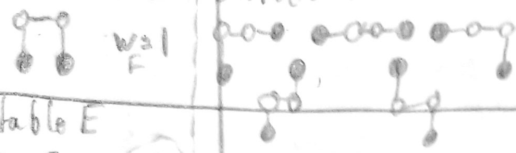
Lecture 25: Heat capacity / applications

- Heat capacity of a 'folding' hair pin (RNA/protein)

F (Folded) | Unfolded (U)



$W_F = 1$ | $W_U = 5$

say $E_F = \varepsilon \frac{J}{mol}$

Stable E

$E_F = 0$

$$Z = W_F e^{-\frac{0}{RT}} + W_U e^{-\frac{\varepsilon}{RT}}$$

$$P_F = \frac{W_F}{Z} \qquad P_U = \frac{W_U e^{-\frac{\varepsilon}{RT}}}{Z}$$

$$\frac{P_U}{P_F} = \frac{W_U e^{-\varepsilon/RT}}{W_F} = \frac{5 e^{-\varepsilon/RT}}{1}$$

$F \rightleftharpoons U$

$$K = \frac{[U]}{[F]} = \frac{P_U}{P_F}$$

Average E:

$$E = \sum p_j E_j = P_F E_F + P_U E_U$$

$$= 0 + \frac{W_U e^{-\frac{\varepsilon}{RT}} \varepsilon}{Z}$$

$$= \frac{W_U e^{-\frac{\varepsilon}{RT}} \varepsilon}{W_F + W_U e^{-\varepsilon/RT}}$$

$$C_V = \frac{\partial E}{\partial T} = \frac{1}{R}\left(\frac{\varepsilon}{T}\right)^2 P_U P_F$$ (use quotient rule to evaluate derivative)

Quotient rule: $\frac{\partial}{\partial x}\left(\frac{f(x)}{g(x)}\right) = \frac{f'g - g'f}{g^2}$

Microcanonical (constant E) partition function W

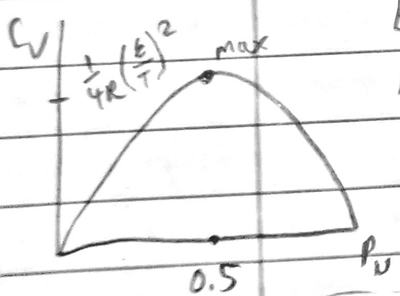
Canonical (constant T) partition function Z

For constant T,

$$\sum p_j = 1 = \sum_j \frac{W_j e^{-E_j/kT}}{Z} \qquad Z = \sum_j W_j e^{-E_j/kT}$$

$$= \sum_j W_j e^{-E_j/RT} \quad \text{(if } E_j \text{ in J/mol)}$$

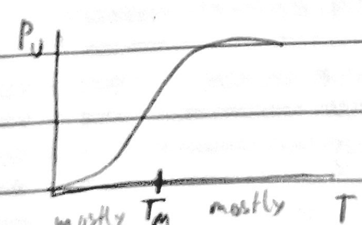
$$C_V = \frac{1}{R}\left(\frac{\varepsilon}{T}\right)^2 P_U(1 - P_U)$$



Experimentally, measuring heat capacity can give us the unfolded energy ε.

$$P_U = 1 - P_F = 1 - \frac{W_F}{W_F + W_U e^{-\varepsilon/RT}} = \frac{W_U e^{-\varepsilon/RT}}{W_F + W_U e^{-\varepsilon/RT}}$$

$$= \frac{\frac{W_U}{W_F} e^{-\varepsilon/RT}}{1 + \frac{W_U}{W_F} e^{-\varepsilon/RT}}$$



slope at T_m:

$$\frac{\partial P_U}{\partial T} \propto \frac{W_U}{W_F}$$

Cooperative transition (2 states, could have been different if more states)