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°, 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 φ. 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*$_-$ and *gauche*$_+$ states at $\varphi = \pm 120$ degrees, as shown in Fig 1.

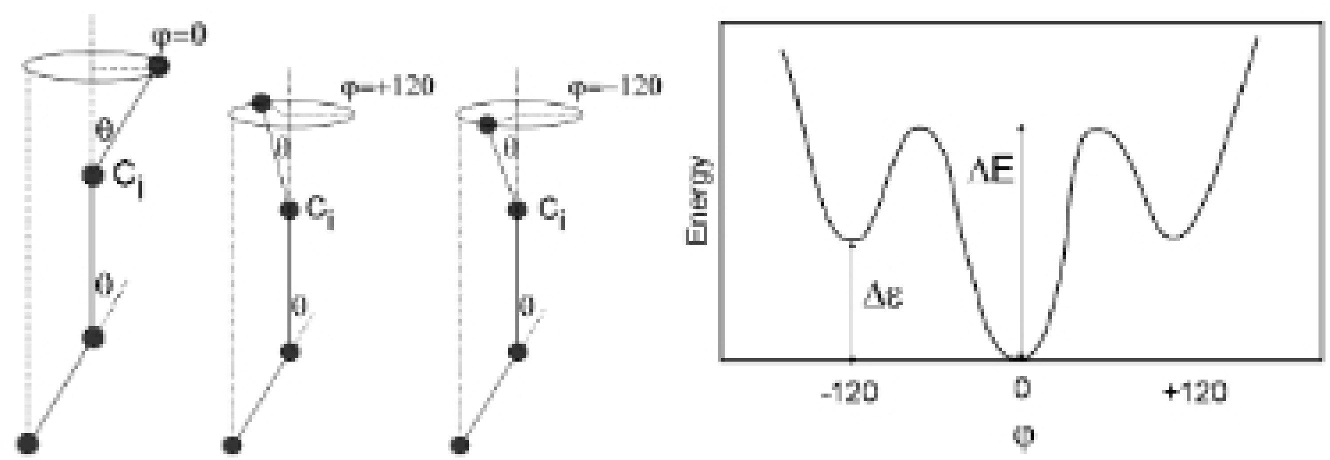

Figure 1: Trans, gauche- and gauche+ configurations, and their energetic sates

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

$$l_p = l_0 \exp(\Delta\epsilon/kT) \tag{1}$$

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, ΔE. In analogy to the structural or spatial counterpart, we may think in terms of a persistence time, τ_p

$$\tau_p = \tau_0 \exp(\Delta E/kT) \tag{2}$$

where τ_0 is an attempt frequency.

On timescales smaller than τ_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.

$$\begin{aligned}
\langle R^2 \rangle &= \langle \overrightarrow{R_n}.\overrightarrow{R_n} \rangle \\
&= \left\langle \left(\sum_{i=1}^{n} \overrightarrow{r_i} \right) \cdot \left(\sum_{j=1}^{n} \overrightarrow{r_j} \right) \right\rangle \\
&= \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \overrightarrow{r_i}.\overrightarrow{r_j} \rangle \\
&= l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle
\end{aligned} \tag{3}$$

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 $i \neq j$.

$$\langle R^2 \rangle = nl^2 \tag{4}$$

2.1.1 Equivalent Freely Jointed Chain

We may represent an ideal polymer chain which for which we account for local interactions via C_∞ 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 $\langle R^2 \rangle = Nb^2 = C_\infty n l^2$, so that

$$\begin{aligned} N &= \frac{R_{max}^2}{C_\infty n l^2} \\ b &= \frac{C_\infty n l^2}{R_{max}} \end{aligned} \tag{5}$$

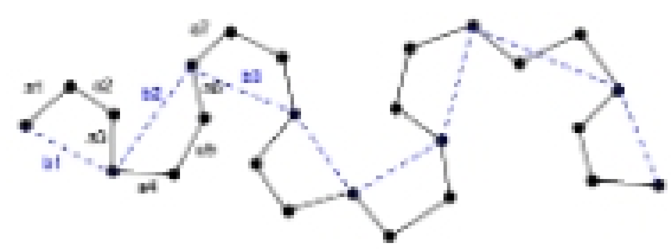

Figure 2: Equivalent freely jointed chain

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.

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

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

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

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

For saturated carbon chains, $\theta = 68°$ 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 θ is small and we make approximations for $\cos\theta$ and $\ln(\cos\theta)$ as used in the derivation for the freely rotating chain.