Lecture 4: Real chains and Flory Theory

A. Polymer - Gas Analogy

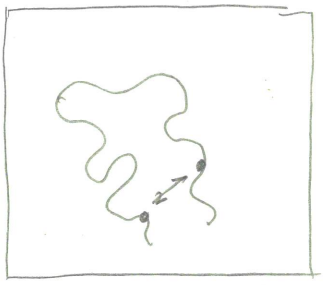
* In the last two lectures, we looked at polymer conformations and free energies assuming that chains were ideal. By ideal we meant that monomers did not interact. This is the polymer equivalent of an ideal gas.

* Was this unrealistic? useless? Our analysis of ideal chains revealed the impact of chain connectivity of long molecules.

  - Polymer size: $R^2 \simeq Nb^2$
  - Effective FJC & Universality
  - Gaussian chain & Entropic elasticity
  - Free Energy: $\Delta F(R) \simeq \frac{3kT}{2}\frac{R^2}{Nb^2}$

* Do we need to account for monomer-monomer interactions? If so, how?

* We will approach the problem using the "polymer-gas" analogy. This theory postulates that monomer-monomer interactions in a solvent can be treated like particles in a gas, neglecting chain connectivity.



* most intrachain interactions occur between distally located parts of the molecule.

(far apart in contour length, but close in space).

* A dilute solution is like a gas. Stat mech: McMillan-Mayer theory addresses this. (see Hill ch. 19).

* For a flexible chain, their movements are nearly completely uncorrelated.

* Why treat like a gas? very dilute. What is the volume fraction of monomers in a coil?

$$\phi = \frac{v_{mon} \cdot N}{V_{coil}} = \frac{b^3 N}{R^3} = \frac{N b^3}{N^{3/2} b^3} = N^{-1/2}$$

- For N large (e.g. $N = 1000$ is typical), $\phi \ll 1$.
- A gas of monomers seems appropriate.

* Can we just neglect it altogether? Is the energy really small?

# of contacts between monomers: $N\phi$

$$\#\text{contacts} = N^{1/2} \gg 1$$

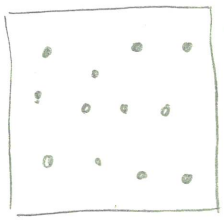
- Not that small, so we better not neglect them.
- Energy $\propto$ # of contacts

B. The Virial Expansion

* In the statistical mechanics of gases, there is a famous expression that we can use to get the free energy due to interparticle interactions. This expression is the virial expansion. It has other names as well: Mayer expansion or a cluster expansion.(*)

(*) Mayer's approach is restricted to pair-wise additive potentials. Ursell expansions are not limited in this way.

* Consider a monoatomic gas in a box:



N atoms
box volume, V
temperature, T

$$F - F_0 = -k_B T \ln Z \qquad F_0 = -k_B T \ln Z_0, \quad Z_0 = \frac{V^N}{N!\,\lambda_{TH}^{3N}}$$

(Z: configurational partition function; Z_0: ideal gas.)

$$Z = \frac{1}{V^N} \int d\underline{r}_1 \cdots \int d\underline{r}_N \exp\left[-\beta U(\{\underline{r}_i\})\right]$$

* We will assume that the potential, U, is pairwise additive:

$$U(\{\underline{r}_i\}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij}) = \sum_{i<j} u(r_{ij})$$

- Common assumption, even for simulations.
- Perfect model of 2-body collisions. Models 3-body collisions as:

$$u(r_{12}) + u(r_{13}) + u(r_{23})$$

- so, still has n-body collisions, but approximates them.
- Ad-hoc approximation. Could introduce significant error. In practice, error appears to be small, but people are still studying this.
- Costly to remove this assumption
- In a solution for a polymer, $u(r_{ij})$ is some potential of mean force. (ie. takes into account solvent, coarse-grained monomers, etc.)

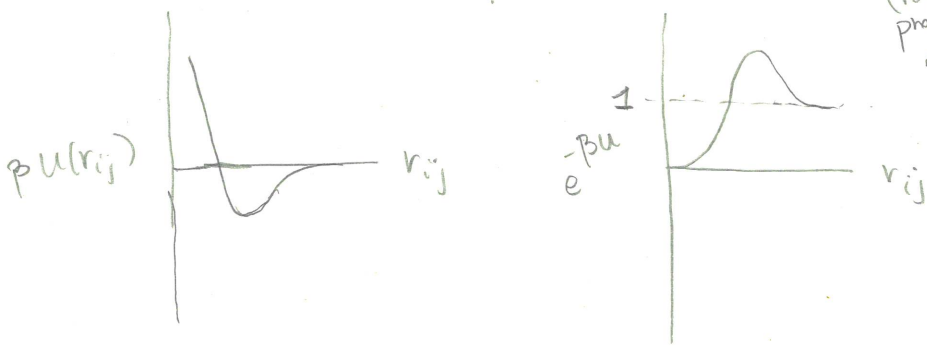
+ Back to our cluster expansion:

$$Z = \frac{1}{V^N} \int d\underline{r}_1 \cdots \int d\underline{r}_N \exp\left[-\beta \sum_{i<j} u(r_{ij})\right]$$

- using the properties of exponentials, we can turn this into a product.

$$Z = \frac{1}{V^N} \int d\underline{r}_1 \cdots \int dr_N \prod_{i=1}^{N-1} \prod_{j=i+1}^{N} \exp\left[-\beta u(r_{ij})\right]$$

- we would like to turn this product into a series, but the exponentials are a problem.

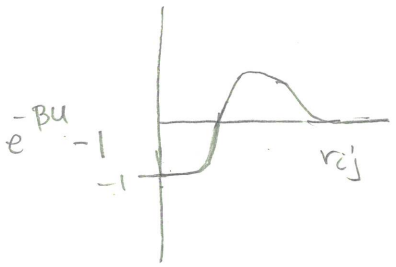


- If we do a series with terms like

$$\int e^{-\beta u(\underline{r}_{12})}\, d\underline{r}_{12}$$

the integrals won't converge. We need a different basis for our integrals. Otherwise, we are adding up a bunch of diverging integrals.

- Mayer solved this problem. Can you guess how?



$$f(r_{ij}) = e^{-\beta u(r_{ij})} - 1$$

"Mayer f-function"

- Integrals of $\int f(\underline{r}_{ij})\, d\underline{r}_{ij}$ converge!

$$\Rightarrow \quad 1 + f(r_{ij}) = e^{-\beta u(r_{ij})}$$

$$Z = \frac{1}{V^N} \int d\underline{r}_1 \cdots \int d\underline{r}_N \underbrace{\prod_{i=1}^{N-1} \prod_{j=i+1}^{N} \left[1 + f(r_{ij})\right]}$$

- Now, we need to expand out this form. This is the worst "FOIL" problem you can think of.

$$(1+f_{12})(1+f_{13})(1+f_{14})\cdots(1+f_{1N})$$
$$\times\ (1+f_{23})(1+f_{24})\cdots(1+f_{2N})$$
$$\times\ \cdots$$
$$\times\ \cdots \qquad (1+f_{N-1,N})$$

Example: (suppose $N=3$. You can use this to see what the terms are like)

$$(1+f_{12})(1+f_{13})(1+f_{23}) = (1+f_{12}+f_{13}+f_{12}f_{13})(1+f_{23})$$

underline: 2 molecules
squiggle: 3 molecules

$$= 1 + \underline{f_{12}} + \underline{f_{13}} + \underline{f_{12}f_{13}} + \underline{f_{23}} + \underline{\underline{f_{12}f_{23}}} + \underline{\underline{f_{13}f_{23}}} + \underline{\underline{f_{12}f_{13}f_{23}}}$$

$$Z = \frac{1}{V^N}\int d\underline{r}_1 \cdots \int d\underline{r}_N \left[1 + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} f_{ij} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{k=i}^{N-1}\sum_{l=k+1}^{N} f_{ij}f_{kl} + \cdots \right]$$

($ij \neq kl$) messy counting so only count each one once.

$\sum_{i<j}\sum_{k<l}$

* The last step of the derivation is to simplify the integrals for each term. There are many fewer degrees of freedom.

$$\int d\underline{r}_1 \cdots \int d\underline{r}_N [1] = V^N$$

$$\int d\underline{r}_1 \cdots \int d\underline{r}_N \sum_{i<j} f_{ij} = V^{N-1}\frac{N(N-1)}{2}\int d\underline{r}_{ij}\, f(\underline{r}_{ij})$$

This gets messy for more than 2 molecules, because integrals simplify into others... I'll skip those details ("reducible integrals", "irreducible integrals")

* Finally, Z becomes: (using the fact that $N-1 \approx N$ for large N)

$$Z = 1 + \frac{N^2}{2V}\beta_1 + \frac{N^3}{3V^2}\beta_2 + \cdots$$

$$\beta_1 = \frac{1}{V}\int d\underline{r}_1 \int d\underline{r}_2\, f(\underline{r}_{12}) = \int d\underline{r}_{12}\, f(\underline{r}_{12}) = \int_0^\infty f(r)\, 4\pi r^2\, dr$$

$$\beta_2 = \frac{1}{2V}\iiint d\underline{r}_1\, d\underline{r}_2\, d\underline{r}_3\, f(r_{12})\, f(\underline{r}_{13})\, f(\underline{r}_{23})$$

* Comments:

- See why it is a "cluster expansion." It is an expansion in the # of molecules in a collision.

  B_1: pairs

  B_2: triples

- Note that Z/V is a function of density:

  $\rho = N/V$

$$\frac{Z}{V} = \frac{1}{V} + \frac{\rho^2}{2} B_1 + \frac{\rho^3}{3} B_2 + \cdots$$

- Our expansion is good at low density. It is like an asymptotic expansion in the fact that it gets better as $\rho \to 0$. However, this expansion is even better. It <u>can converge</u> as # of terms $\to \infty$ for low ρ too.

- B_k are called "virial coefficients."

  B_1: 2nd virial coefficient

  B_2: 3rd " "

- Can write the free energy ($F - F_{ideal}$)

$$\Delta F = -k_B T \ln Z \quad \text{or} \quad \frac{\Delta F}{kT} = -\ln Z$$

recall $\ln(1+x) \approx x$ for x small

$$-\frac{\Delta F}{k_B T} \simeq \frac{V}{2}\rho^2 B_1 + \frac{V}{3}\rho^3 B_2 + \cdots$$

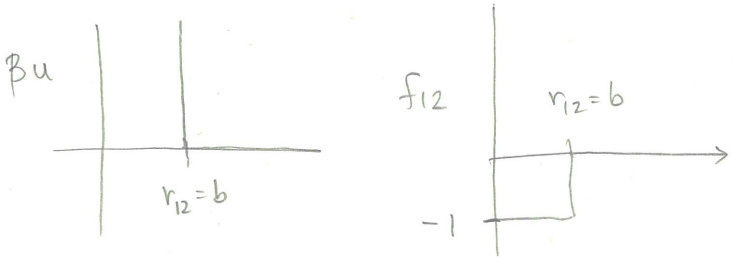
$$\boxed{-\frac{\Delta F}{k_B T V} \simeq \frac{1}{2}\rho^2 B_1 + \frac{1}{3}\rho^3 B_2 + \cdots}$$

(free energy density)

C. Excluded volume

* Let's step back and think about polymers for a minute again. We want to take into account the energy of interaction between distal monomers.

* Suppose we had an FJC with spherical monomers of size b. What is β_1?



$$\beta_1 = \int_0^\infty f_{12}(r) \cdot 4\pi r^2 dr = \int_0^b -4\pi r^2 dr = -\frac{4}{3}\pi b^3$$

- negative volume of the space prohibited from overlap between two monomers.

* The excluded volume

$$v = -\beta_1 = -\int f(\underline{r}_{12})\, d\underline{r}_{12}$$

is the net two body interaction between monomers

$v > 0$ - net repulsion

$v < 0$ - net attraction

$v = 0$ - no net interaction

* what are the cases in solution?

monomers prefer solvent to self:

- $v \simeq b^3$ – "athermal" solvent (hard core repulsion only)
- $0 < v < b^3$ – "good" solvent (net repulsion, polymer swells)

$v \approx 0$ – "theta" solvent. attraction ≈ repulsion balance.

monomers prefer self to solvent.

- $-b^3 < v < 0$ – "poor" solvent. attraction dominates.
- $v \approx -b^3$ – "non-solvent". limit of strong attraction

Do temp. dependence here.

* what happens to our free energy when we put in excluded volume?

$$\frac{\Delta F}{V} \simeq k_B T \left(v c_n^2 + w c_n^3 \right)$$

→ drop coefficients b/c we are doing physics ☺

c_n: monomer number density $= \frac{nN}{V}$ (n: # of chains, N: D.O.P.)

w: 3-body interaction coefficient ($w \simeq b^6$ for athermal).

• for single chain $n = 1$, $V = R^3$

$$\boxed{\frac{\Delta F}{V} \simeq k_B T \left(v \frac{N^2}{R^6} + w \frac{N^3}{R^9} + \dots \right)}$$

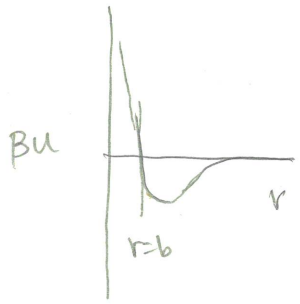
$V \propto R^3$

2-body term

3-body term.

$$\boxed{\Delta F \simeq k_B T \left(v \frac{N^2}{R^3} + w \frac{N^3}{R^6} + \dots \right)}$$

* In addition to changing with solvent quality, the excluded volume can change with temperature.



$$v = -\int_0^\infty f(r)\, 4\pi r^2 dr \qquad f(r) = e^{-\beta U(r)} - 1$$

* for $r<b$, $U \gg kT \Rightarrow f(r) \simeq -1$

for $r>b$, $U \ll kT \Rightarrow f(r) \simeq -\beta U(r)$

$\left(e^{-x} \simeq 1-x \quad \text{when} \quad x \ll 1\right)$

* So, the excluded volume becomes:

$$v = -\int_0^b (-4\pi r^2)\, dr - \int_b^\infty -\beta U(r)\, 4\pi r^2 dr$$

$$= \frac{4}{3}\pi b^3 + \frac{1}{T}\int_b^\infty \frac{U(r)}{k_B} \cdot 4\pi r^2 dr$$

$\frac{4}{3}\pi b^3$: repulsive interactions

$\frac{1}{T}\int_b^\infty \frac{U(r)}{k_B} \cdot 4\pi r^2 dr$: $\theta \simeq \frac{-1}{k_B b^3}\int_b^\infty U(r) r^2 dr$

$U(r)<0$, add (-) so $\theta > 0$

Net attractive interactions in units of temperature.

$$\boxed{v \simeq b^3\left(1 - \frac{\theta}{T}\right)}$$

- when $\theta = T$, $v = 0$. "Theta temperature" The chains are ideal
- $\theta < T$: good solvent
- $\theta > T$: poor solvent

D. Flory Theory

* with a free energy of interaction for monomers, we are now ready to find R (rms end-to-end distance) of a "real" polymer chain.

* This way of finding a polymer size is called "Flory Theory".

* Let the total free energy be the sum of entropic terms (from ideal chain) and the interaction term we just derived.

$$F_{ent} = \frac{3}{2} k_B T \frac{R^2}{Nb^2} \simeq k_B T \frac{R^2}{Nb^2} \qquad \text{(drop coeffs)}$$

$$F_{int} \simeq k_B T \, v \frac{N^2}{R^3} \qquad \text{(2-body term only.}$$

$$F = F_{int} + F_{ent}$$

$$F = k_B T \left(v \frac{N^2}{R^3} + \frac{R^2}{Nb^2} \right)$$

* Flory theory postulates that the equilibrium polymer size will be a balance of those entropic & enthalpic effects. We will solve for this size by minimizing the free energy:

$$\frac{\partial F}{\partial R} = 0$$

$$\frac{\partial F}{\partial R} = k_B T \left(-3\nu N^2 R^{-4} + \frac{2R}{Nb^2} \right) = 0$$

↓ drop coeffs

$$-\frac{\nu N^2}{R^4} + \frac{R}{Nb^2} \simeq 0$$

$$R^5 \simeq \nu N^3 b^2$$

$$\boxed{R \simeq \nu^{1/5} b^{2/5} N^{3/5}}$$

* suppose $\nu = b^3$ (athermal solvent)

$$\boxed{R \simeq b N^{3/5}}$$

* Comments:

- Flory theory predicts a swollen coil for $\nu > 0$. Repulsive interactions cause the coil to be significantly larger
- Is it really bigger? Yes!

$$\frac{R}{R_{id}} = \frac{b N^{3/5}}{b N^{1/2}} = N^{1/10}$$

- when are the interactions "large enough" to swell the coil? when

$$F_{int}(R_{id}) >> k_B T$$

$$\nu \frac{N^2}{(R_{id})^3} >> 1$$

$$\frac{b^3 N^2}{(b N^{1/2})^3} >> 1 \quad \rightarrow \quad \boxed{N^{1/2} >> 1}$$

↙ same as criteria from part A.

* what about $v=0$? $\Rightarrow$ Have ideal case. $R = bN^{1/2}$

* what happens if $v<0$?

$$\frac{\partial F}{\partial R} = 0 = k_BT\left(3|v|N^2R^{-4} + \frac{2R}{Nb^2}\right)$$

$$\frac{|v|N^2}{R^4} + \frac{2R}{Nb^2} \simeq 0$$

$$R^5 \simeq -|v|N^3b^2$$

↖ can't be negative?

minimum is at $\underline{R=0}$.

- This isn't physical! We need another term in the free energy. Entropy is causing the chain to shrink, and so is net attraction. We need some repulsion.

$$F_{int} \simeq k_BT\left(v\frac{N^2}{R^3} + w\frac{N^3}{R^6}\right)$$

3-body term.

$v<0$, $w \simeq b^6 > 0$

- Excluded volume is attractive, but the three body term is still repulsive.

- What terms should we balance?

entropy: $\frac{R^2}{Nb^2} \ll 1$ $\qquad R \ll R_{id} \simeq Nb^2$

↖ this term is small, so we should just balance 2 & 3-body terms

$$F \simeq k_B T \left(v \frac{N^2}{R^3} + w \frac{N^3}{R^6} \right) \qquad v = -|v|$$

$$\frac{\partial F}{\partial R} \simeq +3 \frac{|v| N^2}{R^4} - \frac{6 w N^3}{R^7} \simeq 0$$

$$\frac{|v| N^2}{R^4} \simeq \frac{w N^3}{R^7} \Rightarrow R^3 \simeq \frac{wN}{|v|}$$

$$\boxed{R \simeq \left(\frac{wN}{|v|} \right)^{1/3}} \quad \text{or} \quad \boxed{R \simeq b N^{1/3}}$$

$v = -b^3$

$w = b^6$

* This makes sense! In a bad/non-solvent the coil collapses due to attractive interactions.
* However, it can't collapse "all the way." It collapses to its "dry" volume:

$$V_{dry} \simeq N b^3 \rightarrow R \simeq V_{dry}^{1/3}$$

* Summary:

Good solvent/athermal: $R \sim b N^{3/5}$

Ideal / Theta solvent: $R \sim b N^{1/2}$

Poor / Non-solvent: $R \sim b N^{1/3}$