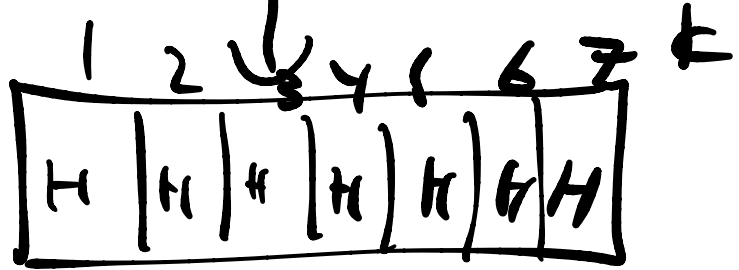
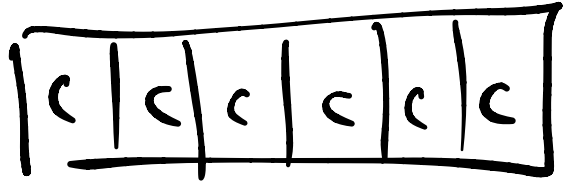
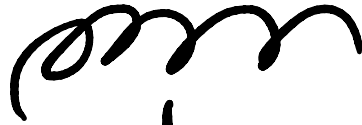


# Helix/coil model

(Zimm-Bragg)



$$q = (1 + e^{-\beta \epsilon}) \quad \epsilon_c = 0 \quad \epsilon_h = \epsilon$$

ind:  $Q = q^k = (1 + q)^k$   
 $= \sum w(\epsilon) e^{-\beta \epsilon}$

$$= \sum W(\epsilon) e^{-\beta \epsilon}$$

$$= \sum_{i=0}^{N_H} \binom{K}{i} e^{-\beta \epsilon_i}$$

$$\epsilon_i = i \epsilon$$

$$P_H = e^{-\beta \epsilon} / q$$

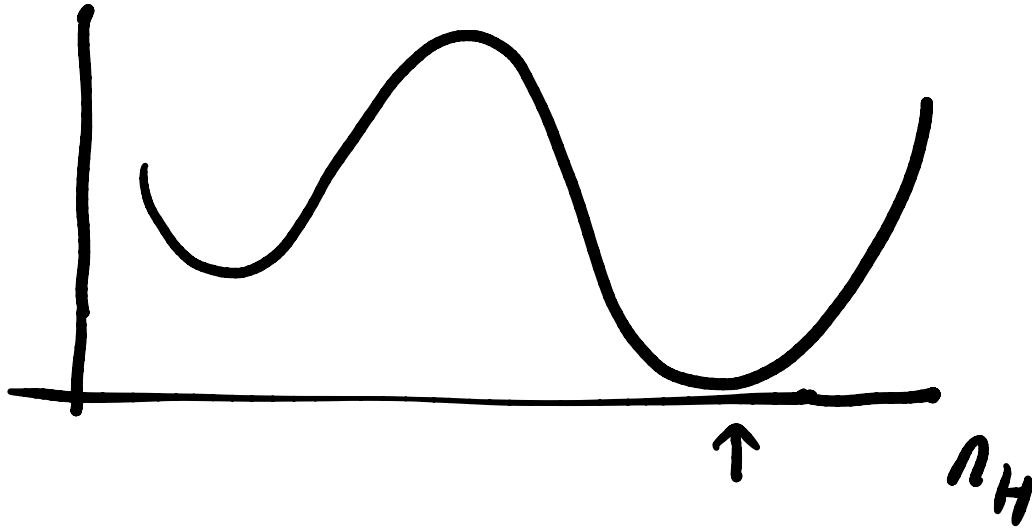
$$P_C = e^{-\beta \cdot 0} / q$$

$$A \rightleftharpoons B$$

$$K_{eq} = P_H / P_C = e^{-\beta \epsilon}$$

$$(1 + e^{-\beta \epsilon})^K$$
$$= \sum \binom{N}{n} (e^{-\beta \epsilon})^n$$

$$A = -RT \ln Q$$



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

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

$$f_H = ?$$

$$\langle i \rangle / N$$

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

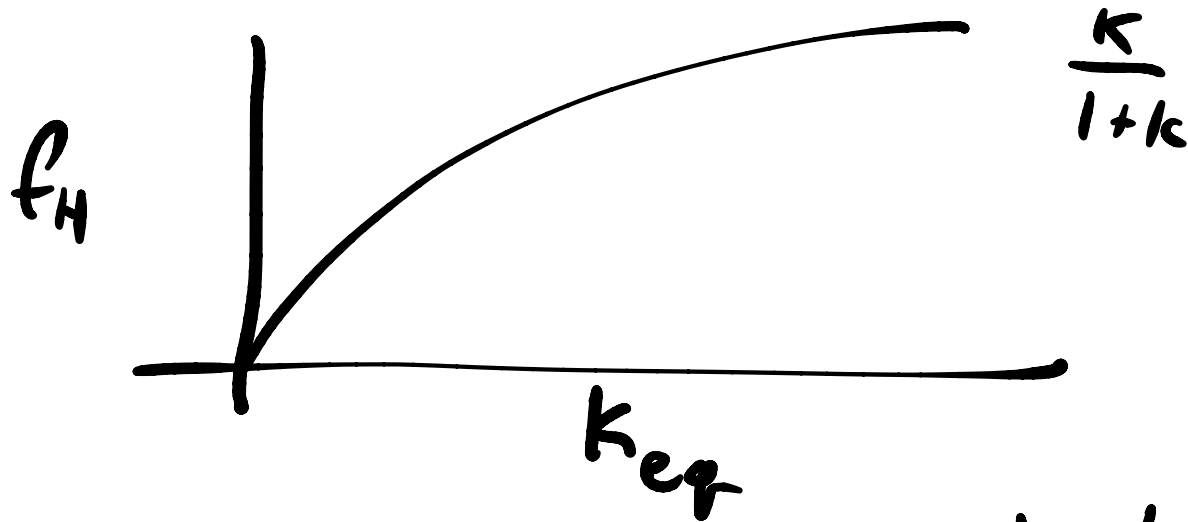
$$\frac{\partial \ln Q}{\partial k} = \frac{1}{Q} \cdot \sum_i i \binom{N}{i} k_{eq}^{i-1} = f_H \cdot N / k_{eq}$$

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

$$\begin{aligned}
 &= k \cdot \frac{1}{1+k} \cdot \frac{N}{N} = \frac{K e_f}{1 + K e_f} & A \geq B \\
 &= \frac{[H] / [C]}{1 + [H]^2 / [C]} & C \geq H \\
 &= \frac{[H]}{[H] + [C]}
 \end{aligned}$$

$$E = \sum_{i=1}^n \langle i \rangle \cdot \epsilon$$

$$-\frac{\partial \ln Q}{\partial \beta} = E$$



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

big  $k$  is  $\epsilon \ll 0$

20+ amino acids

$K_H$  for each one

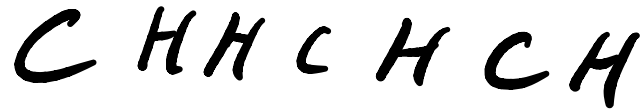
$K_i$  for each type

HEAMS

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

Glycine,  $K_G \approx 1$

# Interactions



non interaction

$$BF = P_C \cdot P_H \cdot P_H \cdot P_C \cdot P_H \cdot P_C \cdot P_H$$

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

coupling

$\approx$

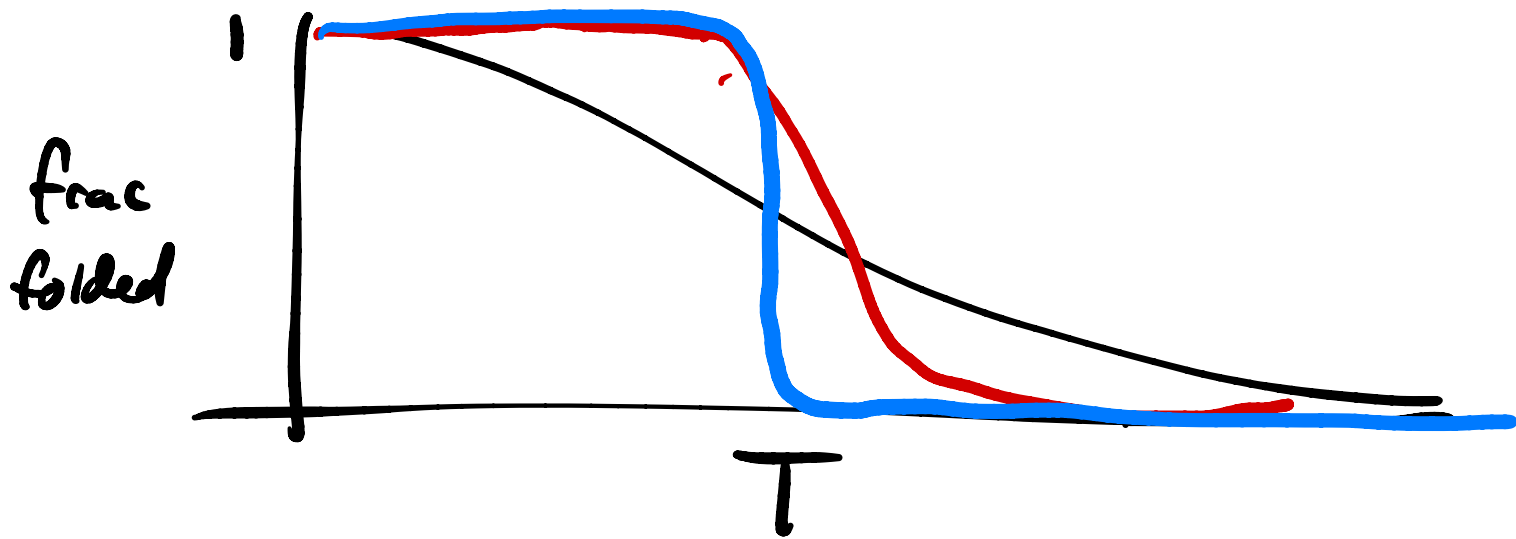


C H H C H C H

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

C C H H H H C

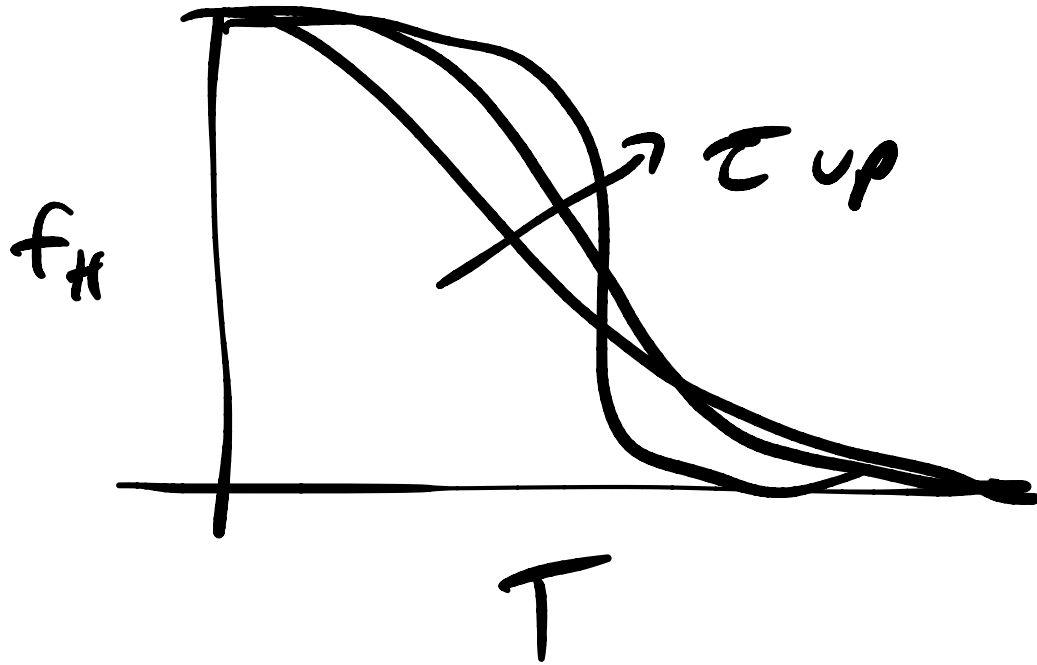
$$1 \cdot 1 \cdot k \cdot (kz)^3 \cdot 1 = k^4 z^3$$



Zimmer Bragg

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

$$Z \sim e^{+\beta J S_i S_{i+1}}$$



(fill solution:  
transfer  
matrices)

how does  $k, \tau$  effect  
 $T_m$ , steepness

# Zipper model

only have all Hs adjacent

C C C C C C

no Hs

H H H C C C

3 Hs

C H H H C C

C C H H H C

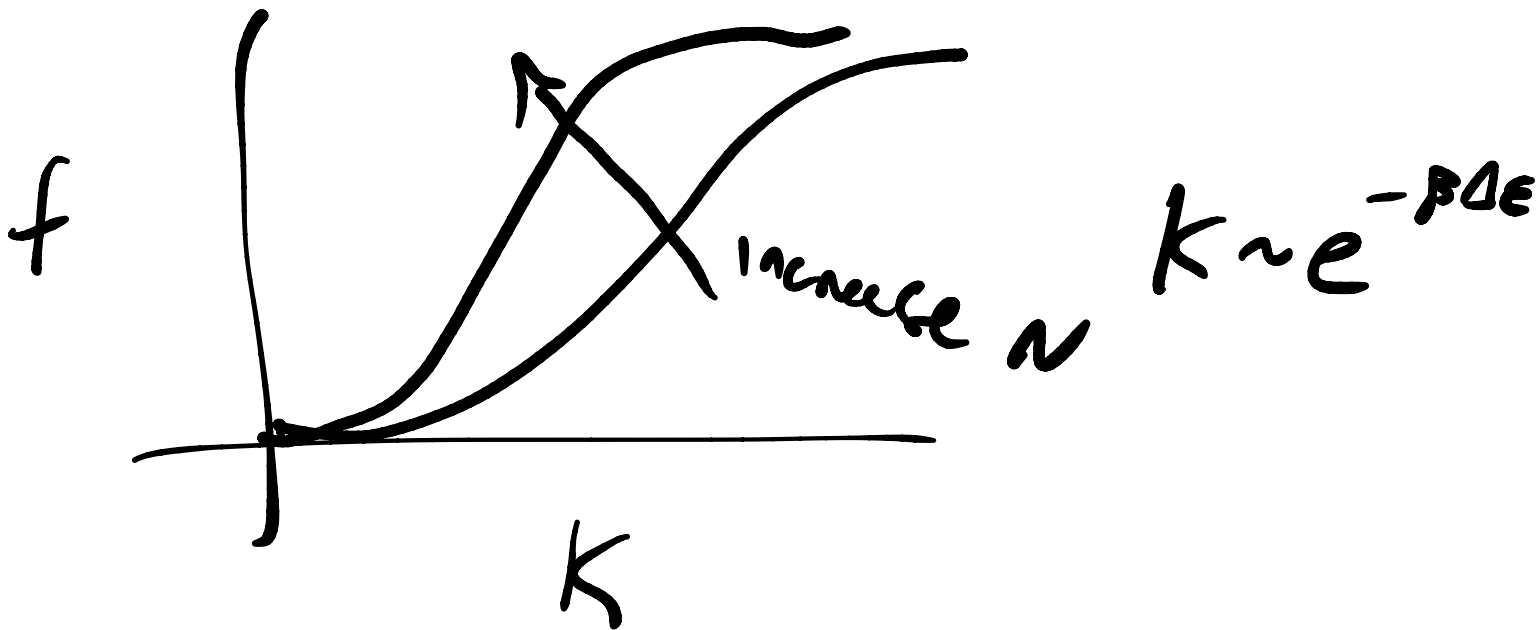
C C C H H H

|

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

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

$$f_H = \frac{k}{z} \frac{\partial \ln Q}{\partial k} = \sim$$



# Ligand Binding



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

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

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

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

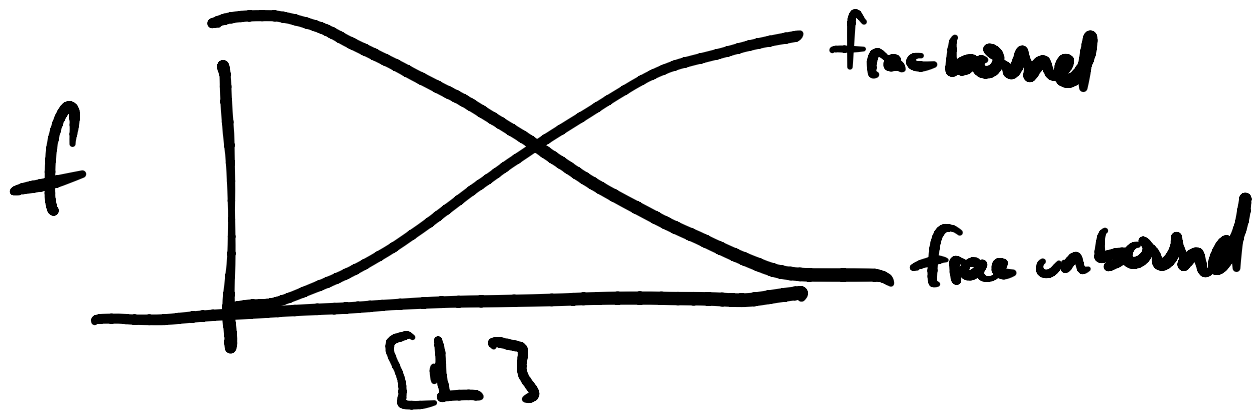
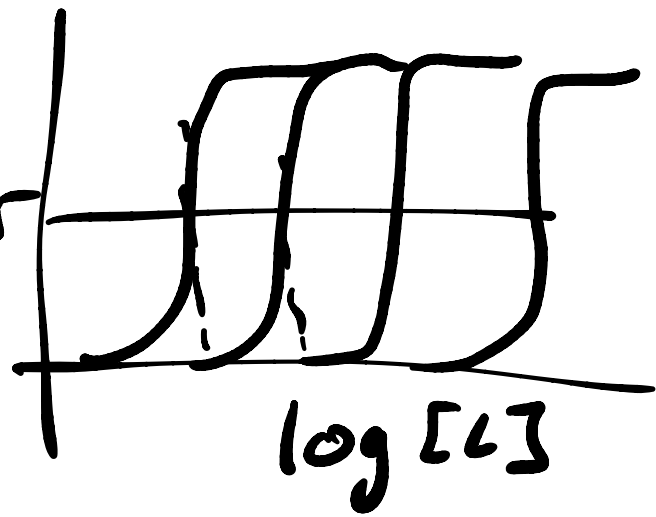
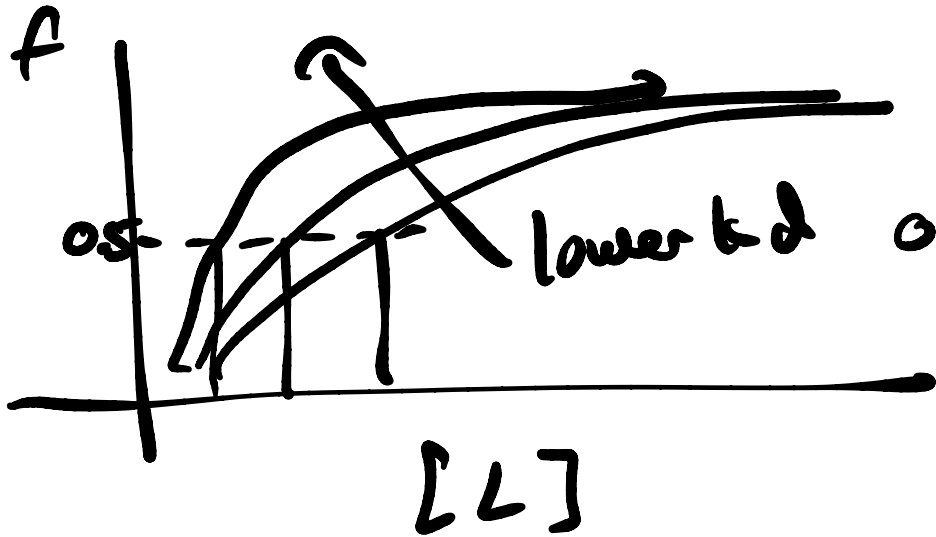
"K"

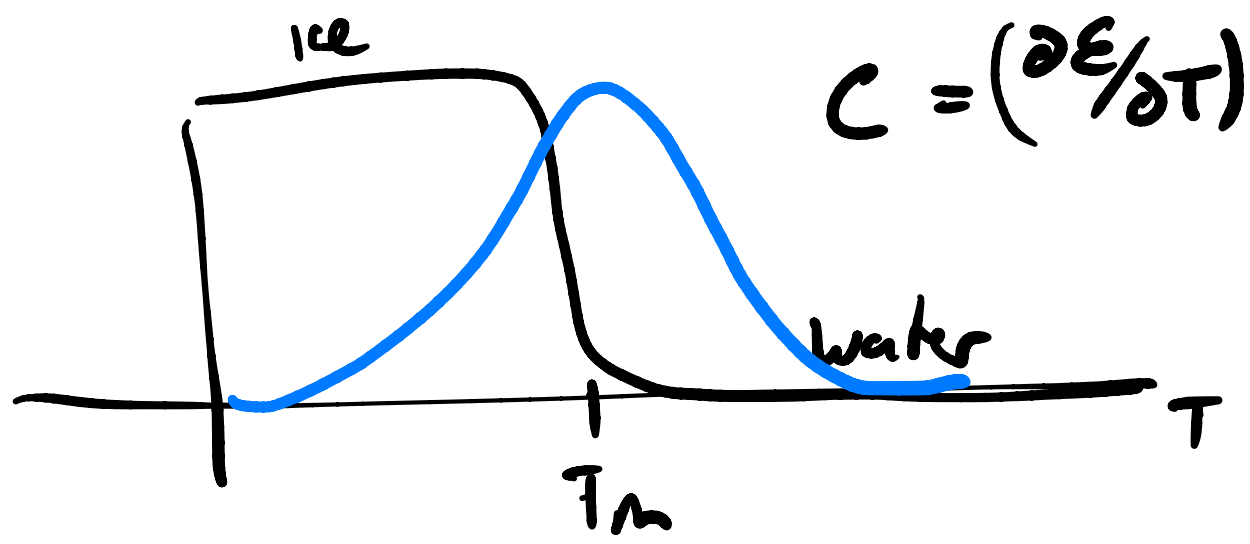
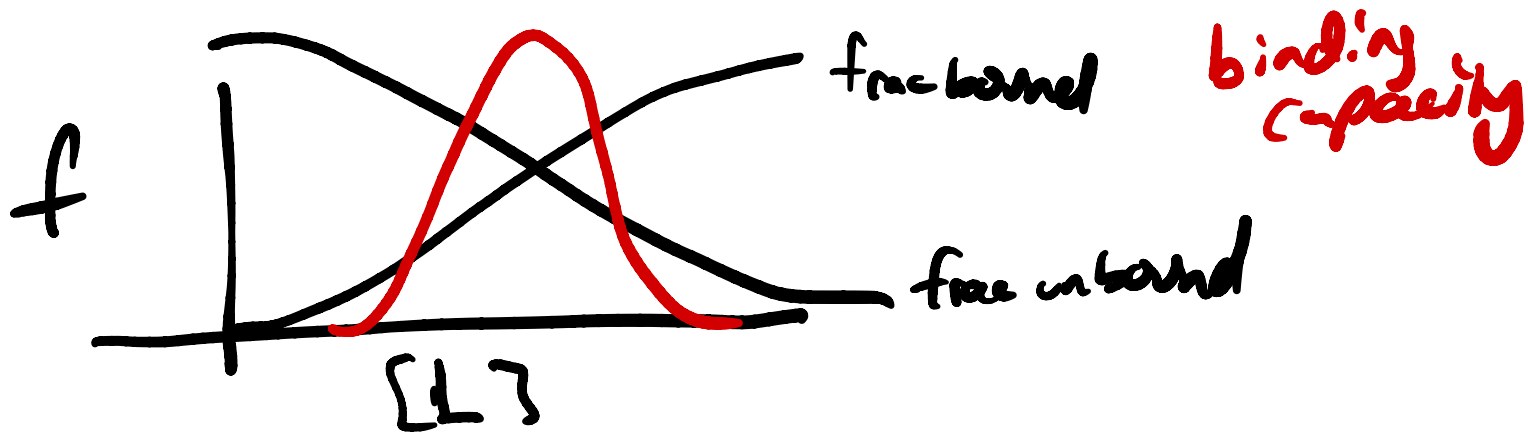
$$K_d = \frac{[M][L]}{[ML]}$$

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

$K_d$  is when protein half bound







was plotting vs  $[L]$

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

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

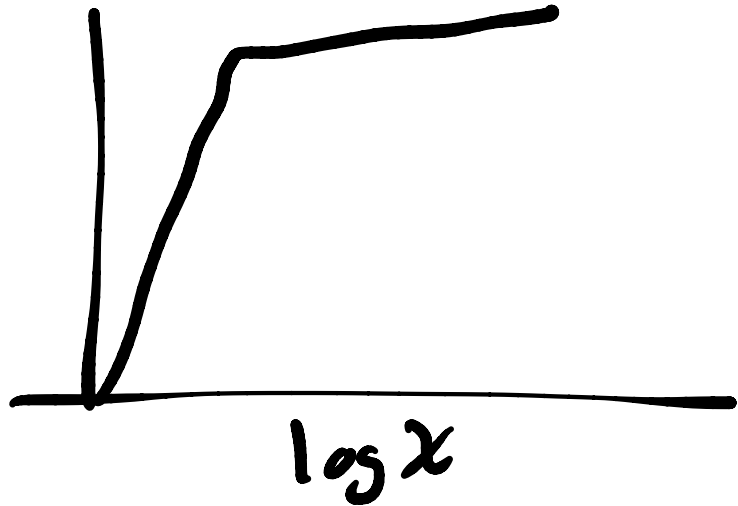
$$[M]_{\text{tot}} = [M] + [ML]$$

$$K_b = \frac{[ML]}{[M] \cdot [L]} = \frac{[ML]}{([M]_{\text{tot}} - [ML])([L]_{\text{tot}} - [ML])}$$

Solve for  $M_L$ , fit  $K_b$

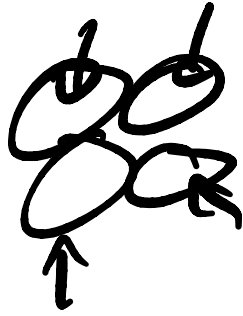


$M_{tot} \ll K_d$   
Weak binder  
very low conc

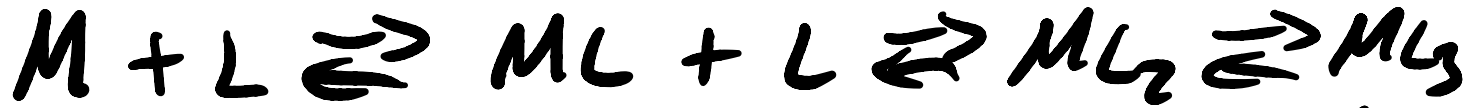


Strong binder  
Saturating conc

Case of multiple binding sites



hemoglobin



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

$$K_b^2 = \frac{[ML_2]}{[ML][L]} \quad \leftarrow$$

etc

Stepwise or concerted  
positive, negative cooperativity