Solution 3
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(Gaussian) Freely Jointed Chain with Varying Step Length

For better understanding the role of the parameter a, let us consider $d = 3$ for a moment. In this case,

$$p(\vec{r}) = \frac{e^{-\frac{r_x^2}{2a^2}}}{(2\pi a^2)^{\frac{1}{2}}} \cdot \frac{e^{-\frac{r_y^2}{2a^2}}}{(2\pi a^2)^{\frac{1}{2}}} \cdot \frac{e^{-\frac{r_z^2}{2a^2}}}{(2\pi a^2)^{\frac{1}{2}}} \ ,$$

therefore

$$a^2 = \langle r_x^2 \rangle = \langle r_y^2 \rangle = \langle r_z^2 \rangle \ ,$$

and $\langle \vec{r}^2 \rangle = 3\,a^2 = d\,a^2$.
As for the end to end distance, there are two different ways to compute it:
Fast way: a random walk is a sequence of N *independent* steps $\{\vec{r}_i\}_{i=1}^N$, each taken with probability $p(\vec{r})$. Such a distribution probability has mean 0 and variance da^2. By making use of the Central Limit Theorem, we can thus conclude that the end-to-end vector will be distributed as a Gaussian with zero mean and variance Nda^2. We thus obtain

$$P(\vec{R}_e) = \frac{e^{-\frac{\vec{R}_e^2}{2Na^2}}}{(2\pi N a^2)^{\frac{d}{2}}} \ . \tag{1}$$

Explicit way: the probability distribution that the N steps fall into the set $\vec{r}_1, \ldots, \vec{r}_N$ is given by

$$p(\{\vec{r}_i\}_{i=1}^N) = \prod_{i=1}^N p(\vec{r}_i) \ .$$

The probability of the end-to-end distance $\vec{R}_e$ is the sum of the probabilities of the random walks having $\sum_{i=1}^N \vec{r}_i = \vec{R}_e$, i.e.

$$P(\vec{R}_e) = \int \prod_{i=1}^N d\vec{r}_i p(\vec{r}_i) \left[\delta\Big(\sum \vec{r}_i - \vec{R}_e\Big) \right] \ .$$

The presence of the δ function suggests to compute the Fourier transform of $P(\vec{R}_e)$,

$$\begin{aligned}
\tilde{P}(\vec{k}) &= \int d\vec{R}_e e^{-i\vec{k}\cdot\vec{R}_e} P(\vec{R}_e) = \int d\vec{R}_e e^{-i\vec{k}\cdot\vec{R}_e} \int \prod_{i=1}^N d\vec{r}_i p(\vec{r}_i) \left[\delta\Big(\sum \vec{r}_i - \vec{R}_e\Big) \right] \\
&= \int \prod_{i=1}^N d\vec{r}_i p(\vec{r}_i) \left[e^{-i \sum_{i=1}^N \vec{k}\cdot\vec{r}_i} \right] = \tilde{p}^N(\vec{k}) \ ,
\end{aligned}$$

where

$$\tilde{p}(\vec{k}) = \int d\vec{r} e^{-i\vec{k}\cdot\vec{r}} \frac{e^{-\frac{\vec{r}^2}{2a^2}}}{(2\pi a^2)^{\frac{d}{2}}} = \int \frac{d\vec{r}}{(2\pi a^2)^{\frac{d}{2}}} e^{-\frac{1}{2}\left(\frac{\vec{r}+i\vec{k}a^2}{a}\right)^2 - \frac{1}{2}a^2\vec{k}^2} = e^{-\frac{1}{2}a^2\vec{k}^2} \ .$$

Finally,

$$P(\vec{R}_e) = \int \frac{d\vec{k}}{(2\pi)^d} e^{i\vec{k}\cdot\vec{R}_e} \tilde{p}^N(\vec{k}) = \int \frac{d\vec{k}}{(2\pi)^d} e^{-\frac{1}{2}Na^2\vec{k}^2 + i\vec{k}\vec{R}_e}$$
$$= \int \frac{d\vec{k}}{(2\pi)^d} e^{-\frac{1}{2}\left(\sqrt{N}a\vec{k} - i\frac{\vec{R}_e}{\sqrt{N}a}\right)^2 - \frac{1}{2}\frac{\vec{R}_e^2}{Na^2}} = \frac{1}{(2\pi)^d}\left(\frac{2\pi}{Na^2}\right)^{\frac{d}{2}} e^{-\frac{1}{2}\frac{\vec{R}_e^2}{Na^2}}$$
$$= \frac{e^{-\frac{\vec{R}_e^2}{2Na^2}}}{(2\pi Na^2)^{\frac{d}{2}}} \, ,$$

which is the same result as above. Now, as for the average value of the end-to-end distance, we can proceed in several ways:

1. Remembering that $\left\langle \vec{r}^2 \right\rangle = da^2$, since $\vec{R}_e = \sum_i \vec{r}_i$ we easily get

$$\left\langle \vec{R}_e^2 \right\rangle = \left\langle \left(\sum_{i=1}^{N} \vec{r}_i \right)^2 \right\rangle = \left\langle \sum_{i,j=1}^{N} \vec{r}_i \cdot \vec{r}_j \right\rangle = \left\langle \sum_i \vec{r}_i^2 + \sum_{i\neq j} \vec{r}_i \cdot \vec{r}_j \right\rangle =$$
$$= \sum_i \left\langle \vec{r}_i^2 \right\rangle + \sum_{i\neq j} \left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle = Nda^2 + 0 = Nda^2 \, .$$

Once again $\vec{R}_e^2$ is proportional to N as all *ideal chains* previously studied.

2.

$$\left\langle \vec{R}_e^2 \right\rangle = \int d\vec{R}_e P(\vec{R}_e) \vec{R}_e^2 = \int d\vec{R}_e \frac{e^{-\frac{\vec{R}_e^2}{2Na^2}}}{(2\pi Na^2)^{\frac{d}{2}}} \vec{R}_e^2 = \frac{1}{(2\pi Na^2)^{\frac{d}{2}}} \frac{d}{d\left(-\frac{1}{2Na^2}\right)} \int d\vec{R}_e e^{-\frac{\vec{R}_e^2}{2Na^2}} =$$
$$= \frac{1}{(2\pi Na^2)^{\frac{d}{2}}} \frac{d}{d\left(-\frac{1}{2Na^2}\right)} \left(2Na^2\pi\right)^{\frac{d}{2}} = -\frac{1}{(2Na^2)^{\frac{d}{2}}} \frac{d}{d\left(\frac{1}{2Na^2}\right)} \left(\frac{1}{2Na^2}\right)^{-\frac{d}{2}} =$$
$$= \frac{1}{(2Na^2)^{\frac{d}{2}}} \frac{d}{2} \left(\frac{1}{2Na^2}\right)^{-\frac{d}{2}-1} = \frac{d}{2} 2Na^2 = Nda^2 \, .$$

Equivalent Freely Jointed Chain

From the actual values of $\langle R_{end}^2 \rangle$ and R_{max} we calculate N and b in such a way that

$$\begin{cases} \langle R_{end}^2 \rangle = Nb^2 \\ R_{max} = Nb \end{cases} \quad \Longrightarrow \quad \begin{cases} b = \dfrac{\langle R_{end}^2 \rangle}{R_{max}} \\ N = \dfrac{R_{max}^2}{\langle R_{end}^2 \rangle} \end{cases} .$$

Applying this formula we get

$$R_{max} = nl \, , \quad b = l\frac{1+\epsilon}{1-\epsilon}$$

for the model of homework 2,

$$R_{max} = nl\cos\left(\frac{\theta}{2}\right) \, , \quad b = \frac{1}{\cos\left(\frac{\theta}{2}\right)} l \frac{1+\cos\theta}{1-\cos\theta} \tag{2}$$

for the freely rotating chain with fixed bond, and

$$R_{max} = nl\cos\left(\frac{\theta}{2}\right) \, , \quad b = \frac{7.4nl^2}{nl\cos\left(\frac{\theta}{2}\right)} \approx 13.7\text{Å}$$

for a polyethylene chain with a fixed bond angle $\theta = 68°$.
As for the double-stranded DNA, since $l \ll b$ we expect it to be a very stiff polymer, i.e. we expect θ to be small. Plugging this approximation in Eq. (2), we have

$$\frac{b}{l} = \frac{1+\cos\theta}{\cos(\theta/2)(1-\cos\theta)} \approx \frac{2-\theta^2/2}{(1-\theta^2/8)(\theta^2/2)} \approx \frac{2-\theta^2/2}{\theta^2/2} \,.$$

Hence,

$$\frac{\theta^2}{2}\left(\frac{b}{l}\right) = 2 - \frac{\theta^2}{2}$$

and

$$\theta = \sqrt{\frac{4l}{b+l}} \approx 0.11 \text{ rad} \approx 6.3°.$$