

Homework 2 Solutions

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■ Problem 1 (6 points)

To calculate the characteristic ratio for a freely-rotating chain with fixed bond angle θ , recall the general expression for the mean squared end-to-end distance of a chain model:

$$\langle r^2 \rangle = n l^2 + \sum \langle \vec{l}_i \vec{l}_j \rangle$$

where n is the number of chain segments, l is the length of each segment, and \vec{l}_i is the vector orientation of the i th segment. The sum is over $i, j = 1$ to n .

Let's first note a few things about this sum. The first is that by symmetry the dot product does not depend on the absolute values of i and j but the relative value, $k = j - i$. Thus, we can write the second term as

$$2 \sum_{k=i}^{n-1} (n-k) \langle \vec{l}_i \vec{l}_{i+k} \rangle$$

where the factor $(n-k)$ comes from the fact that in a linear chain of length n there are $(n-k)$ different segments of length k .

Now, we need to evaluate this dot product. Through simple geometric arguments it can be shown to be

$$\langle \vec{l}_i \vec{l}_{i+1} \rangle = l^2 \cos(\theta)$$

Moreover, for $k = 2$

$$\langle \vec{l}_i \vec{l}_{i+2} \rangle = l^2 \langle \cos(\theta) \rangle^2$$

By extrapolating the pattern, we can say that

$$\langle \vec{l}_i \vec{l}_{i+k} \rangle = l^2 \langle \cos(\theta) \rangle^k$$

and our mean squared end-to-end distance becomes

$$\langle r^2 \rangle = n l^2 + 2 \sum_{k=i}^{n-1} (n-k) \langle \vec{l}_i \vec{l}_{i+k} \rangle = n l^2 + 2 l^2 \sum_{k=i}^{n-1} (n-k) \alpha^k$$

where we have defined $\alpha = \langle \cos(\theta) \rangle$.

Evaluating this sum for $n = 4$ yields

$$\langle r^2 \rangle = n l^2 + 2 l^2 (3 \alpha + 2 \alpha^2 + \alpha^3)$$

The characteristic ratio is defined as $\langle r^2 \rangle / n l^2$; thus,

$$C_4 = \frac{4 l^2 + 2 l^2 (3 \alpha + 2 \alpha^2 + \alpha^3)}{4 l^2} = 1 + (6 \alpha + 4 \alpha^2 + 2 \alpha^3) / 4$$

The above derivation took a gigantic leap of insight to extrapolate the pattern to k . "Through simple geometric arguments" are code words for through complicated geometric arguments which we don't want to show or some brilliant insight that no one would normally have. However, at the end of the solution set, I have provided a rigorous demonstration of how to do this calculation.

■ Problem 2 (6 points)

Let's start by using the characteristic ratio to calculate the length of the statistical segment.

Recall that for some new length l' the polymer can be divided into a new number of segments n' such that its mean square end-to-end distance is $\langle r^2 \rangle = n' l'^2$.

We can compute n' and l' by recalling the $\langle r^2 \rangle$ is also equal to

$$\langle r^2 \rangle = C n l^2$$

By recalling that the polymer length must be equal in terms of n and l and n' and l' , we can show that

$$n' = n / C \text{ and } l' = C l$$

Thus, if a virtual bond in a polypeptide is 3.8 Å long and the characteristic ratio is 10, the statistical segment length is 38 Å.

Now, we can treat the problem using the freely-jointed chain results.

First, recall that in a freely jointed chain $\langle r^2 \rangle$ (or equivalently $\langle h^2 \rangle$) is simply $n' l'^2$. Thus, if we estimate the end-to-end distance from $\sqrt{\langle r^2 \rangle} = \sqrt{n'} l'$, then we find

$$\sqrt{n'} l' = 50 \text{ \AA} \Rightarrow n' = (50 \text{ \AA} / 38 \text{ \AA})^2 = 1.73$$

In terms of actual chain segments, this is 17.3.

Now we can also estimate the end-to-end distance from the most probable value, r_{mp} . Recall that this is

$$r_{\text{mp}} = \sqrt{\frac{2}{3} n'} l' = 50 \text{ \AA} \Rightarrow n' = 3/2 (50 \text{ \AA} / 38 \text{ \AA})^2 = 2.60$$

Again in terms of actual chain segments this is 26.

■ Problem 3 (6 points)

First we need to calculate the length of a DNA molecule of molecular weight 125×10^6 Daltons. Recalling that each base pair of double stranded DNA is on average 630 Daltons, this implies that the DNA is 2.0×10^5 bp long. With a length of 3.4 Å/bp, this implies that the molecule is 6.7×10^5 Å or $67 \mu\text{m}$.

Recall that the persistence length of dsDNA is 530 Å, which implies that the Kuhn length, the length of a statistical segment is 1060 Å. Thus, the T4 DNA has $(6.7 \times 10^5 \text{ Å}) / (1060 \text{ Å}) = 632$ statistical segments.

Further recall that the radius of gyration, R_G , is

$$R_G = \frac{\langle r^2 \rangle^{1/2}}{\sqrt{6}} = \sqrt{\frac{n'}{6}} l' = \sqrt{\frac{632}{6}} 1060 \text{ Å} = 1.09 \times 10^4 \text{ Å} = 1.09 \mu\text{m}$$

Thus, the volume per molecule is

$$V = \frac{4}{3} \pi R_G^3 = \frac{4}{3} \pi (1.09 \mu\text{m})^3 = 5.4 \mu\text{m}^3$$

The concentration of the DNA in this sphere is

$$C = \frac{m}{V} = (125 \times 10^6 \frac{\text{g}}{\text{mol}}) (1000 \frac{\text{mg}}{\text{g}}) (\frac{1}{6.023 \times 10^{23}} \frac{\text{mol}}{\text{molecules}}) \frac{1}{5.4 \mu\text{m}^3} \frac{1 \times 10^{12} \mu\text{m}^3}{\text{mL}} = 0.038 \text{ mg/mL}$$

Thus, neglecting excluded volume and finite packing volume effects, the solution of DNA would have to be at a concentration of ~ 0.04 mg/mL to equal the "effective" concentration of the DNA within the radius of gyration of a single molecule.

Several affects might be important for concentrations beyond this point. First of all, our entire stastical treatment has ignored self-interactions of different portions of the chain. When the concentration of DNA molecules exceeds this value, these effects may become important. These interactions may lead to a smaller radius of gyration or perhaps to the aggregation of multiple DNA molecules and perhaps the precipitation of the DNA.

■ Problem 4 (6 points)

We start by computing the mean square end-to-end distance of λ DNA. The genome of the λ bacteriophage is ~ 48 kilobase-pairs long. With a length of 3.4 Å/bp, it is thus

$$L = (4.8 \times 10^4 \text{ bp}) (3.4 \text{ Å/bp}) = 1.6 \times 10^5 \text{ Å} = 16 \mu\text{m}$$

Recalling that the persistence length of DNA is 530 Å and the the mean square end-to-end distance for a worm-like chain is

$$\langle R^2 \rangle = 2PL = 2(530 \text{ Å})(1.6 \times 10^5 \text{ Å}) = 1.7 \times 10^8 \text{ Å}^2 = 1.7 \mu\text{m}^2$$

Of course this equation only applies when $L \gg P$, which in this case it is.

Now to calculate the probability of ring closure, we need to calculate the probability that this molecule of DNA will have an end-to-end distance h less than 10 \AA . Recall that the probability of observing an end-to-end distance r in a freely jointed chain is

$$P(r) dr = 4\pi \left(\frac{3}{2\pi Nl^2}\right)^{3/2} e^{-\frac{3r^2}{2Nl^2}} r^2 dr$$

where N is the number of statistical chain segments and l is the statistical chain segment length. If the DNA is long enough, as we showed above, then it effectively behaves as a freely jointed chain with a statistical segment length, the Kuhn length, of $2P$. In other words, $Nl^2 = 2PL$. Using this in the above probability distribution we find that

$$P(r) dr = 4\pi \left(\frac{3}{4\pi PL}\right)^{3/2} e^{-\frac{3r^2}{4PL}} r^2 dr$$

Now to calculate the probability of having an end-to-end length less than 10 \AA , we simply integrate this distribution from 0 length to 10 \AA .

$$P(r < 10 \text{ \AA}) = \int_0^{10 \text{ \AA}} P(r) dr$$

However, we can make a very nice simplification by noticing that for the range of integration, the exponential is very small, i.e. $\frac{3r^2}{4PL} \ll 1$, and we can expand it to first order and keep only the constant term, i.e.

$$e^{-r^2} \approx 1 \text{ for } r \ll 1$$

Thus, our probability becomes

$$\begin{aligned} P(r < 10 \text{ \AA}) &= \int_0^{10 \text{ \AA}} 4\pi \left(\frac{3}{4\pi PL}\right)^{3/2} e^{-\frac{3r^2}{4PL}} r^2 dr \approx 4\pi \left(\frac{3}{4\pi PL}\right)^{3/2} \int_0^{10 \text{ \AA}} r^2 dr = 4\pi \left(\frac{3}{4\pi PL}\right)^{3/2} \frac{1}{3} (10 \text{ \AA})^3 \\ &= \frac{4}{3} \pi \left(\frac{3}{4\pi 530 \text{ \AA} \cdot 1.6 \times 10^6 \text{ \AA}}\right)^{3/2} (10 \text{ \AA})^3 = 6 \times 10^{-10} \end{aligned}$$

In other words it is incredibly unlikely.

For those less inclined to expand functions to lower order, we can calculate the integral using error functions.

The full integral is a rather nasty expression

$$P(r < 10 \text{ \AA}) = \int_0^{10 \text{ \AA}} 4\pi \left(\frac{3}{4\pi PL}\right)^{3/2} e^{-\frac{3r^2}{4PL}} r^2 dr = \frac{1}{\sqrt{PL}} \left(\sqrt{PL} \operatorname{Erf}\left(\frac{1}{2} \sqrt{\frac{3}{PL}} 10 \text{ \AA}\right) - \sqrt{\frac{3}{\pi}} 10 \text{ \AA} e^{-\frac{3(10 \text{ \AA})^2}{4PL}} \right)$$

which when evaluated gives a probability of 6×10^{-10} identical to that above!

■ Problem 5 (6 points)

Since extension increases with applied force, it is reasonable to assume that low extensions implies low forces. In particular, we assume that we are in a force range where the product $Fb/k_B T \ll 1$. In this limit, we can expand the coth to lowest order. It is important to note that this is not a Taylor series since it has a pole, i.e. it diverges for very small argument. This is actually a Laurent series, and we will see that this expansion is valid because the pole will cancel with an additional term in the expression.

For small arguments the $\coth(a) = \frac{1}{a} + \frac{1}{3}a + O[a]^2$. When we combine this with the expression for the average extension

$$\langle x \rangle = L(\coth(Fb/k_B T) - k_B T / Fb) \approx L(k_B T / Fb + \frac{1}{3} Fb/k_B T - k_B T / Fb) = \frac{1}{3} \frac{Lb}{k_B T} F$$

Inverting this relationship and recalling that a simple Hookean spring obeys $F = \kappa x$, we can show that the polymer behaves exactly as a spring at low force and extension with a spring constant of

$$\kappa = 3 \frac{k_B T}{Lb}$$

The work done in extending a simple spring is $W = \frac{1}{2} \kappa x^2$; thus, the work done in extending the polymer from 1% to 3% of its contour length, L , is

$$W = \frac{1}{2} \kappa (x_2^2 - x_1^2) = \frac{1}{2} 3 \frac{k_B T}{Lb} \left(\left(\frac{3}{100} L \right)^2 - \left(\frac{1}{100} L \right)^2 \right) = \frac{3}{2} \frac{k_B T}{b} L \frac{8}{100^2} \approx 0.0012 k_B T \frac{L}{b}$$

The change in Gibbs free energy, ΔG , is equal to the mechanical work done on the system, i.e. $W = \Delta G = \Delta H - T \Delta S$. Even though this system behaves like a simple spring, there is no potential energy in a simple freely jointed chain model and, thus, no change in enthalpy. This implies that $W = -T \Delta S$! In other words, in order to stretch this polymer, we had to do work against entropy! This type of system is known as an entropic spring, and it is the continual bombardment of solvent molecules and the thermal energy that they impart to the polymer that gives it an effective stiffness that resists forces that try to extend it!

Thus, using the result derived above we can determine the change in entropy upon stretching of this polymer

$$-T \Delta S = W \Rightarrow -T \Delta S = 0.0012 k_B T \frac{L}{b} \Rightarrow \Delta S = -0.0012 k_B \frac{L}{b}$$

■ Problem 6 (6 points)

Before we derive the full expression, recall that the mean square end-to-end distance in a worm like chain model can be expressed in integral form as

$$\langle R^2 \rangle = \int_0^L \int_0^L \langle \vec{r}(s) \vec{r}(s') \rangle ds ds' = \int_0^L \int_0^L e^{-|s-s'|/P} ds ds' = 2 \int_0^L \int_s^L e^{-(\eta-s)/P} ds d\eta$$

where in the last step we changed the way in which we label variables. s picks a position along the contour of the polymer while η is a measure of the distance from s along increasing length. Thus, by integrating over all values of s and all remaining lengths from s to the end of the polymer (and recalling that for every forward pair there is a reverse pair, i.e. $-\eta$, hence the factor of 2), we can express this integral in a more manageable fashion. Integrating in steps, over η first yields

$$\langle R^2 \rangle = 2 \int_0^L \int_s^L e^{-(\eta-s)/P} ds d\eta = 2 \int_0^L (P - P e^{-(L-s)/P}) ds = 2PL(1 - \frac{P}{L}(1 - e^{-L/P}))$$

Now, we need to calculate this property for a polymer with two different regions of different persistence length: one region of length l with persistence length P_1 and a second region of length $L-l$ with persistence length P_2 . Again our mean square end-to-end distance is expressed by

$$\langle R^2 \rangle = \int_0^L \int_0^L \langle \vec{r}(s) \vec{r}(s') \rangle ds ds'$$

However, it is important to note that there are three possibilities for $\langle \vec{t}(s) \vec{t}(s') \rangle$.

- 1: Both $\vec{t}(s)$ and $\vec{t}(s')$ are in the P_1 region
- 2: Both $\vec{t}(s)$ and $\vec{t}(s')$ are in the P_2 region
- 3: $\vec{t}(s)$ and $\vec{t}(s')$ in different regions

Mathematically this can be expressed by breaking our integral up into three separate integrals over different bounds.

$$\int_0^L \int_0^L \langle \vec{t}(s) \vec{t}(s') \rangle ds ds' = \int_0^l \int_0^l \langle \vec{t}(s) \vec{t}(s') \rangle ds ds' + \int_l^L \int_l^L \langle \vec{t}(s) \vec{t}(s') \rangle ds ds' + 2 \int_0^l \int_l^L \langle \vec{t}(s) \vec{t}(s') \rangle ds ds'$$

where each corresponds to each of the cases above and the factor of two in the last term comes from the fact that there are two possible choices for which vector is in which region.

The first two integrals are the same as the integral we did above. The first one in particular is clear. The second integral requires us to recall that we could have labeled any specific value of s as zero, thus integrating from l to L is the same as integrating from 0 to $L-l$. Thus the first two terms are

$$\int_0^l \int_0^l \langle \vec{t}(s) \vec{t}(s') \rangle ds ds' = 2 P_1 l \left(1 - \frac{P_1}{l} (1 - e^{-l/P_1})\right)$$

$$\int_l^L \int_l^L \langle \vec{t}(s) \vec{t}(s') \rangle ds ds' = 2 P_2 (L-l) \left(1 - \frac{P_2}{(L-l)} (1 - e^{-(L-l)/P_2})\right)$$

Finally, we turn to the last integral. To do this integral, we need to recognize that the correlation terms, $e^{-s/P}$, are multiplicative. If we want the correlation between two vectors, \vec{t}_A and \vec{t}_C a distance $s + s'$ apart this is the same as the product of the individual correlations between a third vector \vec{t}_B a distance s from \vec{t}_A and s' from \vec{t}_B .

$$\text{If } \langle \vec{t}_A \vec{t}_B \rangle = e^{-s/P} \text{ and } \langle \vec{t}_B \vec{t}_C \rangle = e^{-s'/P} \text{ then } \langle \vec{t}_A \vec{t}_C \rangle = e^{-(s+s')/P} = e^{-s/P} e^{-s'/P} = \langle \vec{t}_A \vec{t}_B \rangle \langle \vec{t}_B \vec{t}_C \rangle$$

Thus, we can write $\langle \vec{t}(s) \vec{t}(s') \rangle = \langle \vec{t}(s) \vec{t}(l) \rangle \langle \vec{t}(l) \vec{t}(s') \rangle$, where we are now essentially referencing all vectors to the tangent vector at the interface between the two regions. Thus, the integral is

$$\begin{aligned} 2 \int_0^l \int_l^L \langle \vec{t}(s) \vec{t}(s') \rangle ds ds' &= 2 \int_0^l \int_l^L \langle \vec{t}(s) \vec{t}(l) \rangle \langle \vec{t}(l) \vec{t}(s') \rangle ds ds' = 2 \int_0^l \int_l^L e^{-(l-s)/P_1} e^{-(s'-l)/P_2} ds ds' \\ &= 2 \int_0^l e^{-(l-s)/P_1} P_2 (1 - e^{-(L-l)/P_2}) ds = 2 P_1 P_2 (1 - e^{-l/P_1}) (1 - e^{-(L-l)/P_2}) \end{aligned}$$

Thus, the full expression is

$$\langle R^2 \rangle = 2 P_1 l \left(1 - \frac{P_1}{l} (1 - e^{-l/P_1})\right) + 2 P_2 (L-l) \left(1 - \frac{P_2}{(L-l)} (1 - e^{-(L-l)/P_2})\right) + 2 P_1 P_2 (1 - e^{-l/P_1}) (1 - e^{-(L-l)/P_2})$$

■ Calculation of Correlation Term for Problem 1

In order to calculate the correlation term for problem 1, we need to devise a way of evaluating the dot product for all vectors separated by k segments. The formal way to do this is to use rotation matrices.

Let's start by considering the $\langle \vec{t}_i \vec{t}_{i+1} \rangle$ term, i.e. $k = 1$. For simplicity let's choose a coordinate system in which $\vec{t}_i = 0 e_x + 0 e_y + l e_z$, where $e_{x,y,z}$ are the unit vectors that define our Cartesian coordinate system. However, we could also decide that in a new coordinate system vector \vec{t}_{i+1} is aligned completely in the z 'direction, i.e.

$\vec{l}_{i+1} = 0 e_x' + 0 e_y' + l e_z'$. The dot product is simple if we first rotate the original coordinate system into the new coordinate system, i.e. $e_x, e_y, e_z \rightarrow e_x', e_y', e_z'$ or vice versa. There is a well defined way to do this.

If we have a vector in the original coordinate system, then to rotate it into the primed coordinate system, we first must rotate it around the z axis of the original coordinate system by an angle ψ so that it is in the xz plane. We can then rotate it around the new y axis by an angle θ , so that it is now completely aligned in the z direction. These rotations can be formally done with the following rotation matrices:

$$\text{In}[81] := \mathbf{Rz}[\psi] := \begin{pmatrix} \mathbf{Cos}[\psi] & \mathbf{Sin}[\psi] & 0 \\ -\mathbf{Sin}[\psi] & \mathbf{Cos}[\psi] & 0 \\ 0 & 0 & 1 \end{pmatrix};$$

$$\text{In}[82] := \mathbf{Ry}[\theta] := \begin{pmatrix} \mathbf{Cos}[\theta] & 0 & -\mathbf{Sin}[\theta] \\ 0 & 1 & 0 \\ \mathbf{Sin}[\theta] & 0 & \mathbf{Cos}[\theta] \end{pmatrix};$$

Thus, if we have a vector $\vec{l}_{i+1} = \begin{pmatrix} 0 \\ 0 \\ l \end{pmatrix} = 0 e_x' + 0 e_y' + l e_z'$, we can show that it will have coordinates

$$\vec{l}_{i+1} = -l \mathbf{Sin}[\theta] e_x + 0 e_y + l \mathbf{Cos}[\theta] e_z$$

in the new coordinate system by applying the two rotation matrices above.

$$\text{In}[83] := \mathbf{Ry}[\theta] . \mathbf{Rz}[\psi] . \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} // \mathbf{Simplify} // \mathbf{MatrixForm}$$

$$\text{Out}[83] // \mathbf{MatrixForm} = \begin{pmatrix} -1 \mathbf{Sin}[\theta] \\ 0 \\ 1 \mathbf{Cos}[\theta] \end{pmatrix}$$

Note: this is not the same answer we would get if we computed things in simple spherical coordinates. This is because once we rotate around z our y axis is changed.

Now that this vector is rotated into the original coordinate system the dot product is simple

$$\text{In}[84] := (0 \ 0 \ 1) . \begin{pmatrix} -1 \mathbf{Sin}[\theta] \\ 0 \\ 1 \mathbf{Cos}[\theta] \end{pmatrix} // \mathbf{Simplify} // \mathbf{MatrixForm}$$

$$\text{Out}[84] // \mathbf{MatrixForm} = (1^2 \mathbf{Cos}[\theta])$$

To take the average of this dot product, we have to recall that the angle θ is fixed while the angle ψ could take on any value between 0 and 2π . Thus the probability of observing any value of ψ is $\frac{1}{2\pi}$. Remember that formally

$$\langle \vec{l}_i \vec{l}_{i+1} \rangle = \int d\psi \vec{l}_i \vec{l}_{i+1} p(\psi)$$

which in this case is simply

$$\langle \vec{l}_i \vec{l}_{i+1} \rangle = \int d\psi \vec{l}_i \vec{l}_{i+1} p(\psi) = \int d\psi l^2 \cos[\theta] \frac{1}{2\pi} = l^2 \cos[\theta]$$

Now let's consider the more complicated case of $k = 2$. In this case, we can extend the above argument to an additional coordinate system, a double prime coordinate system. Thus, to rotate the original vector into this coordinate system, we need to perform the same rotation twice, first to the prime coordinate system, then from the prime coordinate system to the double prime coordinate system. This gives

$$\text{In}[85] := \mathbf{Ry}[\theta] \cdot \mathbf{Rz}[\psi_2] \cdot \mathbf{Ry}[\theta] \cdot \mathbf{Rz}[\psi_1] \cdot \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} // \text{Simplify} // \text{MatrixForm}$$

Out[85]//MatrixForm=

$$\begin{pmatrix} -2 l \cos[\theta] \cos\left[\frac{\psi_2}{2}\right]^2 \sin[\theta] \\ l \sin[\theta] \sin[\psi_2] \\ l (\cos[\theta]^2 - \cos[\psi_2] \sin[\theta]^2) \end{pmatrix}$$

Where we have labeled two different ψ angles, ψ_1 and ψ_2 , since the orientation of these two segments depends on two angles. We can now take the dot product

$$\text{In}[86] := \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} -2 l \cos[\theta] \cos\left[\frac{\psi_2}{2}\right]^2 \sin[\theta] \\ l \sin[\theta] \sin[\psi_2] \\ l (\cos[\theta]^2 - \cos[\psi_2] \sin[\theta]^2) \end{pmatrix} // \text{Simplify} // \text{MatrixForm}$$

Out[86]//MatrixForm=

$$(l^2 (\cos[\theta]^2 - \cos[\psi_2] \sin[\theta]^2))$$

This is a more complicated expression than above, and to find the average value we must integrate over both ψ_1 and ψ_2 , both of which are equally likely on the range of 0 to 2π .

$$\text{In}[87] := \int_0^{2\pi} \frac{1}{2\pi} \left(\int_0^{2\pi} \frac{1}{2\pi} l^2 (\cos[\theta]^2 - \cos[\psi_2] \sin[\theta]^2) d\psi_1 \right) d\psi_2$$

$$\text{Out}[87] = l^2 \cos[\theta]^2$$

For the $k = 3$ case we now need to do three rotations, thus our dot product will be

$$\text{In}[88] := \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \cdot \mathbf{Ry}[\theta] \cdot \mathbf{Rz}[\psi_3] \cdot \mathbf{Ry}[\theta] \cdot \mathbf{Rz}[\psi_2] \cdot \mathbf{Ry}[\theta] \cdot \mathbf{Rz}[\psi_1] \cdot \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} // \text{Simplify} // \text{MatrixForm}$$

Out[88]//MatrixForm=

$$(l^2 (\cos[\theta]^3 - \cos[\theta] (\cos[\psi_3] + \cos[\psi_2] (1 + \cos[\psi_3])) \sin[\theta]^2 + \sin[\theta]^2 \sin[\psi_2] \sin[\psi_3]))$$

and to perform the average we need to integrate over all three ψ angles

$$\text{In}[89] := \int_0^{2\pi} \frac{1}{2\pi} \left(\int_0^{2\pi} \frac{1}{2\pi} \left(\int_0^{2\pi} \frac{1}{2\pi} l^2 (\cos[\theta]^3 - \cos[\theta] (\cos[\psi_3] + \cos[\psi_2] (1 + \cos[\psi_3]))) \sin[\theta]^2 + \sin[\theta]^2 \sin[\psi_2] \sin[\psi_3] \right) d\psi_1 \right) d\psi_2 \right) d\psi_3$$

$$\text{Out}[89] = l^2 \cos[\theta]^3$$

To generalize this argument to all k , we can write

$$\langle \vec{l}_i \vec{l}_{i+k} \rangle = \int d\psi_1 \frac{1}{2\pi} \int d\psi_2 \frac{1}{2\pi} \dots \int d\psi_k$$

$$\frac{1}{2\pi} (0 \ 0 \ l) (R_y[\theta] R_z[\psi_k]) \dots (R_y[\theta] R_z[\psi_2]) (R_y[\theta] R_z[\psi_1]) \begin{pmatrix} 0 \\ 0 \\ l \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ l \end{pmatrix}$$

$$(0 \ 0 \ l) \left(\int d\psi_1 \frac{1}{2\pi} R_y[\theta] R_z[\psi_1] \right) \left(\int d\psi_2 \frac{1}{2\pi} R_y[\theta] R_z[\psi_2] \right) \dots \left(\int d\psi_k \frac{1}{2\pi} R_y[\theta] R_z[\psi_k] \right)$$

In the last line we recognized that because each rotation matrix depends on a different ψ_i , we can perform each average before taking the matrix product! Thus, if we calculate the average of one rotation

$$\text{In}[90] := \int_0^{2\pi} \frac{1}{2\pi} \mathbf{Ry}[\theta] \mathbf{Rz}[\psi] d\psi // \text{MatrixForm}$$

$$\text{Out}[90] // \text{MatrixForm} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \cos[\theta] \end{pmatrix}$$

we can derive the result for arbitrary k

$$\langle \vec{l}_i \vec{l}_{i+k} \rangle = (0 \ 0 \ l) \langle R_y[\theta] R_z[\psi] \rangle^k \begin{pmatrix} 0 \\ 0 \\ l \end{pmatrix} = (0 \ 0 \ l) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \cos^k[\theta] \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ l \end{pmatrix} = l^2 \cos^k[\theta]$$