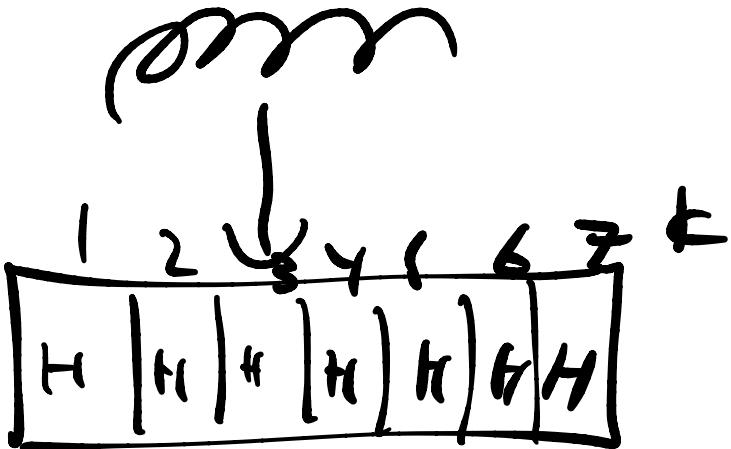
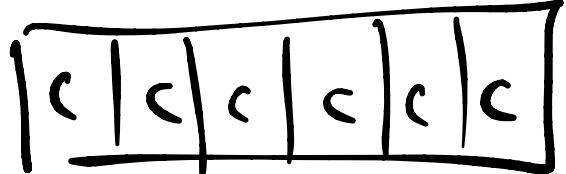
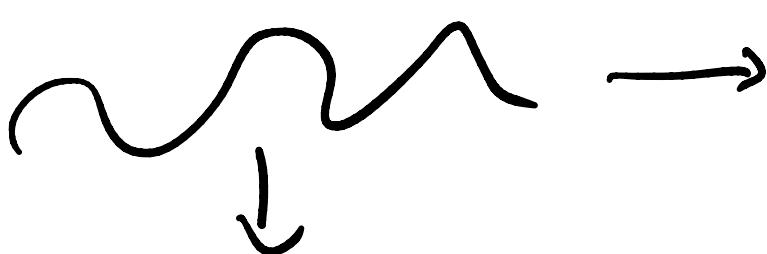


Helix/coil model

(Zimm-Bragg)



$$q = (1 + e^{-\beta E}) \quad E_C = 0 \quad E_H = \epsilon$$

Ind:

$$Q = \frac{q^k}{\sum w(E) e^{-\beta E}} = (1 + q)^k$$

$$\begin{aligned}
 &= \sum w(\epsilon) e^{-\beta \epsilon} \\
 &= \sum_{i=0}^{N_H} \binom{k}{i} e^{-\beta \epsilon_i} \\
 &\quad = \sum \binom{N}{n} (e^{-\beta \epsilon})^n
 \end{aligned}$$

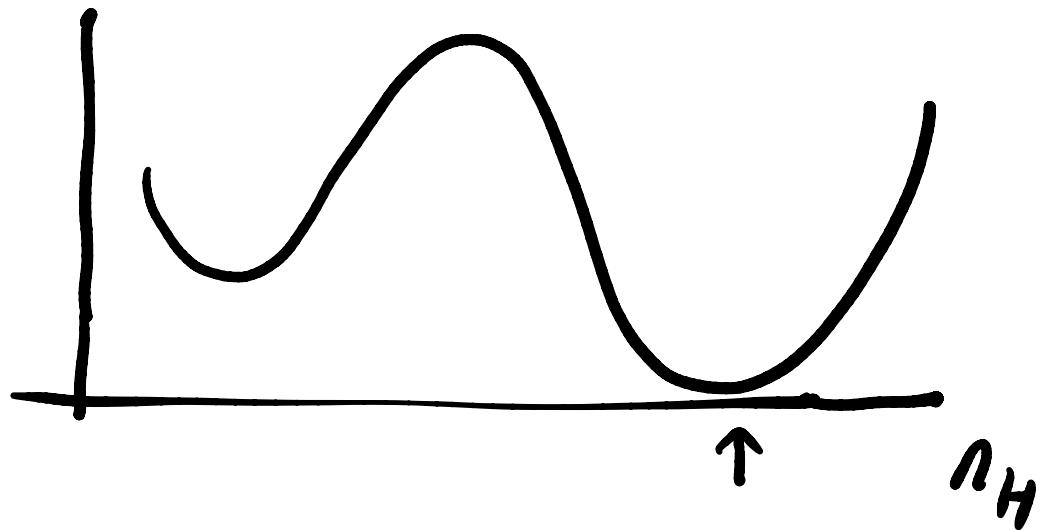
$$\epsilon_i = i\epsilon$$

$$\begin{aligned}
 P_H &= e^{-\beta \epsilon} / q \\
 P_C &= e^{-\beta \cdot 0} / q
 \end{aligned}$$

$$A \geq B$$

$$K_{ef} = \frac{P_H}{P_C} = e^{-\beta \epsilon}$$

$$A = -RT \ln Q$$



$$Q = (1 + k_{eq})^N$$

$$= \sum_{i=0}^N \binom{N}{i} k_{eq}^i$$

$$f_H = ?$$

$$\langle i \rangle_N$$

$$\langle i \rangle = \sum_i i P(i) = \sum_i i \binom{N}{i} k_{eq}^i$$

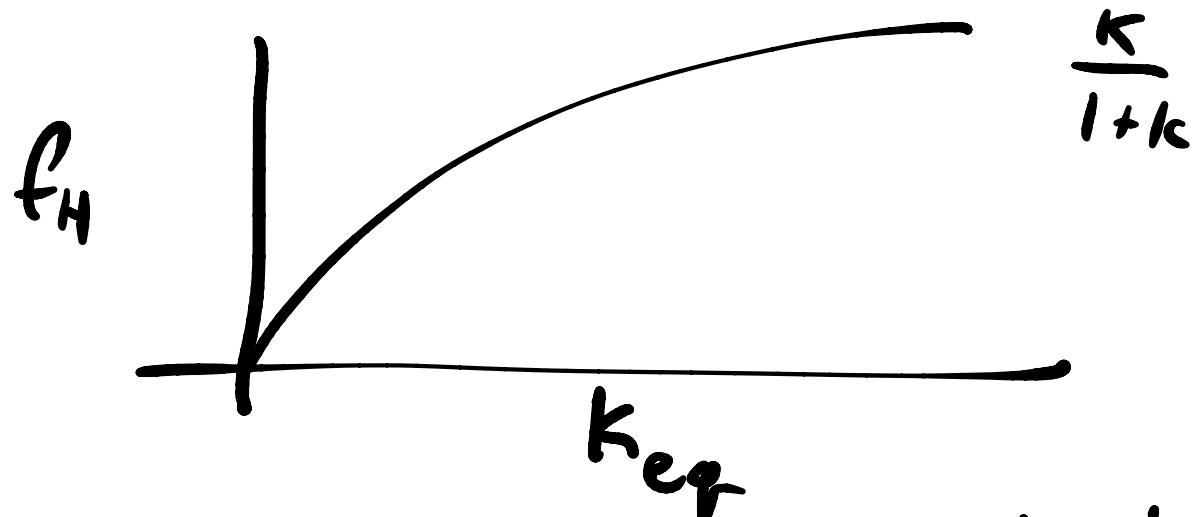
$$\frac{\partial \ln Q}{\partial k} = \frac{1}{Q} \cdot \sum_i i \binom{N}{i} k_{eq}^{i-1} = f_H \cdot N / k_{eq}$$

$$f_H = \frac{k}{N} \frac{\partial \ln Q}{\partial k} \quad \text{if } Q = (1+k)^N$$

$$\begin{aligned} &= k \cdot \frac{1}{1+k} \cdot \frac{N}{N} = \frac{k_{eq}}{1+k_{eq}} \quad A \overset{?}{\in} B \\ &= \frac{[H]/[C]}{1 + \frac{[H^3]/[C]}{[C]}} \quad C \overset{?}{\in} H \\ &= \frac{[H]}{[H]+[C]} \end{aligned}$$

$$\epsilon = \underbrace{\langle \cdot \rangle}_{n_H} \cdot \epsilon$$

$$-\frac{\partial \ln Q}{\partial P} = \epsilon$$



$$k_{eq} = e^{-\beta \epsilon}$$

b.g k is
 $\epsilon \ll 0$

20+ amino acids

ϵ_H for each one

k_i for each type

HEAMS

$$Q = (1 + K_H)(1 + K_E)(1 + F_A) \dots$$

Glycine, $K_G \approx 1$

Intrachains



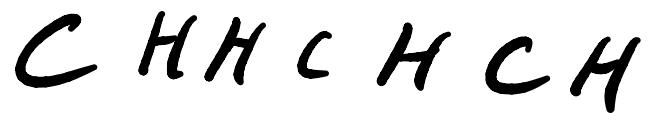
non interaction

$$BF = P_C \cdot P_H \cdot P_{H_1} \cdot P_C \cdot P_H \cdot P_C \cdot P_{H_1}$$

$$= 1 \cdot K \cdot K \cdot 1 \cdot K \cdot 1 \cdot K = K^4 = K^{n_H}$$

coupling

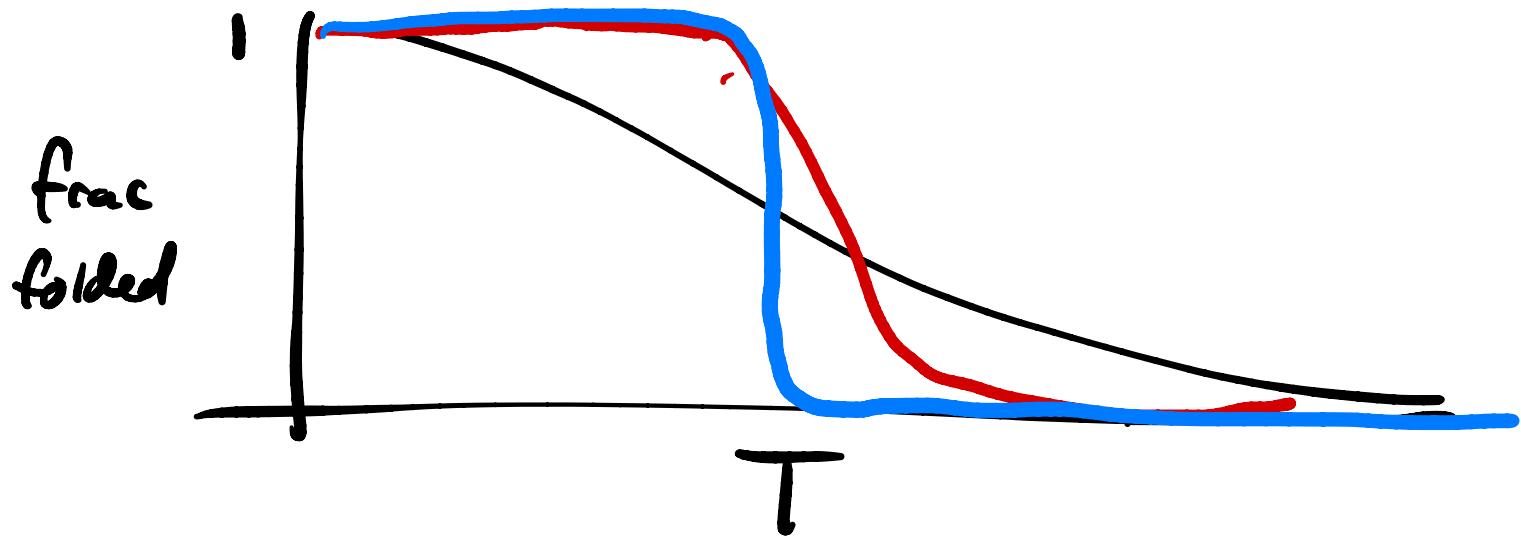
\approx



$$1 \cdot k \cdot (kz) \cdot 1 \cdot k \cdot 1 \cdot k = k^4 z$$



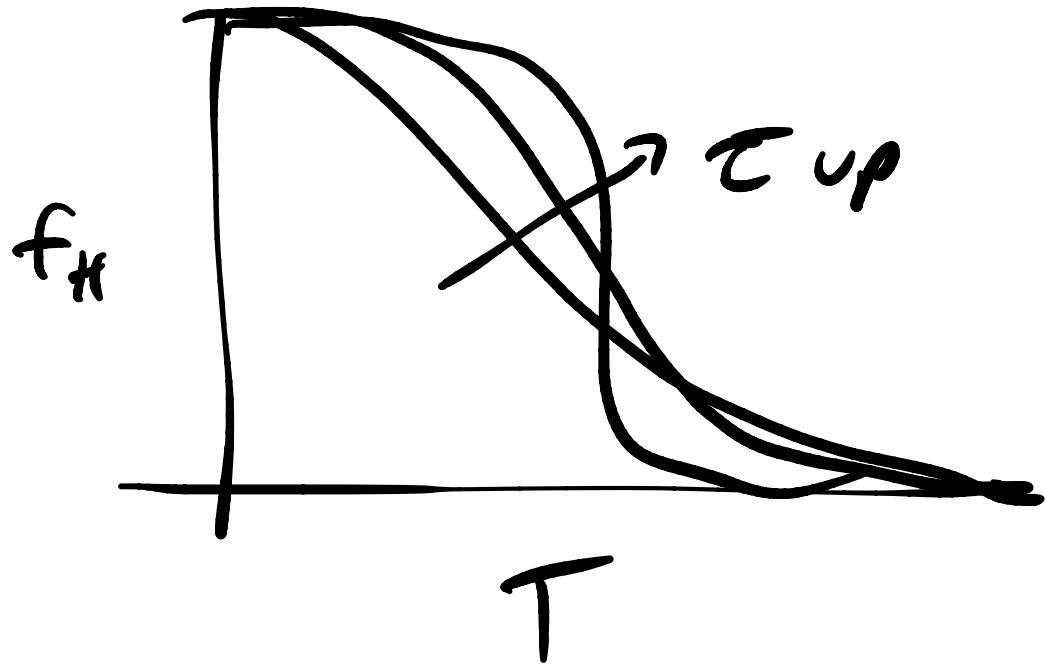
$$1 \cdot 1 \cdot k \cdot (kz)^3 \cdot 1 = k^4 z^3$$



Zimm Bragg

$$K \sim e^{+\beta h s_i}$$

$$\gamma \sim e^{+\beta J s_i s_{i+1}}$$



(full solution
transfer
matrices)

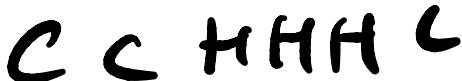
how does k, τ effect
 T_m , steepness

Zipper model

only have all Hs adjacent



3 Hs

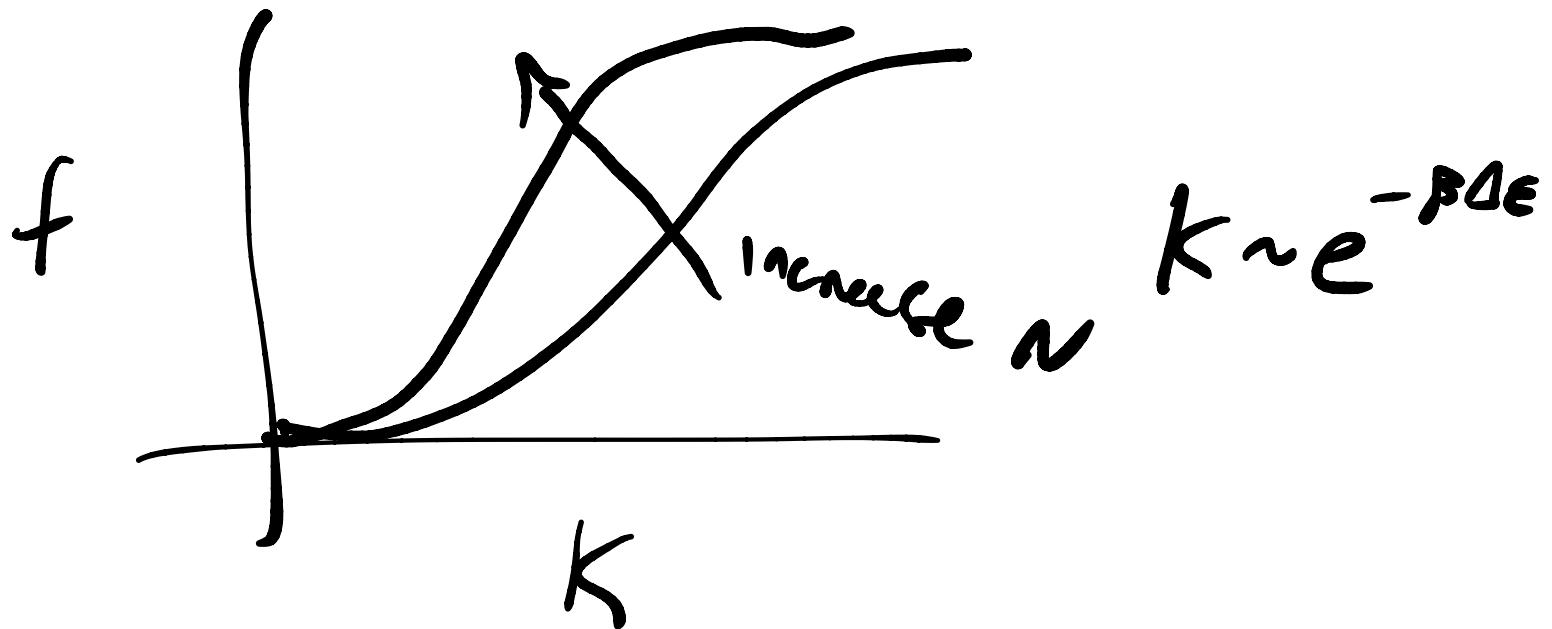


1

$$Q = \sum_{n_H=0}^N K^{n_H} \varepsilon^{(n_H-1)} \cdot (N-n_H+1)$$

$$= \frac{1}{\varepsilon} \sum_{n_H=0}^N (\varepsilon^{-1})^{n_H} (N-n_H+1)$$

$$f_H = \frac{1}{N} \frac{\partial \ln Q}{\partial K} = \text{~~~~~}$$



Ligand Binding



$$K_b = \frac{[ML]}{[M][L]} \quad \text{units } \frac{1}{M}$$

$$K_d = \frac{1}{K_b} = \frac{[M][L]}{[ML]} , M$$

$$f_{\text{protein band}} = \frac{[ML]}{[ML] + [M]} = \frac{k_B[M][L]}{k_B[M][L] + [M]}$$

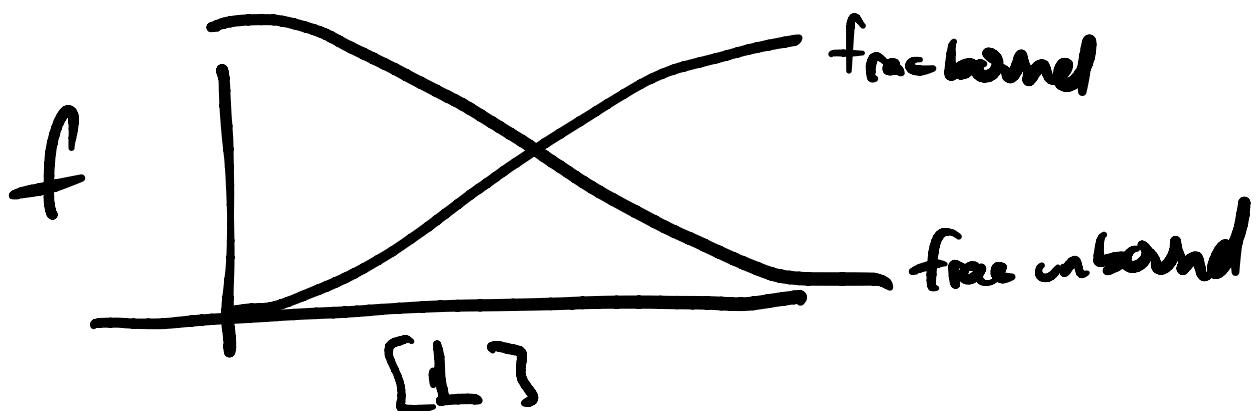
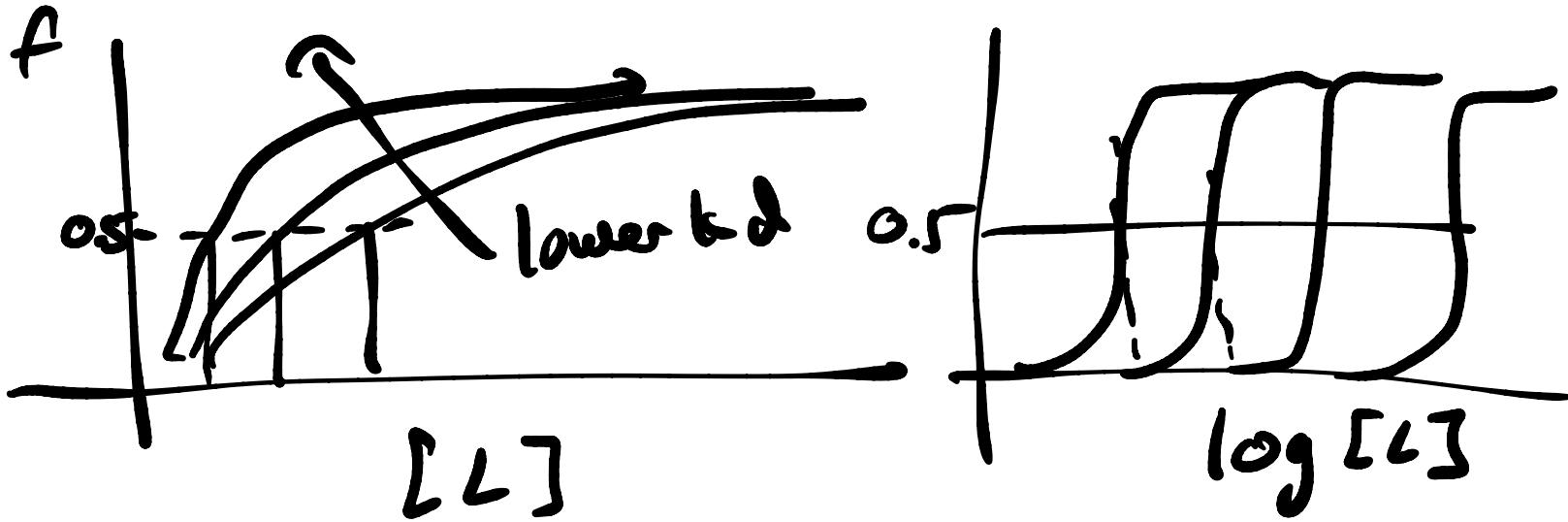
$$= \frac{k_B[L]}{k_B[L] + 1}$$

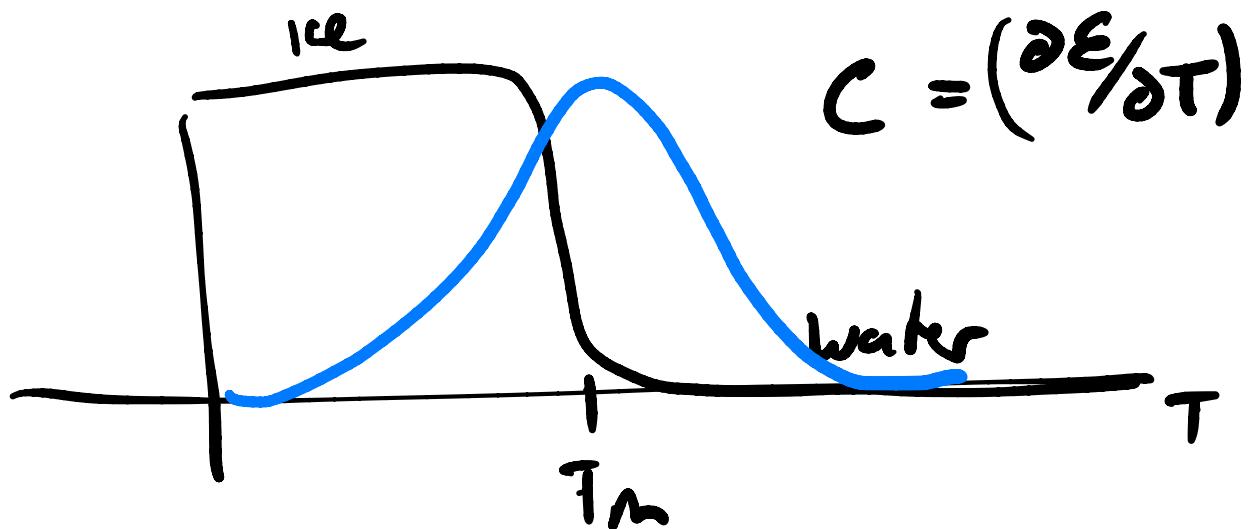
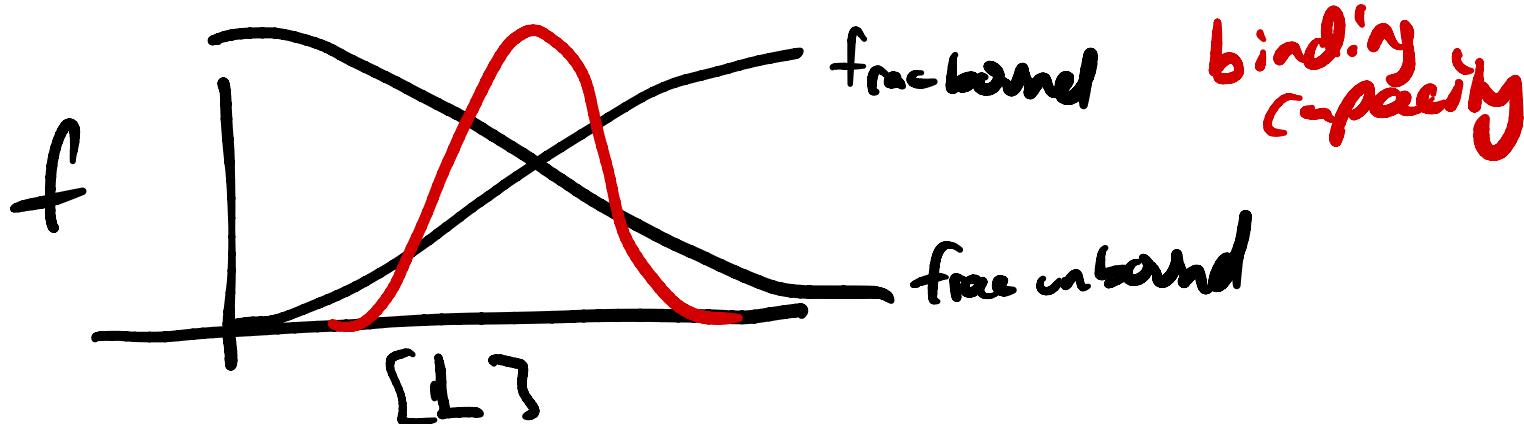
" k "

$$K_d = \frac{[M][L]}{[ML]}$$

$$= \frac{1}{1 + K_d / [L]}$$

K_d is when protein half band





Was plotting vs $[L]$
in expt, you don't control $[L]$

$$[L]_{\text{tot}} = [L] + [ML] \quad (409 - 411)$$

$$[M]_{\text{tot}} = [M] + [ML]$$

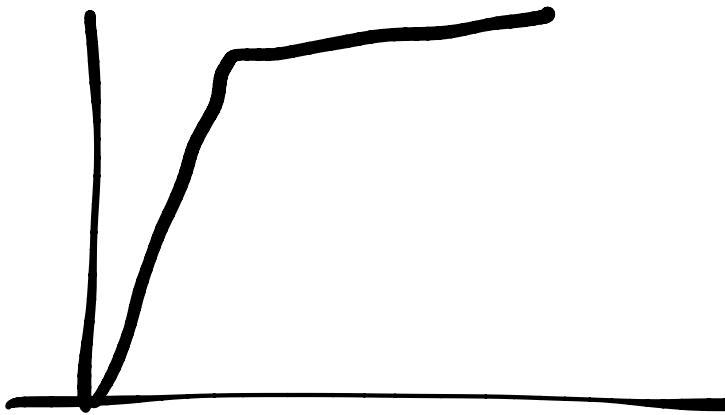
$$k_b = \frac{\Sigma MLJ}{[M] \cdot [L]} = \left(\frac{\Sigma MLJ}{[M]_{\text{tot}} - [ML]([L]_{\text{tot}} - [ML])} \right)$$

Solve for M_L , fit k_b



$M_{tot} \ll K_d$

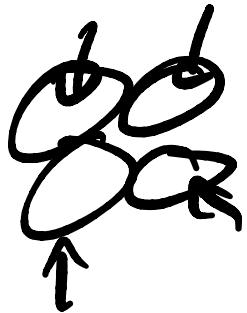
Weak binder
very low conc



$\log x$

Strong binder
saturation conc

Case of multiple binding sites



hemoglobin



$$K_b^1 = \frac{[ML]}{[M][L]} \quad K_b^2 = \frac{[ML_2]}{[ML][L]} \quad K_b^3 = \frac{[ML_3]}{[ML_2][L]}$$

etc

Stepwise or concerted
positive, negative cooperativity