Lecture 4:
Ideal polymer chains – 3 Different Models

Prof. Mark W. Tibbitt – ETH Zürich – 03 March 2022

1 Suggested reading

- *Polymer Physics* – Rubinstein and Colby: Chapter 2

- *Principles of Polymer Chemistry* – Flory: Chapter 10

- *Introduction to Polymer Physics* – Doi: Chapter 1

2 Three Different Models of Ideal Polymer Chains

The Freely Jointed Chain model or random walk model presented in Lecture 3 ignores bonding and sterics and is non-physical in its origin. As we will see, this model still functions extremely well in many cases. Here, we explore three other models of ideal polymer chains. The first will be referred to as the **Mathematician's Ideal Chain**, which is effectively a reformulation of the Freely Jointed Chain from a different approach. As before, all models are 'ideal' in that we do not account for any energetic interactions between monomers along the backbone of the polymer. The Mathematician's Ideal Chain states that $\langle r^2 \rangle = N\ell^2$ as before. The second model will be referred to as the **Chemist's Ideal Chain**. This model includes an effective parameter C_∞ that is used to correct for the non-physical aspects of the Freely Jointed Chain and Mathematician's Ideal Chain and increases the root-mean-square end-to-end distance based on known or estimated constraints. The Chemist's Ideal Chain states that $\langle r^2 \rangle = N\ell^2 C_\infty$. By inspection, $C_\infty = 1$ for the Freely Jointed Chain. The third model will be referred to as the **Physicist's Ideal Chain**. Here, we re-scale the values of N and ℓ to N_K and b to approximate chains as Freely Jointed Chains. In this model, $\langle r^2 \rangle = N_K b^2$.

3 Mathematician's Ideal Chain

As stated above, the Mathematician's Ideal Chain is essentially the same as the Freely Jointed Chain model, but viewed from a different mathematical formalism. In this model, we again assume that we have a polymer chain composed of N monomers that can each be represented as vectors in 3D space with a fixed length $|\vec{r}_i| = \ell$. Thus, the end-to-end distance vector $\vec{r}$ can be calculated as:

$$\vec{r} = \vec{r}_1 + \vec{r}_2 + \vec{r}_3 + \cdots = \sum_{i=1}^{N} \vec{r}_i. \tag{1}$$

Each $\vec{r}$ is non-zero; however, as the chains are randomly oriented with no preferential direction $\langle \vec{r} \rangle = 0$.

Therefore, as we have done before, we consider $\langle \vec{r}^2 \rangle$ instead. The easiest way to compute this is to expand $\langle \vec{r}^2 \rangle$ in vector notation as the dot product of the vectors $\{\vec{r}_i\}$ for the monomers that compose the chain:

$$\langle \vec{r} \cdot \vec{r} \rangle = \langle \sum_{i=1}^{N} \vec{r}_i \cdot \sum_{j=1}^{N} \vec{r}_j \rangle. \tag{2}$$

Eq. 2 computes the mean-square end-to-end distance and is better visualized in matrix form. Each row represents the dot product of $\vec{r}_i$ with each $\vec{r}_j$. Thus, we will have an $N \times N$ matrix as shown below:

$$\langle \vec{r} \cdot \vec{r} \rangle = \left\langle \begin{bmatrix} \vec{r}_1 \cdot \vec{r}_1 & \vec{r}_1 \cdot \vec{r}_2 & \vec{r}_1 \cdot \vec{r}_3 & \cdots & \vec{r}_1 \cdot \vec{r}_N \\ \vec{r}_2 \cdot \vec{r}_1 & \vec{r}_2 \cdot \vec{r}_2 & \vec{r}_2 \cdot \vec{r}_3 & \cdots & \vec{r}_2 \cdot \vec{r}_N \\ \vec{r}_3 \cdot \vec{r}_1 & \vec{r}_3 \cdot \vec{r}_2 & \vec{r}_3 \cdot \vec{r}_3 & \cdots & \vec{r}_3 \cdot \vec{r}_N \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \vec{r}_N \cdot \vec{r}_1 & \vec{r}_N \cdot \vec{r}_2 & \vec{r}_N \cdot \vec{r}_3 & \cdots & \vec{r}_N \cdot \vec{r}_N \end{bmatrix} \right\rangle \tag{3}$$

We recall that by definition for an ideal chain $\langle \vec{r}_i \cdot \vec{r}_j \rangle_{i \neq j} = 0$. Therefore, all of the cross terms are equal to zero. Further, the dot product of a vector with itself is the magnitude squared so $\langle \vec{r}_i \cdot \vec{r}_j \rangle_{i=j} = \ell^2$ Thus, all of the diagonal terms are equal to ℓ^2. So the matrix above reduces to:

$$\langle \vec{r} \cdot \vec{r} \rangle = \langle r^2 \rangle = \begin{bmatrix} \ell^2 & 0 & 0 & \cdots & 0 \\ 0 & \ell^2 & 0 & \cdots & 0 \\ 0 & 0 & \ell^2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \ell^2 \end{bmatrix} \tag{4}$$

Summing over all of the terms now becomes trivial and we arrive at the relationship that

$$\boxed{\langle r^2 \rangle = N\ell^2} \tag{5}$$

as derived previously for the Freely Jointed Chain model.

4 Chemist's Ideal Chain

Another model of ideal polymer chains, that is the model ignores energetic interactions between monomers along the chain, is that of the Chemist's ideal chain, which includes information about known bond angles into the Freely Jointed Chain model.

The first approximation is the **Freely Rotating Chain** model, which fixes all bond lengths ℓ and bond angles θ but assumes all torsional angles ϕ are equally probable about each bond along the backbone. Therefore, to calculate the mean-square end-to-end distance we must calculate the correlations between $\vec{r}_i$ and $\vec{r}_j$ because as before:

$$\langle \vec{r} \cdot \vec{r} \rangle = \langle \sum_{i=1}^{N} \vec{r}_i \cdot \sum_{j=1}^{N} \vec{r}_j \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \vec{r}_i \cdot \vec{r}_j \rangle. \tag{6}$$

Given a fixed bond angle θ one can show geometrically that:

$$\langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle = \ell^2(-\cos\theta) \tag{7}$$

$$\langle \vec{r}_i \cdot \vec{r}_{i+2} \rangle = \ell^2(-\cos\theta)^2 \tag{8}$$

$$\langle \vec{r}_i \cdot \vec{r}_{i+3} \rangle = \ell^2(-\cos\theta)^3 \ldots \tag{9}$$

And, in general, that:

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = \ell^2(-\cos\theta)^{|j-i|} \tag{10}$$

Therefore Eq. 3 for the freely rotating chain model becomes:

$$\langle \vec{r} \cdot \vec{r} \rangle = \ell^2 \begin{bmatrix} 1 & -\cos\theta & \cos^2\theta & \cdots & (-\cos\theta)^{N-1} \\ -\cos\theta & 1 & -\cos\theta & \cdots & (-\cos\theta)^{N-2} \\ \cos^2\theta & -\cos\theta & 1 & \cdots & (-\cos\theta)^{N-3} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ (-\cos\theta)^{N-1} & (-\cos\theta)^{N-2} & (-\cos\theta)^{N-3} & \cdots & 1 \end{bmatrix} \tag{11}$$

We will not show all of the math here, but this sum reduces to:

$$\langle r^2 \rangle = N\ell^2 \left(\frac{1-\cos\theta}{1+\cos\theta} \right) \tag{12}$$

We will often write this as:

$$\boxed{\langle r^2 \rangle = N\ell^2 C_\infty} \tag{13}$$

The freely rotating chain model then defines $C_\infty = \frac{1-\cos\theta}{1+\cos\theta}$. We can also take into account that rotation about each bond is not completely free and often there are select torsional angles ϕ that are favorable, for example $gauche_-, trans,$ and $gauche_+$ in a carbon atom chain, and this is called the **Hindered Rotation** model. We can take this into account using a similar strain of logic for taking the $\langle \cos\phi \rangle$ from the Boltzmann distribution, which will be introduced explicitly later. Again summing over all terms with the new assumptions, we can show that:

$$\langle r^2 \rangle = N\ell^2 \left(\frac{1 - \cos\theta}{1 + \cos\theta} \right) \left(\frac{1 + \langle \cos\phi \rangle}{1 - \langle \cos\phi \rangle} \right) \tag{14}$$

Therefore, in the hindered rotation model $C_\infty = \left(\frac{1-\cos\theta}{1+\cos\theta} \right) \left(\frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle} \right)$. Physically, C_∞ will increase the end-to-end distance of a polymer as $C_\infty \geq 1$ for real polymers, $\theta > 90°$ implies $C_\infty > 1$. $\theta = 90°$ is equivalent to the Freely Jointed Chain model. Typical values for C_∞ range from ~ 1–20 and can be thought of as the number of monomers that are felt by each monomer.

5   Physicist's Ideal Chain

The physicist, and often we will take this view, is most interested in how the properties of an object scales and finds clever ways to reformulate the dimensions of an object to a frame that is easier to compute. In the Chemist's Ideal Chain, the physicist sees a Freely Jointed Chain on a slightly different scale. One can simply rescale the degree of polymerization N and monomer length ℓ to arrive at an **equivalent Freely Jointed Chain** of a different dimension. One way to think about this, is that we consider the term C_∞, as stated above, as the number of monomers that are felt by each monomer. Thus, if we redefine the 'monomer' as $b = C_\infty \ell$, clumping together the monomers that 'feel' each other, we can rescale the system to a new dimension that behaves as if the 'monomers' b are not influenced by each other. On this scale, the polymer will behave identically to the Freely Jointed Chain model with Gaussian behavior as before. This strategy was originally developed by Kuhn and the effective monomer b is referred to as the Kuhn monomer. We also need to rescale the degree of polymerization to the number of Kuhn monomers:

$$N_K = \frac{N}{C_\infty}. \tag{15}$$

Therefore, we can rewrite the mean-square end-to-end distance in Kuhn monomers as:

$$\boxed{\langle r^2 \rangle = N_K b^2 = N\ell^2 C_\infty} \tag{16}$$

We will use this reformulation commonly throughout the course and this is a powerful way to convert a more complicated view of a polymer chain into a much simpler form without losing any of the real physics of the system. Importantly, all three of these models show the same scaling factor for the size of these objects

$$\boxed{\langle r^2 \rangle^{\frac{1}{2}} \propto N^{\frac{1}{2}}} \tag{17}$$

This is the scaling factor of size with respect to degree of polymerization for ideal polymer chains. We will explore this in other models in our discussion of 'real' polymer chains and, in general, we will be interested in understanding how the size of the object scales with N

$$\langle r^2 \rangle^{\frac{1}{2}} \propto N^{\nu} \tag{18}$$

where $\nu = 0.5$ for ideal polymer chains.

6   Radius of gyration

We have used up to now the mean-square end-to-end distance as a measure of the size of a polymer chain. This is quite effective for the linear polymer chains that we have looked at so far. More complex geometries are not easy to formulate as an end-to-end distance, for example star, comb, or ring polymers. For these and other polymers, we often calculate the square **radius of gyration** r_g^2 as a general measure of polymer size. The square radius of gyration of a polymer is defined as the average square distance between monomers $(\vec{r}_i)$ in a conformation and the center of mass $(\vec{r}_c)$:

$$r_g^2 \equiv \frac{1}{N} \sum_{i=1}^{N} (\vec{r}_i - \vec{r}_c)^2, \tag{19}$$

where the position vector of the center of mass of the polymer is the number-average of all of the monomer vectors

$$\vec{r}_c \equiv \frac{1}{N} \sum_{i=1}^{N} \vec{r}_i. \tag{20}$$

It can be shown that be a bit of algebra one can rewrite the square radius of gyration as

$$r_g^2 = \frac{1}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} (\vec{r}_i - \vec{r}_j)^2, \tag{21}$$

where the 2 accounts for double counting and we have $\frac{1}{N^2}$ because of the double sum. As before, we will average over the possible conformations for a polymer chain as it is a rapidly fluctuating object in free space, so we often are interested in the mean-square radius of gyration

$$\langle r_g^2 \rangle = \frac{1}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle (\vec{r}_i - \vec{r}_j)^2 \rangle. \tag{22}$$

This equation will be useful in computing one of the exercise problems. For a linear polymer chain, we can show that

$$\langle r_g^2 \rangle = \frac{N\ell^2}{6} = \frac{\langle r^2 \rangle}{6}. \tag{23}$$

Throughout this course, we will most often refer to the mean-square end-to-end distance of a polymer though we may use radius of gyration interchangeably.