Lecture 25

Last time: Stat mech at constant T

const E (extensive) | const T (intensive)

$E(S)$ $\longrightarrow$ $F(T)$ or $G(T)$

counts accessible microstates $\{W(E)$ $\longrightarrow$ $Z(T) = e^{-F(T)/k_BT}\}$ counts over all microstates at temp T

log for convenience $\{S = k_B \ln W$ $\longrightarrow$ $-\frac{F}{T} = k_B \ln Z$

$P_j = \frac{1}{W}$ $\longrightarrow$ $P_j = \frac{1}{Z} \cdot \underbrace{w_j e^{-E_j/k_BT}}_{\text{Boltzmann factor}}$ free energy counts micro states

Note: $\Lambda = -\frac{F}{T}$ is the Massieu function

Alternate related ways of writing $Z(T)$:

$\sum P_j = 1$ (total probability) $\Rightarrow \sum \frac{1}{Z} w_j e^{-E_j/k_BT} = 1 \Rightarrow Z = \sum w_j e^{-E_j/k_BT}$

Thus, states at higher energy are less accessible at higher T and count less

$Z \to w_0 = 1$ as $T \to 0$

Sometimes, the sum is written over every single microstate at energy E_j i.e. repeated w_j times rather than lumping w_j microstates at energy E_j together:

$$Z(T) = \underset{\text{every single microstate}}{\sum} \underbrace{e^{-E_j/k_BT} = e^{-F/k_BT}}_{\text{connects the micro and macro world}}$$

Today: Protein folding using $Z(T)$

Q: What is the formula for the K_{eq} of protein folding or unfolding and the heat capacity for the reaction?

A: Steps 1-2-3: formula for system - formula from P1 and P2 - combine

① Macrostate "F" folded hairpin

$E_F = 0$

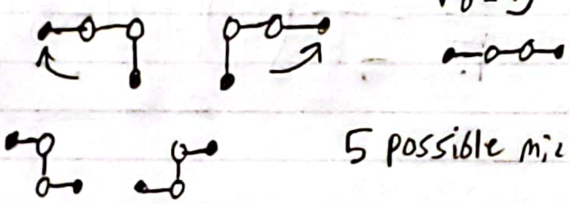
favorable interaction of energy ε

$W_F = 1$

Macrostate "U" unfolded hairpin

$E_U = +\varepsilon$

$W_U = 5$



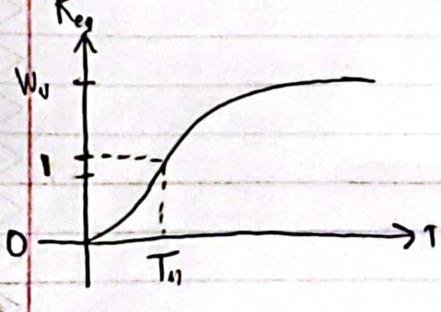
5 possible microstates

② $$Z(T) = W_F e^{-E_F/RT} + W_U e^{-E_U/RT}$$

$$= (1 \cdot 1) + W_U e^{-\varepsilon/RT} \quad (W_U = 5 \text{ in our example})$$

$$\rho_F = \frac{1}{Z}, \quad \rho_U = \frac{W_U e^{-\varepsilon/RT}}{Z}$$

Reaction: $F \rightleftharpoons U \Rightarrow \frac{[U]}{[F]} = \frac{\rho_U}{\rho_F} = K_{eq} = W_U e^{-\varepsilon/RT}$



$$K_{eq} = 1 = W_U e^{-\varepsilon/RT} \Rightarrow T_m = \frac{\varepsilon}{R\ln(W_U)}$$

"tug of war"

Heat capacity of (un) folding

To get C_v, let's get $E(T)$ first

$$\langle E \rangle = \sum P_j E_j = \frac{1}{Z} \cdot 0 + \frac{5 \cdot e^{-\varepsilon/kT}}{Z} \cdot \varepsilon$$

$$\therefore E(T) = \varepsilon \cdot \frac{5e^{-\varepsilon/kT}}{1 + 5e^{-\varepsilon/kT}} \quad \begin{array}{l} \rightarrow 0 \text{ as } T \rightarrow 0 \\ \rightarrow \frac{5}{6}\varepsilon \text{ as } T \rightarrow \infty \end{array}$$

$$C_V = \frac{\partial E}{\partial T} = \frac{1}{k} \left(\frac{\varepsilon}{T}\right)^2 \rho_u (1 - \rho_u)$$