Lecture 3: Ideal chain distributions & Free Energy

A. The equivalent FJC.

* In the last lecture, we saw that all polymer models have the same size behavior at large n:

$$\langle R_e^2 \rangle = C_\infty n \ell^2$$

* The fact that different models give rise to equivalent behavior is called the principle of universality. The principle of universality is a corrollary to the PPH.

PPH – Conformational entropy (& energy) dominates the behavior of macromolecules

Universality – Key properties of polymers are independent of their chemical identity (or polymer model) in the large-n limit. Only a few parameters contain chemical dependence, e.g. C_∞.

* If all models behave the same, then lets use the simplest one: the FJC!

* Let's map the other models to an "equivalent FJC."

- Postulate: $Re^2 = \langle R_e^2 \rangle$ and contour length L are universal in the long n limit.

- Result:

	polymer model	Equiv. FJC
Re^2	$C_\infty n \ell^2$	Nb^2
L	$n \ell \cos(\theta/2)$	Nb

map: solve 2 EQ, 2 unknowns

$$b = \frac{\langle R_e^2 \rangle}{L} = \frac{C_\infty \ell}{\cos(\theta/2)}$$

$$N = \frac{L^2}{\langle R_e^2 \rangle} = \frac{L}{b} = \frac{n \cos^2(\theta/2)}{C_\infty}$$

- we get 2 parameters out of the equivalent FJC.

  - b: the statistical segment length or kuhn length. b is a measure of chain flexibility. It is in units of length, unlike C_∞ which is in units of repeat units (monomers)

  - N: the number of kuhn lengths or number of statistical segments, N is a normalized number of monomers. Sometimes: # of kuhn monomers.

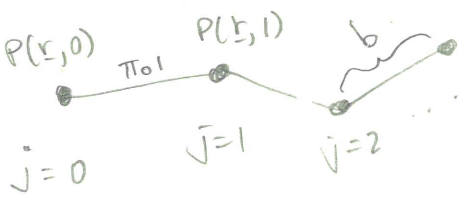
polymer	b (Å)	
PEO	6.0	} θ(1nm)
PI	6.5	
PS	6.7	
dsDNA	1000	100 nm

B. End-to-End Distribution (see GHF ; Doi ; Edwards)

* we have a pretty good handle on estimating R for ideal chains. Can we say more? We started out thinking we could get any property if we knew $p(\underline{r}_0, \{\underline{b}_i\})$.

* As we said before, it is not easy to get p. This involves doing (3n+1) integrals. But, for an ideal chain we can make some progress.

* Suppose we knew $P(\underline{r}, 0)$ the probability of the first monomer.



$\underline{n} = \frac{\underline{b}_i}{b}$, unit vector

$j \in [0, N]$ ← big N for FJC

If we know the probability to go from 0 to 1, then we could know $P(\underline{r}, 1)$.

- $\pi_{0,1}$: a transition probability
- $P(\underline{r}, j)$ is not the full $p(r_0, \{\underline{b}_i\}) = p(\{\underline{r}_i\})$ $i \in [0, N]$

It is a reduced distribution. ↓

$$p(\underline{r}, j) = \int \underline{r}_0 \int \underline{r}_1 \cdots \int \underline{r}_{j-1} \int \underline{r}_{j+1} \cdots \int \underline{r}_N \, p(\{\underline{r}_i\})$$

Only the probability of monomer j at point $\underline{r}$.

* How could we get $p(\underline{r}, 1)$?

$$p(\underline{r}, 1) = \int d\underline{n} \, \pi_{01} \, p(\underline{r} - b\underline{n}, 0)$$

(convolution: $P_1 = \pi_{01} * P_0$)

"Chapman-Kolmogorov" Equation
(see in stochastic processes)

$$= \int d\theta \int d\phi \, \pi_{01} \, p(\underline{r} - b\underline{n}, 0) \sin\theta \, d\theta d\phi$$

integral over unit sphere

* Let's find π_{01}:

$$\pi_{01} = \text{const} \qquad \text{(uniform distribution)}$$

$$\int d\underline{n} \, \pi_{01} = 1 \qquad \text{(to be a probability)}$$

$$\int_0^{\pi} d\theta \int_0^{2\pi} d\phi \sin\theta \, \pi_{01} = 1 \quad \Rightarrow \quad 4\pi \pi_{01} = 1$$

$$\boxed{\pi_{01} = \frac{1}{4\pi}}$$

* Therefore we get:

$$p(\underline{r}, 1) = \int d\underline{n} \, \frac{1}{4\pi} \, p(\underline{r} - b\underline{n}, 0)$$

* This applies at <u>all steps</u> along the chain

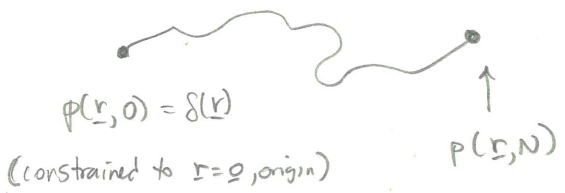
therefore:

$$p(\underline{r}, j) = \frac{1}{4\pi} \int d\underline{n}\; p(\underline{r} - b\underline{n}, j-1)$$

↖ we can get all of the monomers!

* Lets find $p(\underline{r}, N) = p(\underline{R}_e)$.

↖ probability distribution of end to end distance



we "simply" need to chain the CK equations together.

* This is hard w/ lots of integrals. However, it is easy using a Fourier Transform:

Fourier Transform: $\hat{f}(\underline{k}) = \int d\underline{r}\; f(\underline{r})\, e^{-i\underline{k}\cdot\underline{r}}$

Inverse Fourier transform: $f(\underline{r}) = \frac{1}{(2\pi)^3} \int d\underline{k}\; \hat{f}(\underline{k})\, e^{i\underline{k}\cdot\underline{r}}$

$$F\left[\int d\underline{r}'\; g(\underline{r} - \underline{r}')\, h(\underline{r}')\right] = \hat{g}(\underline{k})\, \hat{h}(\underline{k})$$

↖ convolution theorem.

$$F\left[p(\underline{r}, j)\right] = F\left[\frac{1}{4\pi} \int d\underline{n}\; p(\underline{r} - b\underline{n}, j-1)\right]$$

$$\hat{p}(\underline{k}, j) = j_0(b|\underline{k}|)\, \hat{p}(\underline{k}, j-1)$$

↖ $j_0(x) = \frac{\sin x}{x}$, spherical Bessel function

(yay transport!)

$$\hat{p}(\underline{k},1) = j_0(b|\underline{k}|)\,\hat{p}(\underline{k},0)$$

$$\hat{p}(\underline{k},2) = j_0(b|\underline{k}|)\,\hat{p}(\underline{k},1)$$

$$\hat{p}(\underline{k},3) = j_0(b|\underline{k}|)\,\hat{p}(\underline{k},2)$$

$$\hat{p}(\underline{k},N) = j_0(b|\underline{k}|)\,\hat{p}(\underline{k},N-1)$$

$$= [j_0(b|\underline{k}|)]^N \hat{p}(\underline{k},0)$$

3D Dirac Delta

$$F[\delta(\underline{r})] = 1$$

$$p(\underline{r},N) = F^{-1}[\hat{p}(\underline{k},N)]$$

$$\boxed{p(\underline{r},N) = \frac{1}{(2\pi)^3}\int d\underline{k}\,[j_0(b|\underline{k}|)]^N e^{i\underline{k}\cdot\underline{r}}}$$

* Hard to do this integral, but we can approximate it easily when $b|\underline{k}| \ll 1$. $\rightarrow$ $k^{-1} \gg b$ $\quad k = |\underline{k}|$

- when k is large, at larger length scales. This makes sense, we only care about stuff much larger than monomers

$$j_0(bk) = \frac{\sin(bk)}{bk}$$

$$\frac{\sin(x)}{x} \approx 1 - \frac{x^2}{6}$$ (Taylor series, wolframAlpha)

$$j_0(bk) \simeq 1 - \frac{(bk)^2}{6}$$

- Recall $\ln(1-x) \simeq -x$ for $x \approx 1$

so $N \ln(1-x) \approx -Nx$

$$\exp\left[(1-x)^N\right] \approx \exp(-Nx)$$

$$\Rightarrow \left[j_0(bk)\right]^N \approx \exp\left(-\frac{Nb^2k^2}{6}\right)$$

$$\Rightarrow p(\underline{r}, N) = \frac{1}{2\pi^3}\int d\underline{k}\, \exp\left(-\frac{Nb^2k^2}{6}\right) e^{i\underline{k}\cdot\underline{r}}$$

• This integral, we can do!

(F.T. of a Gaussian is a Gaussian)

$$\boxed{p(\underline{r}, N) = \left[\frac{3}{2\pi N b^2}\right]^{3/2} \exp\left(-\frac{3|\underline{r}|^2}{2Nb^2}\right)}$$

* Comments:

• This is a Gaussian distribution (bell curve).

mean: $\underline{r} = 0$

variance: $\frac{Nb^2}{3} = 2R_g^2$

$$p(\underline{r}, N) = \left(\frac{1}{4\pi R_g^2}\right)^{3/2} \exp\left(-\frac{|\underline{r}|^2}{4R_g^2}\right)$$

• This distribution represents conformational entropy! We added them up in our convolutions.

• In spherical coordinates:

$$p(R, N) \cdot 4\pi R^2 dR = 4\pi\left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{R^2}{Nb^2}\right) R^2 dR$$

$p(R, N)$: no vector

(see plot) → very small R and very large R is unlikely.

- For this to work, we need $N \gg 1$ and $R \ll L = Nb$. The distribution is unphysical at large R.

C. Free Energy of an Ideal Chain

*Remember from last time:

$$F = -kT \ln Z$$

$$F(\underline{r}, N) = -kT \ln Z(\underline{r}, N)$$

← Free energy as a function of $\underline{r}$.

- Now, $$P(\underline{r}, N) = \frac{Z(\underline{r}, N)}{\int d\underline{r}\, Z(\underline{r}, N)}$$

→ $\int \exp(-\beta U)\, d\underline{r}$ over all but $\underline{r}, N$

← integral over them all.

$$Z(r, N) = P(\underline{r}, N) \int d\underline{r}\, Z(\underline{r}, N)$$

$$F(\underline{r}, N) = -kT \ln P(\underline{r}, N) - kT \ln \int dr\, Z(\underline{r}, N)$$

$$= -\frac{3}{2} kT \left(\frac{3}{2\pi N b^2} \right) + \frac{3}{2} kT \frac{|r|^2}{Nb^2}$$

$$- kT \ln \int d\underline{r}\, Z(\underline{r}, N)$$

don't depend on $\underline{r}$. $\Rightarrow F(0, N)$

$$\boxed{F(\underline{r}, N) = F(0, N) + \frac{3}{2} kT \frac{|\underline{r}|^2}{Nb^2}}$$

or

$$\Delta F(R) = \frac{3kT}{2} \frac{R^2}{Nb^2}$$

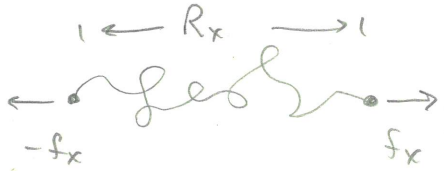
* The chain acts like an "entropic spring" with spring constant:

$$F = \frac{1}{2}kx^2 \qquad \frac{\partial F}{\partial x} = kx$$

$$F = \frac{3kT}{2}\frac{R^2}{Nb^2} \qquad \frac{\partial F}{\partial R} = \frac{3kT}{Nb^2} \cdot R$$

$$\boxed{k = \frac{3kT}{Nb^2}}$$

- $T\uparrow$, chain gets stiffer.
- Metals $T\uparrow$, get softer
- Entropic vs. Enthalpic elasticity

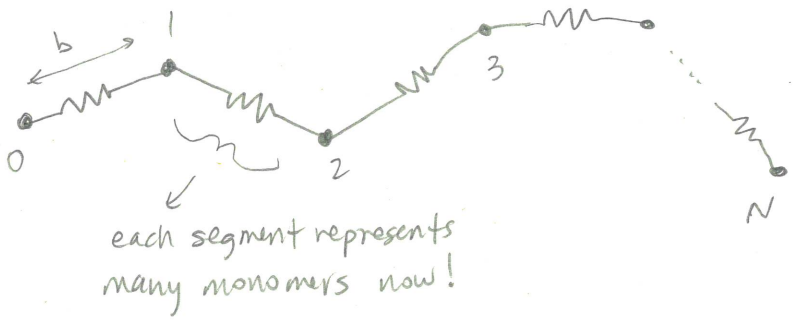


$$|f| \propto \frac{3kT}{Nb^2} \cdot R_x$$

* Conformational entropy resists the chain from being stretched or compressed.

D. The Gaussian chain

* Now we see that if we only care about universal behavior at large N, we get something that looks like a Hookean spring. With this in mind, why even model a complex chain with bond and torsion angles. Instead, we can model a chain as a "bead-spring" model with flexible bonds.



$$U_0 = \sum_{i=1}^{N} \frac{3kT}{2b^2} \left| \underline{r}_{i+1} - \underline{r}_i \right|^2$$

* This model gives

$$\langle \underline{R} \cdot \underline{R} \rangle = Nb^2 \qquad \underline{R} = \underline{r}_N - \underline{r}_0$$

$$P(\underline{r}, N) = \left(\frac{3}{2\pi N b^2} \right)^{3/2} \exp\left(\frac{-3|\underline{r}|^2}{2Nb^2} \right)$$ ← exact

exactly the same as the equivalent FJC in the limit $N \gg 1$, $|r| \ll Nb$.

* In fact:

$$\hat{\pi}_{ij}(\underline{k}) = \exp(-R_g^2 k^2)$$ ← each transition probability is a Gaussian chain. (like the $N \gg 1$ limit of many FJC links)