

# ENAS 606 : Polymer Physics

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## Ideal Chain Conformations and Statistics

### 1 Overview

Consideration of the structure of macromolecules starts with a look at the details of chain level chemical details which can impact the conformations adopted by the polymer. In the case of saturated carbon backbones, while maintaining the desired  $C_{i-1} - C_i - C_{i+1}$  bond angle of  $112^\circ$ , the placement of the final carbon in the triad above can occur at any point along the circumference of a circle, defining a torsion angle  $\varphi$ . We can readily recognize the energetic differences as a function this angle,  $U(\varphi)$  such that there are 3 minima - a deep minimum corresponding the the trans state, for which  $\varphi = 0$  and energetically equivalent *gauche*<sub>-</sub> and *gauche*<sub>+</sub> states at  $\varphi = \pm 120$  degrees, as shown in Fig 1.

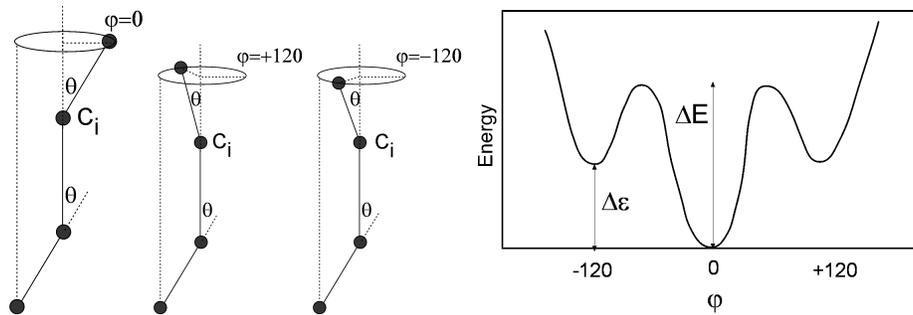


Figure 1: Trans, gauche- and gauche+ configurations, and their energetic states

#### 1.1 Static Flexibility

The static flexibility of the chain in equilibrium is determined by the difference between the levels of the energy minima corresponding the gauche and trans states,  $\Delta\epsilon$ .

If  $\Delta\epsilon < kT$ , the  $g_+$ ,  $g_-$  and  $t$  states occur with similar probability, and so the chain can change direction and appears as a random coil.

If  $\Delta\epsilon$  takes on a larger value, then the  $t$  conformations will be enriched, so the chain will be rigid locally, but on larger length scales, the eventual occurrence of  $g_+$  and  $g_-$  conformations imparts a random conformation.

Overall, if we ignore details on some length scale smaller than  $l_p$ , the persistence length, the polymer appears as a continuous flexible chain where

$$l_p = l_0 \exp(\Delta\epsilon/kT) \quad (1)$$

where  $l_0$  is something like a monomer length.

## 1.2 Dynamic Flexibility

The dynamics of the transition from the  $t$  to  $g_-$  and  $g_+$  states is determined by the activation barrier separating them,  $\Delta E$ . In analogy to the structural or spatial counterpart, we may think in terms of a persistence time,  $\tau_p$

$$\tau_p = \tau_0 \exp(\Delta E/kT) \quad (2)$$

where  $\tau_0$  is an attempt frequency.

On timescales smaller than  $\tau_p$  (at high frequencies,  $\omega > 1/\tau_p$ ), the chain looks inflexible - its conformation doesn't change.

On longer timescales, or smaller frequencies, the chain appears flexible as it is able to sample many different conformational states during the time of observation.

## 2 Ideal Chain Models

Here we consider ideal chains, that like ideal gases, feature no net interaction (repulsive or attractive) among the  $n$  monomers, each with bond length  $l$ . We start with a description of the end to end distance of the chain. Given the random nature of displacements of monomers with respect to each other, the mean end-end distance,  $\langle R \rangle = 0$ . The first non-trivial moment of the distribution of end-end distances is the second moment, so we look at the mean squared end-end distance,  $\langle R^2 \rangle$ , defined in Equation 3.

$$\begin{aligned} \langle R^2 \rangle &= \langle \vec{R}_n \cdot \vec{R}_n \rangle \\ &= \left\langle \left( \sum_{i=1}^n \vec{r}_i \right) \cdot \left( \sum_{j=1}^n \vec{r}_j \right) \right\rangle \\ &= \sum_{i=1}^n \sum_{j=1}^n \langle \vec{r}_i \cdot \vec{r}_j \rangle \\ &= l^2 \sum_{i=1}^n \sum_{j=1}^n \langle \cos \theta_{ij} \rangle \end{aligned} \quad (3)$$

### 2.1 Freely Jointed Chain

- All bond lengths are the same
- There is no correlation between the directions of bond angles, no treatment of torsional angles.  $\langle \cos \theta_{ij} \rangle = 0$  for  $i \neq j$ .

$$\langle R^2 \rangle = nl^2 \quad (4)$$

### 2.1.1 Equivalent Freely Jointed Chain

We may represent an ideal polymer chain for which we account for local interactions via  $C_\infty$  etc. by an equivalent freely jointed chain. The equivalent chain has the same fully extended length of the actual chain,  $R_{max}$ , and the same mean square end-end distance. It is composed of  $N$  subunits of length  $b$  such that  $Nb = R_{max}$  and  $\langle R^2 \rangle = Nb^2 = C_\infty nl^2$ , so that

$$\begin{aligned} N &= \frac{R_{max}^2}{C_\infty nl^2} \\ b &= \frac{C_\infty nl^2}{R_{max}} \end{aligned} \quad (5)$$

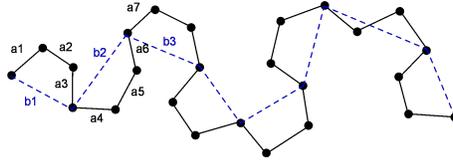


Figure 2: Equivalent freely jointed chain

## 2.2 Freely Rotating Chain

- All bond lengths and angles are the same
- We have to determine the correlation among the bond vectors of the chain, the distance over which the direction of a particular vector may persist.

Correlations are transferred along the direction of bond vectors.

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = l^2 (\cos \theta)^{|j-i|} \quad (6)$$

$$\begin{aligned} \langle R^2 \rangle &= nl^2 + l^2 \sum_{i=1}^n \left( \sum_{k=1}^{i-1} \cos^k \theta + \sum_{k=1}^{n-i} \cos^k \theta \right) \\ (\cos \theta)^{|j-i|} &= \exp(|j-i| \ln(\cos \theta)) \\ &= \exp\left(-\frac{|j-i|}{s_p}\right) \end{aligned} \quad (7)$$

where  $s_p$  is a persistence number,  $s_p = -1/\ln(\cos \theta)$ . This leads to the final result that

$$\langle R^2 \rangle = nl^2 \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) = C_\infty nl^2 \quad (8)$$

For saturated carbon chains,  $\theta = 68^\circ$  so  $C_\infty \approx 2$ .

### 2.2.1 Worm-Like Chain Model

For very stiff chains, the worm-like chain model is applied. Here, the bond angle  $\theta$  is small and we make approximations for  $\cos \theta$  and  $\ln(\cos \theta)$  as used in the derivation for the freely rotating chain.

$$\begin{aligned}
s_p &\cong 2/\theta^2 \\
C_\infty &\cong 4/\theta^2 \\
b &\cong l \frac{4}{\theta^2} = 2l_p \\
\langle R^2 \rangle &= 2l_p R_{max} - 2l_p^2 (1 - \exp(-R_{max}/l_p))
\end{aligned} \tag{9}$$

In the limit where the chain is very long compared to its persistence length,  $R_{max} \gg l_p$ .  $\langle R^2 \rangle \cong 2l_p R_{max} = bR_{max}$ . This is the ideal chain limit.

In the limit where the chain is short compared to its persistence length,  $R_{max} \ll l_p$ .  $\langle R^2 \rangle \cong R_{max}^2$ . This is the rod-like limit

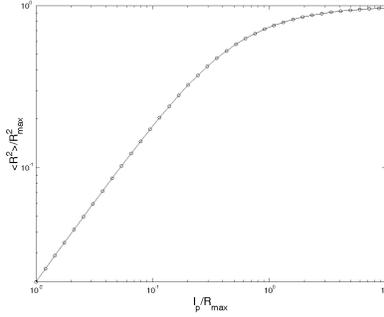


Figure 3: Mean square end to end distance in the WLC model as a function of persistence length, showing the cross over from ideal to rigid rod behavior

### 2.3 Hindered Rotation Chain

- All bond lengths and angles are the same
- Correlations among the bond angles are treated as before.
- Torsional angles are not correlated and can assume continuous values. The mean torsional angle is calculated using Boltzmann weighting of the continuous distribution of  $U(\varphi)$ , as in Figure 1

$$\begin{aligned}
\langle R^2 \rangle &= C_\infty n l^2 \\
C_\infty &= \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) \left( \frac{1 + \langle \cos \varphi \rangle}{1 - \langle \cos \varphi \rangle} \right) \\
\langle \cos \varphi \rangle &= \frac{\int_0^{2\pi} \cos \varphi \exp(-U(\varphi)/kT) d\varphi}{\int_0^{2\pi} \exp(-U(\varphi)/kT) d\varphi}
\end{aligned} \tag{10}$$

### 2.4 Rotational Isomeric States

- All bond lengths and angles are the same
- Correlations among the bond angles are treated as before.
- Each monomer can assume one of a limited number of discrete torsional states,  $t$ ,  $g_-$  or  $g_+$ .

- The probability of sequences of states is modified by relevant energetic penalties
- Successfully applied in statistical mechanics calculations of polymer conformations

### 2.4.1 The Ising Chain

The rotational isomeric state model provides a direct map between calculation of polymer conformations and the familiar 1D Ising model. In this frame, we consider the energy of the chain as

$$U = \sum_{i=2}^n u(\varphi_{i-1}, \varphi_i) \quad (11)$$

where  $u(\varphi_{i-1}, \varphi_i)$  is the pair interaction energy, and bonds are not energetically independent. We calculate the partition function by summing over all configurational states represented by the set of  $\{\varphi_i\}$ , after which the thermodynamic functions follow in the usual manner.

$$\begin{aligned} Z &= \sum_{\{\varphi_i\}} \exp(-U(\varphi_i)/kT) \\ F_p &= -kT \ln Z \\ S_p &= -\partial F_p / \partial T \\ U &= F_p + TS_p \end{aligned} \quad (12)$$

## 3 Radius of Gyration

Instead of the end-end distance, the radius of gyration of the macromolecule,  $R_g$  is more meaningful intuitively as it gives a sense of the size of the polymer coil. It is also the quantity that is experimentally accessed.

The square radius of gyration is the average squared distance of any point in the object (polymer coil) from it's center of mass. This definition, along with the final expression for the calculation of the ensemble average of the quantity is provided in Equation 13.

$$\begin{aligned} R_g^2 &\equiv \frac{1}{N} \sum_{i=1}^N (\vec{R}_i - \vec{R}_{cm})^2 \\ R_{cm} &\equiv \frac{1}{N} \sum_{j=1}^N (\vec{R}_j) \\ R_g^2 &= \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N (\vec{R}_i - \vec{R}_j)^2 \end{aligned} \quad (13)$$

The radius of gyration of an equivalent freely jointed chain is given by  $\langle R_g^2 \rangle = Nb^2/6 = \langle R^2 \rangle / 6$ . That is, the radius of gyration is smaller than the root mean square end-end distance by a factor of  $\sqrt{6}$ . It is instructive to remember that the radius of gyration of a solid sphere is not equivalent to its physical radius. For a sphere,  $R_g^2 = 3R^2/5$ . The radius of gyration for some common polymer architectures and solid objects is provided in Table 1.

## References

- [1] P. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, 1979.

| Object       | $R_g^2$                 |
|--------------|-------------------------|
| Linear chain | $Nb^2/6$                |
| Rings        | $Nb^2/12$               |
| f-arm star   | $((N/f)b^2/6)(3 - 2/f)$ |
| H-polymer    | $(Nb^2/6)89/125$        |
| Sphere       | $3R^2/5$                |
| Disk         | $R^2/2$                 |
| Rod          | $L^2/12$                |
| Cylinder     | $(R^2/2) + (L^2/12)$    |

Table 1: Radii of gyration of some common polymer architectures and solid objects

- [2] M. Rubinstein and R. Colby, *Polymer physics*, Oxford University Press, 2003.
- [3] G. Strobl, *The Physics of Polymers: Concepts for Understanding Their Structures and Behavior*, Springer, 1997.