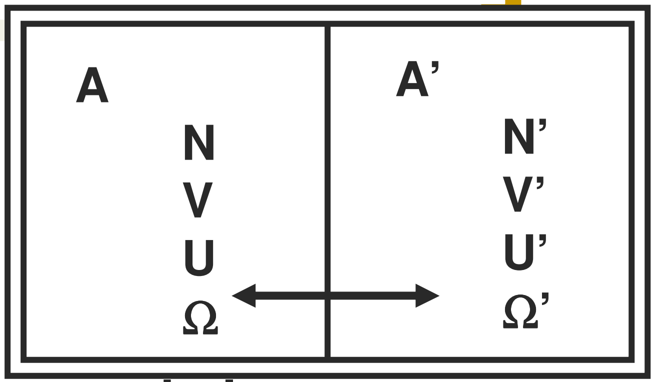
Chapter 3: Systems of Many Particles – Part III

Medical Equipment I

2008-2009

The Boltzmann Factor



- Two isolated systems
  - In thermal contact
- Let system A be a single particle
- Let system A' be a large system
  - "reservoir"
- Transfer of energy → Number of microstates in A and A' change
  - Ratio of number of states ≡ G

The Boltzmann Factor

- Consider system A has two different energies U_r and U_s
- Reservoir A' is very large
  - Its temperature *T'* remains the same
  - Has many energy levels
- Recall that $P(U) = \Omega^*(U) / \Omega^*_{tot}$
- Recall that $\Omega^*(U) = \Omega(U) \cdot \Omega'(U^* - U)$

The Boltzmann Factor

- Then,

$$\frac{P(U_s)}{P(U_r)} = \frac{\Omega^*(U_s)}{\Omega^*(U_r)} = \frac{\Omega(U_s)\cdot\Omega'(U^* - U_s)}{\Omega(U_r)\cdot\Omega'(U^* - U_r)}$$

- Let

$$G = \frac{\Omega(U_s)}{\Omega(U_r)}$$ and $$R = \frac{\Omega'(U^* - U_s)}{\Omega'(U^* - U_r)}$$

The Boltzmann Factor

- Recall that

$$\frac{1}{\tau} \equiv \frac{1}{\Omega}\frac{d\Omega}{dU} \text{ and } \frac{1}{\tau'} \equiv \frac{1}{\Omega'}\frac{d\Omega'}{dU'}$$

- Equilibrium at $\tau = \tau'$,
  - related to absolute temperature
    - k_B= Boltzmann const= 1.38×10^{-23} J K^{-1}
    - T= absolute temperature K

$$\tau' = k_B T'$$

- Consider solving the above equation for Ω'
  - T' is constant

The Boltzmann Factor

$$\frac{1}{\Omega'}\left(\frac{d\Omega'}{dU'}\right)=\frac{1}{k_BT'}\Rightarrow\frac{d\Omega'}{dU'}=\left(\frac{1}{k_BT'}\right)\Omega'$$

- Then,

$$\Omega'(U')=\text{constant}\times e^{U'/k_BT'}$$

- Hence, at equilibrium *T*= *T'*

$$R=\frac{\text{constant}\times e^{(U^*-U_s)/k_BT'}}{\text{constant}\times e^{(U^*-U_r)/k_BT'}}=e^{-(U_s-U_r)/k_BT}$$

The Boltzmann Factor

- *R* is called the "Boltzmann factor"
  - Factor by which the number of microstates in the reservoir decreases when the reservoir gives up energy U_s-U_r
- Relative probability of finding system A with energy U_r or U_s is given by

$$\frac{P(U_s)}{P(U_r)} = G \cdot R = \left[\frac{\Omega(U_s)}{\Omega(U_r)}\right] \cdot e^{-(U_s - U_r)/k_B T}$$

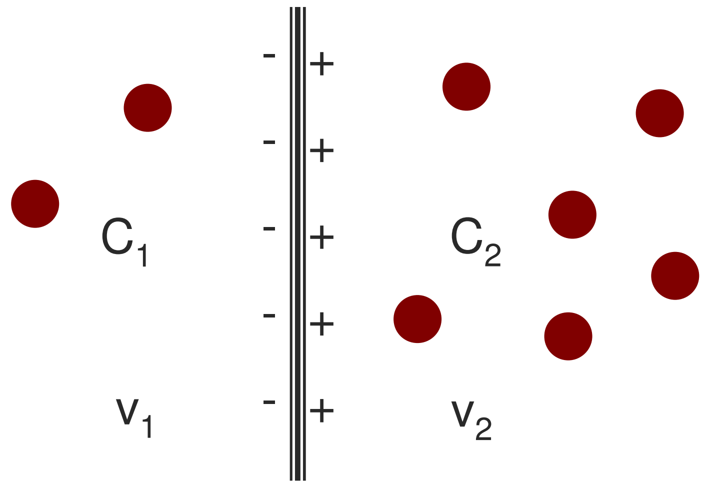
The Boltzmann Factor

- *G* factor: “density of states factor”
  - Property of the system
  - Ex: single atom with discrete energy levels, G=1
  - Degeneracy: G may be different

Example 1: Nernst Equation

- Concentration of ions on the two sides of a semi-permeable membrane and its relation to the voltage across the membrane

$$\frac{P(2)}{P(1)} = \frac{C_2}{C_1}$$



Nernst Equation

- *$U = E_k + E_p$ (E_k is the same)*
  - *Potential energy is $E_p = zev$*
- *Then,*

$$\frac{C_2}{C_1} = e^{-ze(v_2 - v_1)/k_B T}$$

- *Since $R = N_A K_B$ and $F = N_A e$*

Nernst Equation

$$v_2 - v_1 = \frac{RT}{zF} \ln\left(\frac{C_1}{C_2}\right)$$

Example 2: Pressure variation in the atmosphere

- Atmospheric pressure decreases with altitude
- Potential energy: gravitational $= m \times g \times y$

$$\frac{C(y)}{C(0)} = e^{-mgy/k_B T}$$

Assignment

- Problem assignment on web site