Stat Mech Lecture #2

January Friday the 13th

Boltzmann distribution

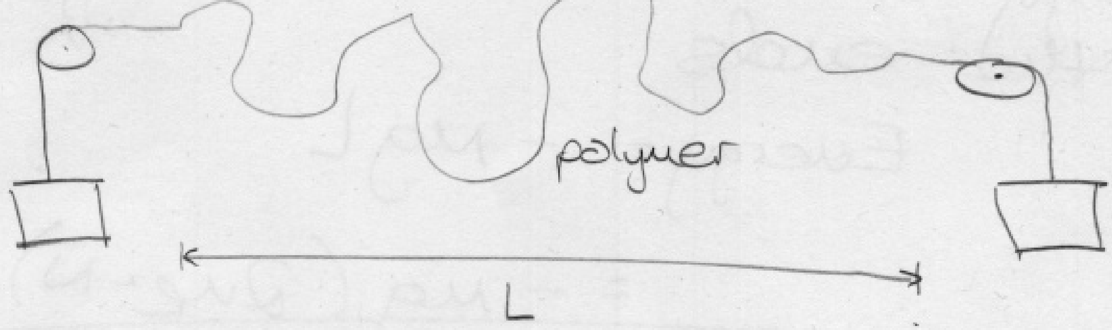
$$p(E_i) = \frac{e^{-\beta E_i}}{Z}, \quad Z \equiv \sum_i e^{-\beta E_i}$$

E_i - energy of microstate i

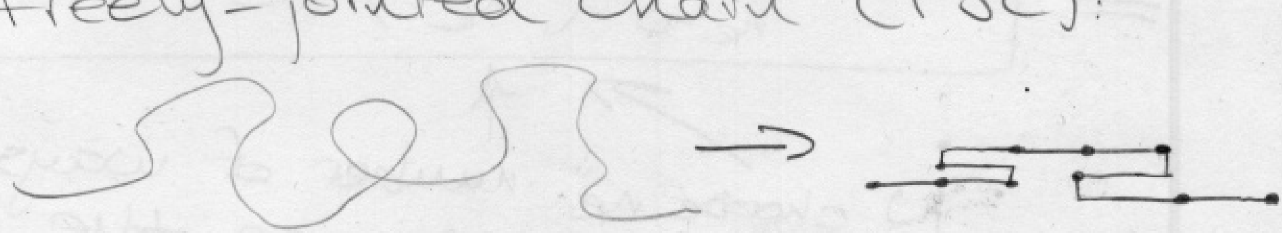
$\beta \equiv 1/k_BT$

$\sum_i$ - sum over all microstates

Example #1: Force-extension of polymers



• map this onto a one-dimensional freely-jointed chain (FJC):



• we could extend our 1d FJC to point at any angle; for now just pointing right or left is enough

• each segment either points right or left

n_R = right-pointing segments
number of

n_L = number of left-pointing segs

a = length of a segment

→ $L = (n_R - n_L)\,a$

→ $N = n_R + n_L$ total # of segments

gives:

$$L = (2n_R - N)\,a$$

- now $Z = \sum_{\text{states}} e^{-E(\text{state})\cdot\beta}$

- energy comes from the weights at the ends

$$\text{Energy} = -Mg\,L$$

$$= -Mg\,(2n_R - N)\,a$$

So $\boxed{Z = \sum_{n_R=0}^{N} \binom{N}{n_R} e^{+\beta\cdot Mga\,(2n_R - N)}}$

"N choose n_R" number of ways to arrange the segments

$$\binom{N}{n_R} = \frac{N!}{n_R!\,(N-n_R)!}$$

• pull out constant factor:

$$= e^{\beta N \mu g a} \sum_{n_R=0}^{N} \binom{N}{n_R} e^{2\beta \mu g a n_R}$$

$$x \equiv e^{2\mu g a \beta}$$

$$y = 1$$

$$= e^{\beta N \mu g a} \underbrace{\sum_{n_R=0}^{N} \binom{N}{n_R} x^{n_R} y^{N-n_R}}_{\text{aha!}}$$

$$= (x+y)^N$$

$$= \left(e^{2\mu g a \beta} + 1\right)^N$$

So $Z = e^{-\beta N \mu g a} \left(1 + e^{2\mu g a \beta}\right)^N$

$$\langle L \rangle = \sum_{n_R=0}^{N} \underbrace{p(n_R)}_{\frac{e^{-\beta E_i}}{Z}} L$$

$$p(n_R) = \frac{\binom{N}{n_R} e^{-\beta \mu g N a} e^{2 n_R \mu g a \beta}}{Z}$$

$$\langle L \rangle = \frac{1}{\left(1+e^{2\beta \mu g a}\right)^N} \sum_{n_R=0}^{N} (2n_R - N)\, a \binom{N}{n_R}$$

$\longrightarrow$ constant ~~factor~~ $\times\, e^{2 n_R \beta \mu g a}$

of $e^{-\mu g a N \beta}$

cancelled!

· we need to evaluate

$$\sum_{n_R=0}^{N} n_R \binom{N}{n_R} x^{n_R} y^{N-n_R} \qquad x = \text{const.} \quad y = 1$$

use a trick:

$$= x \frac{\partial}{\partial x} \underbrace{\sum_{n_R=0}^{N} \binom{N}{n_R} x^{n_R} y^{N-n_R}}_{(x+y)^N}$$

$$= x N (x+y)^{N-1}$$

done!

Now go back and do algebra with $\langle L \rangle$, you will find:

$$\langle L \rangle = Na \frac{e^{2\mu g a \beta} - 1}{e^{2\mu g a \beta} + 1}$$

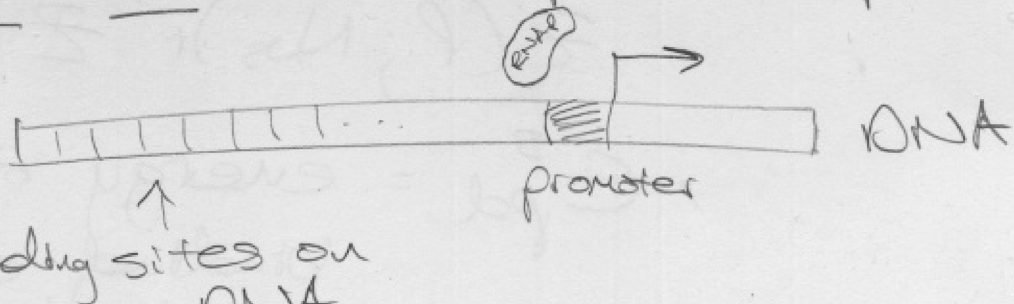
$$\langle L \rangle = Na \tanh(\mu g a \beta)$$

• Or for a general force F instead of gravity mg:

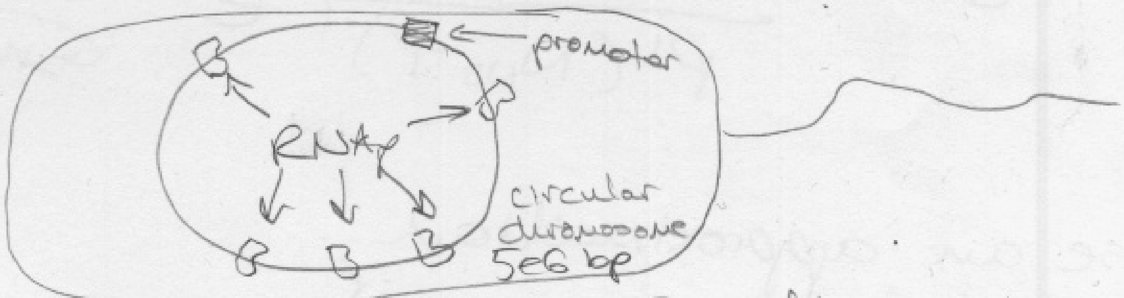
$$\boxed{\langle L \rangle = Na \tanh\left(\frac{Fa}{k_B T}\right)}$$

→ parameter a is called the "persistence length" of the polymer - a material property

Example #2: RNAp and promoter



goal: calculate probability that RNAp is bound to the promoter



E. coli

• R = # of RNAp's in the cell

• N_{NS} = # of nonspecific binding sites

• fact: essentially <u>all</u> RNAp's are bound to DNA, <u>all</u> the time

N_{NS} = # of boxes

P = # of RNAp to put in boxes

P_{bound} = probability that our promoter box is occupied

$$P_{bound} = \frac{\text{weights of states where promoter box is occupied}}{\text{weights of all states}}$$

$$= \frac{Z(P-1; N_{NS})\, e^{-\beta\epsilon^{s}_{pd}}}{Z(P; N_{NS}) + Z(P-1; N_{NS})\, e^{-\beta\epsilon^{s}_{pd}}}$$

- ϵ^{s}_{pd} = energy of specific binding of RNAp to DNA promoter

$$Z = \frac{N_{NS}!}{P!\,(N_{NS}-P)!}\, e^{-\beta P \epsilon^{ns}_{pd}}$$

ns → non-specific binding energy

- use an approximation...

$$\longrightarrow \frac{N!}{P!\,(N-P)!} \simeq \frac{N^{P}}{P!} \text{ if } N \gg P$$

and $5e6 \gg 1e3$
base pairs, RNAp's

Now you turn the crank and do some algebra to find P_{bound} with our approximation...

you will get:

$$\boxed{P_{bound} = \frac{1}{1 + \frac{N_{NS}}{P} e^{\beta \Delta \epsilon_{pd}}}}$$

$\rightarrow$ where $\Delta \epsilon_{pd} \equiv \epsilon_{pd}^{s} - \epsilon_{pd}^{ns}$

Isn't stat mech cool??