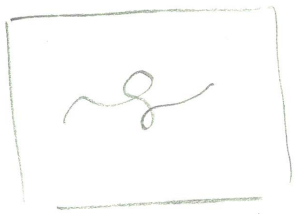
Lecture 2: Ideal Chain Conformations

A. Introduction

* Recall the Polymer physics hypothesis (PPH): conformational entropy (& energy) dominates the behavior of macromolecules.
  - Let's try and understand some of that conformational entropy today.

* We will start by considering an infinitely dilute polymer solution:



single polymer in a solvent bath of infinite extent.

  - For simplicity we will consider an "ideal" or "phantom" chain, i.e. a polymer that does not interact with itself.
  - Notice the parallels with the ideal gas.
  - Key difference: chain connectivity.

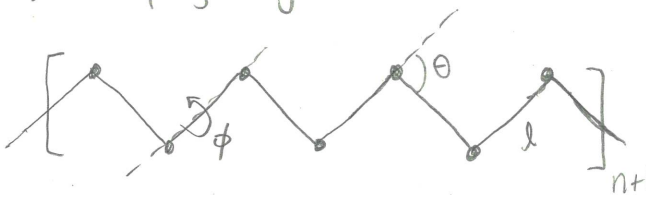
* We will need the formalism of statistical mechanics. Statistical mechanics connects a microscopic description of molecular properties to macroscopic thermodynamic observables.

B. Polymer statistical mechanics

* To say anything using statistical mechanics, we need a molecular model. The model is a simplification of reality. It can be more or less complex.

* The PPH suggests that conformational differences (not electronic states) are what matters for our molecular model of a polymer chain.

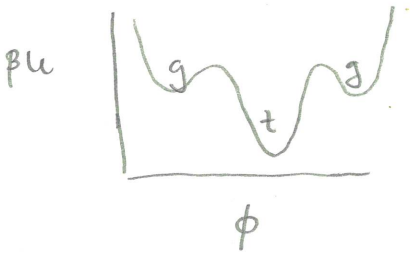
* Consider polyethylene:



n+1 = degree of polymerization

$l = 1.54$ Å (C-C bond length)

$\theta = 71°$ (C-C bond angle)



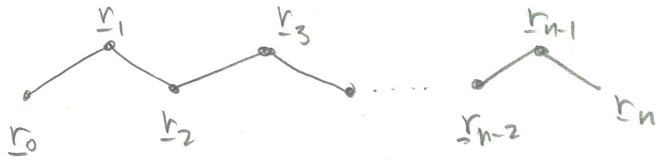
scale < 1 kcal/mol

• Remember: conformational flexibility is governed by torsional rotation

* Mathematically, we can define the conformation by a set of n bond vectors:

$$\{\underline{b}_i\} \quad i \in [1, n]$$

* And by the polymer chain end, $\underline{r}_0$



$$\underline{b}_i = \underline{r}_{i+1} - \underline{r}_i$$

* The joint probability density for observing a conformation (in the nVT ensemble) is given by:

$$P(\underline{r}_0, \{\underline{b}_i\}) = \frac{\exp\left[-\beta U_0(\{\underline{b}_i\})\right]}{Z}$$

↙ Boltzmann distribution

$$Z = \int d\underline{r}_0 \int d\underline{b}_1 \cdots \int d\underline{b}_n \exp\left[-\beta U_0(\{\underline{b}_i\})\right]$$

(*) configurational partition function

$\beta = 1/k_B T$, U_0: potential energy between bonded atoms.
↳ "polymer model"

• This is a consequence of elementary statistical mechanics. If this is mysterious to you, please ask now.

• If we know P, we know everything!

For example:

$$F = -kT \ln Z$$

↖ Helmholtz free energy

(*) Neglects kinetic energy. "configurational" in the stat mech sense.

- we can also get other useful properties, like "ensemble averages":

$$\langle f \rangle = \int d\underline{r}_0 \int d\underline{b}_1 \cdots \int d\underline{b}_n \; P(\underline{r}_0, \{\underline{b}_i\}) \, f(\underline{r}_0, \{\underline{b}_i\})$$

↑ arbitrary function, f.

average is what we would observe macroscopically.

C. Polymer Size

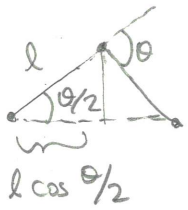
* The size of a polymer in solution is a useful thing to know.

R: polymer size.

v_0: molecular volume.

- we said in lecture 1 that $R >> (v_0 n)^{1/3}$
- we can also infer that $R << L$

L: contour length, fully stretched out length



$L = n l \cos \theta/2$

- $c_2 n^{1/3} << R << c_1 n$

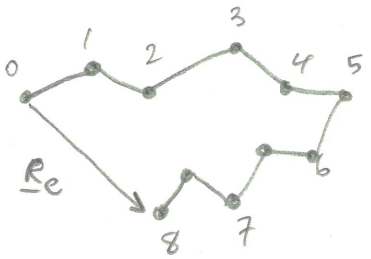
* Let's be more precise. Let

$$\underline{R}_e = \sum_{i=1}^{n} \underline{b}_i$$

$\underline{R}_e$ is the end-to-end distance vector

$$= (\underline{r}_n - \underline{r}_{n-1}) + (\underline{r}_{n-1} + \underline{r}_{n-2}) + \cdots + (\underline{r}_2 - \underline{r}_1) + (\underline{r}_1 - r_0)$$

$$= \underline{r}_n - \underline{r}_0$$



- $\langle \underline{R}_e \rangle$ is <u>not</u> a good measure of size.

  why? Isotropic chain. ↑↓ →← cancel out.

  $\langle \underline{R}_e \rangle = \underline{0}$

- Instead, let's calculate

  $\langle \underline{R}_e \cdot \underline{R}_e \rangle = \langle R_e^2 \rangle$

(✡) I know two ways to do this:

1. Find P. Use our ensemble average formula.
   This is the hard way. (see Fredrickson, p. 27)

2. Use definition of $\underline{R}_e$ and $\underline{b}_i$ and intuition
   This is the easier way.

* To do the calculation, we need to specify the polymer model. The simplest model is a Freely Jointed chain.

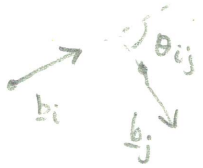
FJC:
- Fixed bond length, l
- no bond angle potential, θ

* The easy way:

$$\langle R_e^2 \rangle = \langle \underline{R}_e \cdot \underline{R}_e \rangle$$

$$= \left\langle \left(\sum_{i=1}^{n} \underline{b}_i \right) \cdot \left(\sum_{i=1}^{n} \underline{b}_i \right) \right\rangle$$

$$= \left\langle \sum_{i=1}^{n} \sum_{j=1}^{n} \underline{b}_i \cdot \underline{b}_j \right\rangle$$



$$= \left\langle \sum_{i=1}^{n} \sum_{j=1}^{n} l^2 \cos\theta_{ij} \right\rangle \qquad |\underline{b}_i| = l$$

↑ does not depend on i or j

$$= l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle$$

↑

no bond angle means the distribution of θ_{ij} is uniform. Because $\cos\theta$ is even, this average must be 0 when $i \neq j$ and 1 when $i = j$.

$$\langle \cos\theta_{ij} \rangle = \delta_{ij}$$

$$= \ell^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \delta_{ij}$$

$$= n\ell^2$$

$$\boxed{\langle R_e^2 \rangle^{1/2} = \ell n^{1/2}}$$

Super important result! ⛤

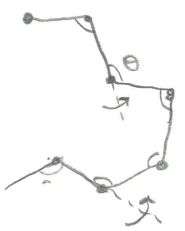
* Comments:

- This is the root-mean-square (rms) end-to-end distance
- when n is big: $n^{1/3} << n^{1/2} << n$
- This kind of path is the same as a random walk. A random walk appears many places in science:
  - path of a diffusing particle
  - price of the stock market
  - contour of a polymer chain
- A random walk is a fractal object. It is a continuous, but non-differentiable, object.

D. other Polymer Models

* The freely jointed chain is not a very realistic polymer model (or is it...?). What happens if we want to be more accurate?

* If we fix the bond angles, but let torsional angles be free, we have a freely rotating chain (FRC) (no gauche, trans)



θ: bond angle

$$\langle R_e^2 \rangle = \langle \underline{R}_e \cdot \underline{R}_e \rangle$$

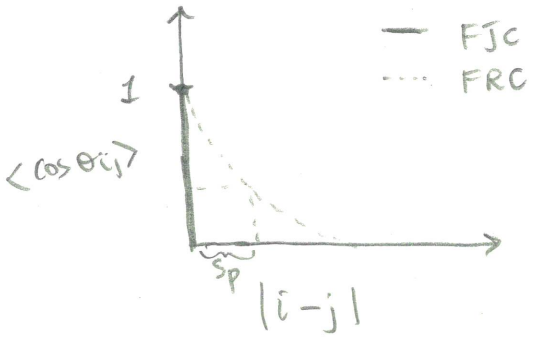
$$= \left\langle \sum_{i=1}^{n} \underline{b}_i \cdot \sum_{j=1}^{n} \underline{b}_j \right\rangle$$

$$= \left\langle \sum_{i=1}^{n} \sum_{j=1}^{n} \ell^2 \cos\theta_{ij} \right\rangle$$

$$= \ell^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle$$

↑ no longer $= \delta_{ij}$

They are correlated.



[Aside: For an FRC

$\langle \cos\theta_{ij} \rangle = |\cos\theta_{ij}|^{|j-i|}$

because cosθ between i & j are independent ∴ so we get a product of cosθ from each bond in between.]

• It can be shown (skipping the algebra) that:

$$\langle \cos\theta_{ij} \rangle = \exp\left(- \frac{|j-i|}{s_p} \right)$$ ← exponentially decays.

$$s_p = - \frac{1}{\ln(\cos\theta)}$$ ← scale (# of bonds) of correlation decay (is a #)

• we still need to sum it up:

$$\sum_{i=1}^{n}\sum_{j=1}^{n} \exp\left(-\frac{|j-i|}{s_p}\right)$$

- If is hard to do this as a finite sum.

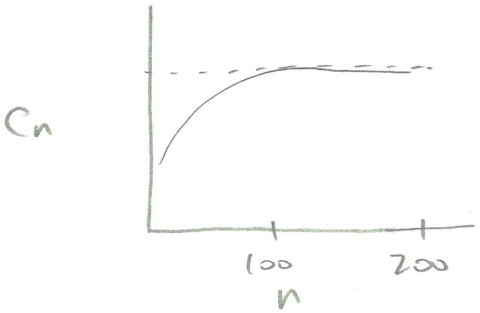
we will call it $n \cdot C_n$

$$C_n = \frac{1}{n}\sum_{i=1}^{n}\sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle$$

$$\boxed{\langle R_e^2 \rangle = C_n \cdot n\, l^2}$$

* Comments:

- Remember, the FJC had a factor of n, so C_n is just a constant.
- C_n is called Flory's characteristic ratio.
- C_n depends on n, but it reaches a stable value as $n \to \infty$. (The exponential converges in an infinite sum.)



- For an FRC,

$$C_\infty = \frac{1+\cos\theta}{1-\cos\theta}, \quad \langle R_e^2 \rangle \simeq C_\infty\, n\, l^2$$

* There are yet more complicated models beyond the FRC.

  - The hindered rotation model takes into account a potential for the torsional angles, $u(\phi_i)$. It's solution is:

$$\langle Re^2 \rangle \simeq C_\infty n \ell^2 \quad (\text{for } n \to \infty)$$

$$C_\infty = \left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle}\right)$$ ← the ϕ_i are independent.

  - The wormlike chain model (FRC with $\theta << 1$)
  - The rotational isomeric state model (discrete ϕ, correlated ϕ)

* In the limit of large n, all models have the form (for an ideal chain):

$$\langle Re^2 \rangle = C_\infty n \ell^2 \quad , \quad \langle Re^2 \rangle^{1/2} \sim n^{1/2}$$

  - C_∞ is a measure of chain flexibility (in units of # of repeat units)
  - $C_\infty \geq 1$ $\quad C_\infty = 1$: Freely jointed chain most flexible

    $C_\infty \approx 2$: FRC

    $C_\infty = 4.8$ 1,4 PI (flexible)

    $C_\infty = 9.5$ PS (stiff)

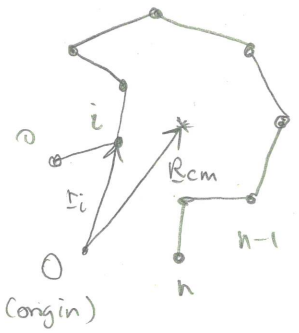
E. Radius of Gyration

* the end-to-end distance is great for theory, but it is hard to get via experiment.
* R_e is also undefined for complex architectures like combs and stars.
* For these reasons, it is useful to define another measure of size, called the radius of gyration:

$$R_g^2 \equiv \frac{1}{(n+1)} \sum_{i=0}^{n} |\underline{r}_i - \underline{R}_{cm}|^2 \quad , R_g = \sqrt{R_g^2}$$

$$\underline{R}_{cm} \equiv \frac{1}{(n+1)} \sum_{j=0}^{n} \underline{r}_j$$

$\underline{R}_{cm}$: center of mass. Assumes monomers have constant molecular weight, $M_j = M_0$.



- R_g is the square distance from the center of mass.

* Using the formula for the center-of-mass, the formula for R_g can be re-written:

$$R_g^2 = \frac{1}{n+1} \sum_{i=0}^{n} \sum_{j=0}^{n} |\underline{r}_i - \underline{r}_j|^2$$

- with this formula, we can interpret the radius of gyration as the average square distance between monomers.

* One can compute the ensemble-averaged R_g for a freely jointed chain:

$$\boxed{\langle R_g^2 \rangle = \frac{Nb^2}{6} = \frac{\langle R_e^2 \rangle}{6}}$$

- $R_g^2 \propto R_e^2$. The differ by only a constant.