Lecture 26

Last time: $Z(t) \rightarrow \rho_j \rightarrow A = \sum \rho_j A_j \rightarrow$ folding!

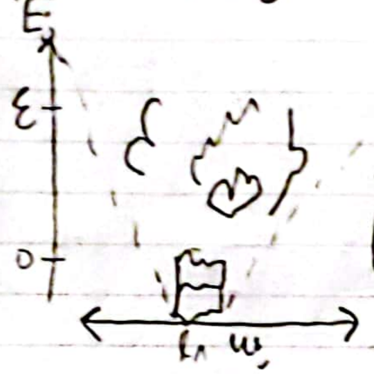
$$Z(T) = \sum \underbrace{e^{-E_j/RT}}_{\text{Boltzmann factor}} = e^{\underbrace{-f(T)/RT}}$$

-free energy counts microstates at constant T

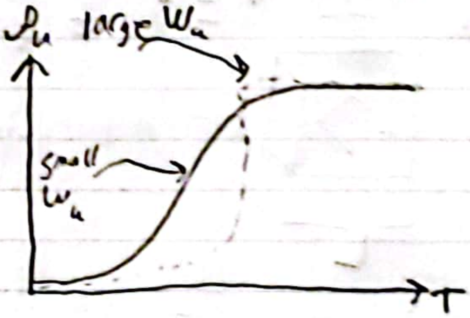
microstates at constant T

ex. protein folding

(1)



$$\begin{cases} w_u >> w_f \\ E_u > E_f \\ w_f = 1 \end{cases}$$



(2) $\rho_j = w_j e^{-E_j/RT} / Z$; $\rho_u = \dfrac{w_u e^{-\varepsilon/RT}}{1 + w_u e^{-\varepsilon/RT}}$

(3) $Z(T) = 1 + w_u e^{-\varepsilon/RT}$, $E = \sum \rho_j E_j = \varepsilon \rho_u$, $C_v = \dfrac{\partial E}{\partial T} \sim \dfrac{1}{R}\left(\dfrac{\varepsilon}{T}\right)^2 \rho_u(1-\rho_u)$

Today: more "laws" using $Z(T)$, $F(T)$, $G(T)$

Q: what is the energy of a gas?

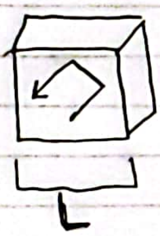
A: ① System + ② universal formula P_1 and P_2 + ③ combine.

② Hw# 54.2 $\left(\beta = \frac{1}{k_B T}, \frac{1}{RT}\right.$ $\quad R = \cancel{A} \cdot k_B$ J/K

J/mol·K $\quad$ mole^{-1} (avogadro's #)

$$Z = e^{-F/kT} = e^{-\beta F} = e^{-\beta(E-TS)} = e^{-\beta E} \cdot e^{+S/R}$$

$$-\frac{\partial Z}{\partial \beta} = +E \cdot Z \Rightarrow E = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} \text{ (Chain rule)}$$

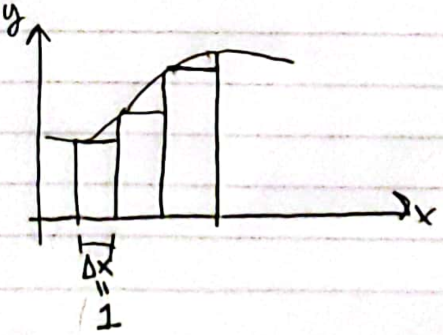
①  For a particle in a box, $E_n = \frac{h^2 n^2}{8mL^2}$ in 1-D

In 3-D, $E_{n_y, n_x, n_z} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$ $\quad n_x = 1, 2, \ldots$ $\quad n_y = 1, 2, \ldots$ $\quad n_z = 1, 2, \ldots$

$Z = \sum_{n_x, n_y, n_z} e^{-\beta E_{n_x, n_y, n_z}}$; let's approximate this sum, "baby calculus in reverse"

$$\int_{x_0}^{x_n} dx\, y(x) \approx \Delta x (y_0 + y_1 + \ldots)$$

do this in reverse



Replacing the triple sum by triple integral,

$$Z(T) \approx \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z\, e^{-\beta \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)}$$

$$Z(T) \approx \int_0^\infty dn_x \, e^{-\beta \frac{h^2}{8mL^2} n_x^2} \cdot \int_0^\infty dn_y \, e^{-\beta \frac{h^2}{8mL^2} \cdot n_y^2} \cdot \int_0^\infty \cdots$$

$$= \left\{ \int_0^\infty dn_x \, e^{-\beta \frac{h^2}{8mL^2} n_x^2} \right\}^3 = \left\{ \left(\frac{2\pi m}{\beta h^2} \right)^{1/2} \right\}^3 = \left(\frac{2\pi m}{\beta h^2} \right)^{3/2}$$

final answer for E:

$$Z_{1\,\text{particle}} = \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} \underbrace{V}_{=L^3}$$

$$Z_{n\,\text{particles}} = \left(\frac{2\pi m}{\beta h^2} \right)^{3N/2} V^N$$

$$\ln Z = -\frac{3}{2} N \ln \beta + \frac{3}{2} N \ln \left(\frac{2\pi m}{h^2} \right) + N \cdot \ln V$$

$$E = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \left(-\frac{3}{2} N \ln \beta \right) = \boxed{+\frac{3}{2} N k_B T = \frac{3}{2} n R T}$$ nice result!