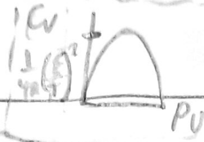
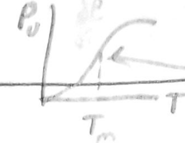
Lecture ~~25~~ 24 review: ($\beta = \frac{1}{RT}$ or $\frac{1}{kT}$ depending on units)

- isolated sys: (const E) $P_j = \frac{1}{W_j}$ ← # of accessible microstates at energy E
- open sys: (const. T) $P_j = \frac{W_j e^{-\beta E_j}}{Z}$ ← # of accessible microstates at temperature T

ex: $PV = nRT$ (using W)

ex: $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$ (using S)





ex: Protein or RNA folding (using W and Z)

F: Folded U: Unfolded

$W_F < W_U$

$E_F < E_U = \varepsilon$

$\frac{\partial P}{\partial T}$ is cooperativity Hill coeff.

Lecture 26: Equipartition: T is the average energy per degree of freedom

$E(S) \to W = e^{-\beta ST}$ $E = \sum_j P_j E_j$

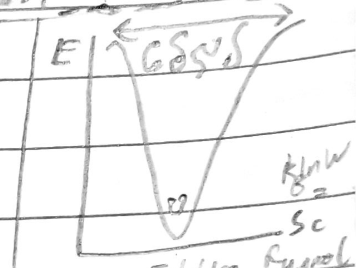
$\downarrow$

$F(T) \to Z = e^{-\beta F} = \sum_j W_j e^{-\beta E_j}$

Boltzmann factor unites microscopic + macroscopic worlds.

- ex: How is the E of particles in a 3D box (3 degrees of freedom per particle) related to T?

two parts: (1) stat mech, (2) QM



1. want a formula for E in terms of $Z(T)$

$$Z = e^{-\beta F} = e^{-\beta E + S/k_B} \to \frac{\partial Z}{\partial \beta} = -E \cdot Z \to E = \frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

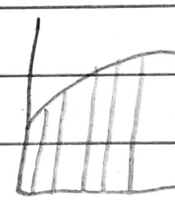
$F = E - TS$

2. Get formula for Z from QM: E of particle in a box

$$E = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) \to Z = \sum_{n_x,n_y,n_z=1}^{\infty} e^{-\beta E} \approx \int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z \, e^{-\frac{\beta h^2}{8mL^2}(n_x^2+n_y^2+n_z^2)}$$

inverse baby calculus trick!

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



approximate integral by sum of areas of finite size boxes.

inverse is reverse, from sum to integral.

$$Z \approx \left(\int_0^{\infty} dx \, e^{-\frac{\beta h^2}{8mL^2}x^2}\right)^3 = \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}} L^3$$

Gaussian function. Integrals of this type have a well-known solution

$$Z = \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}} V = Z(T, V)$$

$$E = \frac{-1}{Z}\frac{\partial Z}{\partial \beta} = -\left(\frac{\beta h^2}{2\pi m}\right)^{\frac{3}{2}} \frac{1}{V} \cdot \left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}} V \cdot \frac{-3}{2}\beta^{-\frac{5}{2}}$$

$\frac{\partial}{\partial x}(x^n) = n x^{n-1}$

$$= \frac{3}{2}\beta^{-1}$$

$$= \frac{3}{2}k_B T \text{ (for 1 particle)}$$

For N particles, $E = N \cdot \frac{3}{2}k_B T = \frac{3}{2}nRT$

For each degree of freedom (3 in this case per particle), $E = \frac{1}{2}k_B T$