Physics of Electronic Polymers

Lecture 1.3:
The Freely Rotating Chain Model

Learning Objectives
By the Conclusion of this Lecture, You Should be Able to:

1. **Manipulate** the general expression for the end-to-end distance in a model polymer chain in to match that of the Freely Rotating Chain Model.

2. **Compare and Contrast** the difference between this model and the one described in Lecture 1.2.

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Freely Rotating Chain is More Realistic Than the Freely Jointed Chain

### Schematic of Polymer Links

Previously we said that the following expression was true for a chain with \( n \) number of links that each had a given length.

\[
\langle h^2 \rangle = \left( \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \right) = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle = \sum_{i=1}^{n} \langle \mathbf{l}_i \cdot \mathbf{l}_i \rangle + \sum_{i=1}^{n} \sum_{j \neq i}^{n} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle
\]

\[
\langle h^2 \rangle = nl^2 + \sum_{i=1}^{n} \sum_{j \neq i}^{n} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle
\]

Now, we place more restrictive bounds on the cross term to develop more realistic models.

### The Freely Rotating Chain

Here, we impose a bound on the value of \( \theta \), but we allow the bond to rotate along the third direction (\( \varphi \)).

Here, we no longer can just cancel the cross term. Instead:

\[
\mathbf{l}_i \cdot \mathbf{l}_j = l^2 \cos \theta \neq 0
\]

For all \( i \) and \( j \).
There are Parallel and Perpendicular Components Now

The Freely Rotating Chain (Continued)

We know that when: $|i - j| = 1$, then: $\vec{l}_i \cdot \vec{l}_j = l^2 \cos \theta$

For larger differences between the $i$ and $j$ units, we need to look at two components, the parallel component and the perpendicular component.

The perpendicular component is more straightforward as it will cancel over large values of $n$. This is because the free rotation of the chain is just as likely to be at any position as another.

The parallel component is more difficult, but it can be shown that the following is true.

$$\vec{l}_i \cdot \vec{l}_j = l^2 \cos \theta |i-j|$$

Then, we can return to our previous expression and say the following. 

$$\sum_{i=1}^{n} \sum_{j \neq i}^{n} (\vec{l}_i \cdot \vec{l}_j) = \sum_{i=1}^{n} \sum_{j \neq i}^{n} l^2 \cos \theta |i-j|$$
The Freely Rotating Chain (Continued)

From this point, we can define a new summation notation by saying that:

\[ g = |i - j| \]

and this converts the summation to the following.

\[
2 \sum_{g=1}^{n-1} l^2 (\cos \theta)^2 (n - g) = 2n l^2 \sum_{g=1}^{n-1} (\cos \theta)^g - 2l^2 \sum_{g=1}^{n-1} g (\cos \theta)^g
\]

The two summation terms have algebraic solutions that can be in the limits that \( n \) is a large number and that \( |\cos \theta| < 1 \). If this is the case, then the expression for the square of the average end-to-end distance reduces to the following.

\[
\langle h^2 \rangle = nl^2 + \sum_{i=1}^{n} \sum_{j \neq i} \langle \vec{l}_i \cdot \vec{l}_j \rangle = nl^2 + 2nl^2 \left( \frac{\cos \theta}{1 - \cos \theta} \right) - 2l^2 \left( \frac{\cos \theta}{(1 - \cos \theta)^2} \right)
\]

\[
\langle h^2 \rangle = nl^2 \left( \frac{1 + \cos \theta}{1 - \cos \theta} - \frac{2}{n} \left( \frac{\cos \theta}{(1 - \cos \theta)^2} \right) \right) \approx nl^2 \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right)
\]
Important Observations Regarding the Freely Rotating Chain

The Freely Rotating Chain (Continued)

\[ \langle h^2 \rangle = nl^2 \left\{ \frac{1 + \cos \theta}{1 - \cos \theta} - \frac{2}{n} \left( \frac{\cos \theta}{(1 - \cos \theta)^2} \right) \right\} \approx nl^2 \left\{ \frac{1 + \cos \theta}{1 - \cos \theta} \right\} \]

- The end-to-end distance of the freely rotating chain scales in the same manner as that of the freely rotating chain.

- However, the freely rotating chain predicts a larger end-to-end distance than the freely jointed chain as the angle will be less than 90 °. This is to be expected as it indicates that it is more physically realistic that the chain will not fold right back onto itself.

- Note that this model was developed for relatively large values of n. As we will see, approximations made here do not necessarily hold at lower values of n. This is important as many electronically-active polymers have lower degree of polymerization values than what is seen commonly in commodity polymeric materials.

Next time we will explain what happens when we take away the free rotation in the final angular coordinate, and how these values can be translated into measurable parameters.