:

- the probabilities for distinct bond angles can be factorized because they are independent, so for example $\langle(\vec{n}_{i-1}\cdot\vec{o}_1)\left(\vec{o}_1\cdot\vec{n}_{i+1}\right)\rangle = \langle(\vec{n}_{i-1}\cdot\vec{o}_1)\rangle\langle(\vec{o}_1\cdot\vec{n}_{i+1})\rangle$;
- *in the case in exam* the projections as e.g. $\vec{o}_1\cdot\vec{n}_{i+1}$ on directions orthogonal to the previous bond have zero mean. Let's see it directly. Let Θ be the angle between $\vec{o}_1$ and $\vec{n}_{i+1}$, and Φ the torsion angle of $\vec{n}_{i+1}$ around $\vec{o}_1$. The *upper half space*, i.e. the one with probability p_+, is now described by $\Phi\in[0,\pi]$ (instead of $\theta<\frac{\pi}{2}$ when considering $\vec{n}_{i+1}$ and $\vec{n}_i$). So

$$\begin{aligned}
\langle\vec{o}_1\cdot\vec{n}_{i+1}\rangle &= \langle\cos\Theta\rangle \\
&= p_+\int_0^\pi d\Phi\int_0^\pi \sin\Theta d\Theta\cos\Theta + p_-\int_\pi^{2\pi} d\Phi\int_0^\pi \sin\Theta d\Theta\cos\Theta \\
&= p_+\pi\cdot 0 + p_-\pi\cdot 0 \\
&= 0 \ .
\end{aligned}$$

The former result can be generalized by iterating the argument we just used. As a result, there is a net "propagation" of a correlation of magnitude ϵ along the backbone, so that we obtain

$$\langle\vec{r}_i\cdot\vec{r}_j\rangle \ = \ l^2\epsilon^{|i-j|} \ .$$

As an example consider the case $j = i+3$, so that $\langle n_i\cdot n_j\rangle = \langle n_i\cdot n_{i+3}\rangle$. We write recursively:

$$\begin{aligned}
\vec{n}_{i+3} &= \vec{n}_{i+2}(\vec{n}_{i+2}\cdot\vec{n}_{i+3}) + \textit{terms whose average is zero} \\
\vec{n}_{i+2} &= \vec{n}_{i+1}(\vec{n}_{i+1}\cdot\vec{n}_{i+2}) + \textit{terms whose average is zero} \\
\vec{n}_{i+1} &= \vec{n}_i(\vec{n}_i\cdot\vec{n}_{i+1}) + \textit{terms whose average is zero.}
\end{aligned}$$

Finally:

$$\begin{aligned}
\langle n_i\cdot n_{i+3}\rangle &= \langle n_i\cdot n_{i+2}(\vec{n}_{i+2}\cdot\vec{n}_{i+3})\rangle \\
&= \langle n_i\cdot n_{i+1}(\vec{n}_{i+1}\cdot\vec{n}_{i+2})(\vec{n}_{i+2}\cdot\vec{n}_{i+3})\rangle \\
&= \langle n_i\cdot n_i(\vec{n}_i\cdot\vec{n}_{i+1})(\vec{n}_{i+1}\cdot\vec{n}_{i+2})(\vec{n}_{i+2}\cdot\vec{n}_{i+3})\rangle \\
&= \langle\vec{n}_i\cdot\vec{n}_{i+1}\rangle\langle\vec{n}_{i+1}\cdot\vec{n}_{i+2}\rangle\langle\vec{n}_{i+2}\cdot\vec{n}_{i+3}\rangle \\
&= \epsilon^3
\end{aligned}$$

3.

Mean-square end-to-end distance:

$$\begin{aligned}
\langle R_{end}^2 \rangle &= \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \vec{r}_i \cdot \vec{r}_j \rangle \\
&= l^2 \sum_{i=1}^{n}\left[\sum_{j=1}^{i-1}\epsilon^{i-j} + 1 + \sum_{j=i+1}^{n}\epsilon^{j-i}\right] \\
&= l^2 \sum_{i=1}^{n}\left[\frac{\epsilon-\epsilon^i}{1-\epsilon} + 1 + \frac{\epsilon-\epsilon^{n-i+1}}{1-\epsilon}\right] \\
&= l^2 \sum_{i=1}^{n}\left[1 + 2\frac{\epsilon}{1-\epsilon} - \frac{\epsilon^i}{1-\epsilon} - \frac{\epsilon^{n-i+1}}{1-\epsilon}\right] \\
&= l^2 n \left(1 + 2\frac{\epsilon}{1-\epsilon}\right) - l^2 2\frac{\epsilon-\epsilon^{n+1}}{(1-\epsilon)^2} \\
&\approx l^2 n \frac{1+\epsilon}{1-\epsilon} \,,
\end{aligned}$$

where the last approximation neglects terms of order 1 (not proportional to n).
Note that this is a result similar to the *freely rotating chain* with $\cos\theta = \epsilon$, with a restriction: $\epsilon < \frac{1}{2}$ which corresponds to $\theta > 60^0$.

Mean-square Radius of gyration
NOTE: $\vec{R}_i$ is the vector position of the $n+1$ monomers ($i = 0...n$), while $\vec{r}_i$ is the bond vector linking monomer $i-1$ with monomer i (i.e. $\vec{r}_i = \vec{R}_i - \vec{R}_{i-1}$).

$$
\begin{aligned}
\langle R^2_{gyr} \rangle &= \frac{1}{(n+1)^2} \sum_{i=0}^{n} \sum_{j=i}^{n} \langle (\vec{R}_i - \vec{R}_j)^2 \rangle \\
&= \frac{1}{(n+1)^2} \sum_{i=0}^{n} \sum_{j=i+1}^{n} \langle \left(\sum_{k=1}^{j-i} \vec{r}_{i+k} \right)^2 \rangle \\
&= \frac{1}{(n+1)^2} \sum_{i=0}^{n} \sum_{j=i+1}^{n} \left((j-i) l^2 + 2((j-i)-1) \langle \vec{r}_i \vec{r}_{i+1} \rangle + \cdots + 2 \langle \vec{r}_i \vec{r}_j \rangle \right) \\
&= \frac{1}{(n+1)^2} \sum_{i=0}^{n} \sum_{m=1}^{n-i} l^2 \left[m + 2 \sum_{k=1}^{m-1} (m-k) \epsilon^k \right] \\
&= \frac{l^2}{(n+1)^2} \sum_{i=0}^{n} \sum_{m=1}^{n-i} \left[m + 2 \left(m\epsilon \frac{1-\epsilon^{m-1}}{1-\epsilon} - \epsilon \frac{d}{d\epsilon} \frac{\epsilon - \epsilon^m}{1-\epsilon} \right) \right] \\
&= \frac{l^2}{(n+1)^2} \sum_{i=0}^{n} \sum_{m=1}^{n-i} \left[m + 2 \left(m\epsilon \frac{1-\epsilon^{m-1}}{1-\epsilon} - \epsilon \left(\frac{1 - m\epsilon^{m-1}}{1-\epsilon} + \frac{\epsilon - \epsilon^m}{(1-\epsilon)^2} \right) \right) \right] \\
&= \frac{l^2}{(n+1)^2} \sum_{i=0}^{n} \sum_{m=1}^{n-i} \left[m + 2 \frac{\epsilon}{1-\epsilon} \left(m - 1 - \frac{\epsilon}{1-\epsilon} + \frac{\epsilon^m}{1-\epsilon} \right) \right] \\
&= \frac{l^2}{(n+1)^2} \frac{n(n+1)(n+2)}{6} \left(1 + 2 \frac{\epsilon}{1-\epsilon} \right) \\
&\qquad + \frac{l^2}{(n+1)^2} \sum_{i=0}^{n} \sum_{m=1}^{n-i} 2 \frac{\epsilon}{1-\epsilon} \left(-1 - \frac{\epsilon}{1-\epsilon} + \frac{\epsilon^m}{1-\epsilon} \right) \\
&= \frac{l^2}{6} \frac{n(n+2)}{n+1} \left(\frac{1+\epsilon}{1-\epsilon} \right) + o(1) \\
&\approx \frac{1}{6} l^2 n \frac{1+\epsilon}{1-\epsilon} \,.
\end{aligned}
$$

Have you noticed that $(\vec{R}_i - \vec{R}_j)$ is the end-to-end distance of a polymer with $|j-i+1|$ monomers? This suggests an alternative way of computing $\langle R^2_{gyr} \rangle$:

$$
\begin{aligned}
\langle R^2_{gyr} \rangle =& \frac{1}{(n+1)^2} \sum_{i=0}^{n} \sum_{j=i}^{n} \left[l^2 (j-i) \left(\frac{1+\epsilon}{1-\epsilon} \right) - 2 l^2 \frac{\epsilon - \epsilon^{j-i+1}}{(1-\epsilon)^2} \right] \\
=& \frac{1}{(n+1)^2} \sum_{i=0}^{n} \sum_{j=i}^{n} \left[l^2 (j-i) \left(\frac{1+\epsilon}{1-\epsilon} \right) \right] + o(1) \\
=& \frac{1}{(n+1)^2} \, l^2 \left(\frac{1+\epsilon}{1-\epsilon} \right) \sum_{i=0}^{n} \frac{(n-i)(n-i+1)}{2} + o(1) \\
=& \frac{1}{(n+1)^2} \, l^2 \left(\frac{1+\epsilon}{1-\epsilon} \right) \frac{n(n+1)(n+2)}{6} + o(1) \\
\approx& \frac{1}{6} l^2 n \frac{1+\epsilon}{1-\epsilon} \,.
\end{aligned}
$$

Bonus: proof of identity (1)

$$
\begin{aligned}
\frac{1}{(n+1)^2}\sum_{i=0}^{n}\sum_{j=0}^{n}(\vec{R}_i-\vec{R}_j)^2 =& \frac{1}{(n+1)^2}\sum_{i=0}^{n}\sum_{j=0}^{n}[(\vec{R}_i-\vec{R}_{cm})-(\vec{R}_j-\vec{R}_{cm})]^2 \\
=& \frac{1}{(n+1)^2}\sum_{i=0}^{n}\sum_{j=0}^{n}[(\vec{R}_i-\vec{R}_{cm})^2-2(\vec{R}_i-\vec{R}_{cm})(\vec{R}_j-\vec{R}_{cm})+(\vec{R}_j-\vec{R}_{cm})^2] \\
=& \frac{2}{n+1}\sum_{i=0}^{n}(\vec{R}_i-\vec{R}_{cm})^2-\frac{2}{(n+1)^2}\sum_{i=0}^{n}(\vec{R}_i-\vec{R}_{cm})\sum_{j=0}^{n}(\vec{R}_j-\vec{R}_{cm}) \\
=& \frac{2}{n+1}\sum_{i=0}^{n}(\vec{R}_i-\vec{R}_{cm})^2
\end{aligned}
$$

The final result can be obtained by noticing that

$$
\begin{aligned}
\frac{1}{n+1}\sum_{i=0}^{n}(\vec{R}_i-\vec{R}_{cm})^2 =& \frac{1}{2(n+1)^2}\sum_{i=0}^{n}\sum_{j=0}^{n}(\vec{R}_i-\vec{R}_j)^2 \\
=& \frac{1}{(n+1)^2}\sum_{i=0}^{n}\sum_{j=i}^{n}(\vec{R}_i-\vec{R}_j)^2 \\
=& \frac{1}{(n+1)^2}\sum_{i=0}^{n}\sum_{j=i+1}^{n}(\vec{R}_i-\vec{R}_j)^2.
\end{aligned}
$$

The last equality is justified by the fact that if $i=j$ then $(\vec{R}_i-\vec{R}_j)^2=0$.