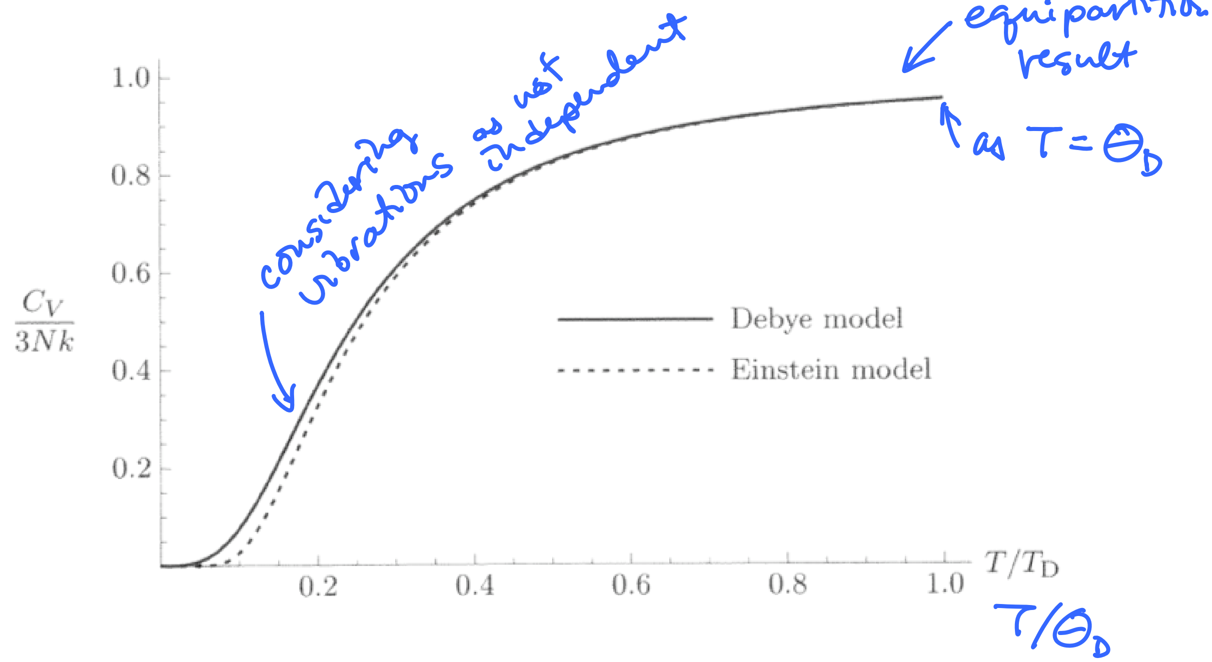
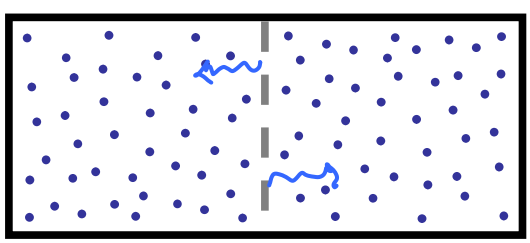
Comparing Model Results



Review

- For two systems in diffusive equilibrium



  – Chemical potential is the same at equilibrium

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

$$\boxed{dU = TdS - PdV + \mu dN}$$

Chemical Potential

- Consider relation

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

→ μ would be negative for increase in N

$$S = Nk\left[\ln\left(V\left(\frac{4\pi mU}{3h^2}\right)^{3/2}\right) - \ln N^{5/2} + \frac{5}{2}\right]$$

$$\frac{\partial S}{\partial N} = k\left[\ln\left(V\left(\frac{4\pi mU}{3h^2}\right)^{3/2}\right) - \ln N^{5/2} + \frac{5}{2}\right] + Nk\left[-\frac{5}{2}\cdot\frac{1}{N}\right]$$

$$= k\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{N3h^2}\right)^{3/2}\right)\right]$$

$$\mu = -kT\ln\left[\frac{V}{N}\underbrace{\left(\frac{4\pi mU}{N3h^2}\right)^{3/2}}_{\sim 7\times10^{30}\,m^{-3}}\right]$$

helium at room T & atmospheric P

$$\frac{V}{N} = 4.2\times10^{-26}\,m^3$$

See Sec 5.3

increase number of particles

$\frac{V}{N}$ decreases

ln term becomes smaller

μ → becomes less negative

↳ more willing to give up particles

Different Types of Particles

- Initially, we assumed only one type of particle in system

- If it contains several different types of particles
  - Need to consider chemical potential for each one

$$\mu_1 \equiv -T\left(\frac{\partial S}{\partial N_1}\right)_{U,V,N_2} \qquad \mu_2 = \left(\frac{\partial U}{\partial N_2}\right)_{S,V,N_1}$$

  - Thermodynamic identity becomes

$$dU = TdS - PdV + \sum_i \mu_i dN_i$$

at eq.

$\mu_{1A} = \mu_{1B}$; $\mu_{2A} = \mu_{2B}$ ...

More on Diffusive Equilibrium

- Now consider system in thermal equilibrium and diffusive equilibrium with reservoir at temperature, T
  - System can exchange particles with environment

- Ratio of probabilities for two different microstates

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}$$

Gibbs Factor

- Starting from $\dfrac{P(s_2)}{P(s_1)} = \dfrac{\Omega_R(s_2)}{\Omega_R(s_1)} = \dfrac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{[S_R(s_2)-S_R(s_1)]/k}$

$\Omega = e^{S/k}$

$dS_R = \frac{1}{T}(dU_R + P\,dV_R - \mu\,dN_R)$

$-dS_R = dS$

$S_R(s_2) - S_R(s_1) = -\frac{1}{T}\left(E(s_2) - E(s_1) - \mu N(s_2) + \mu N(s_1)\right)$

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-[E(s_2)-\mu N(s_2)]/kT}}{e^{-[E(s_1)-\mu N(s_1)]/kT}}$$

$e^{-[E(s)-\mu N(s)]/kT}$ Gibbs factor

Calculating Absolute Probabilities

- Normalizing function for Gibbs factor:
- Grand Partition Function (or Gibbs sum)
  - Sum over all possible states (including all possible *N*)

$\mathcal{Z}$

$$\mathcal{Z} = \sum_s e^{-[E(s)-\mu N(s)]/kT}$$

- Gibbs factor for different types of particles (example two)

$$e^{-[E(s)-\mu_A N_A(s)-\mu_B N_B(s)]/kT}$$

Stat Mech Terminology

- For isolated system (as in the ones just used),
  - All microstates have same probability
  - *Microcannonical ensemble*

fixed U, N

- For system in thermal equilibrium with a reservoir at T,
  - State probabilities determined from Boltzmann factors
  - *Cannonical ensemble*

$\hookrightarrow e^{-E(s)/kT}$

- For system in thermal and diffusive equilibrium with reservoir,
  - State probabilities determined from Gibbs factors
  - *Grand cannonical ensemble*

$\hookrightarrow e^{-[E(s)-\mu N(s)]/kT}$

Quantum Statistics

- Useful application of Gibbs factors
- Consider an ideal gas
  - Partition function derived for N indistinguishable, non-interacting particles

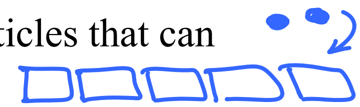
$$Z_{\text{total}} = \frac{1}{N!} Z_1^{\,N}$$

  - Number of single-particle states much greater than number of particles

$$Z_1 >> N$$

System of Non-interacting Particles

- Start with a system of two non-interacting particles that can occupy any of five single-particle states



- Each single particle state has E=0 so each Boltzmann factor is 1 so Z is same as Ω

11000	01010	20000
10100	01001	02000
10010	00110	00200
10001	00101	00020
01100	00011	00002

2x for distinguishable

- If distinguishable particles, Z=25
- If indistinguishable particles, Z=15 - not Boltzmann value

$$Z = \frac{1}{N!} Z_1^N \Rightarrow \frac{5^2}{2!} = 12.5$$

Distribution Functions

- If $Z_1 >> N$ not valid, can use Gibbs factors instead of Boltzmann factors
  - Need to consider if particles are bosons or fermions

- Start with one single-particle state of system,
  - Energy when occupied is ε, when unoccupied is 0
  - If can be occupied by n particles, probability is

$$P(n) = \frac{1}{\cancel{Z}} e^{-(n\varepsilon - \mu n)/kT} = \frac{1}{\cancel{Z}} e^{-n(\varepsilon - \mu)/kT}$$

Fermi-Dirac Distribution

- For a fermion, → cannot share state spin-½ particles
  – n can either be 0 or 1
  – So grand partition function is

$$\mathcal{Z} = 1 + e^{-(\varepsilon-\mu)/kT}$$

  – Average number of particles in state (its occupancy)

$$\bar{n} = \sum_n nP(n) = \frac{e^{-(\varepsilon-\mu)/kT}}{1+e^{-(\varepsilon-\mu)/kT}}$$

$$\bar{n}_{FD} = \frac{1}{e^{(\varepsilon-\mu)/kT}+1} \quad \text{(fermions)}$$

Bose-Einstein Distribution

- For a boson,
  – n can be any non-negative integer $0, 1, 2, \ldots$
  – So grand partition function is

$$\mathcal{Z} = 1 + e^{-(\varepsilon-\mu)/kT} + e^{-2(\varepsilon-\mu)/kT} + \ldots$$

$$= \frac{1}{1-e^{-(\varepsilon-\mu)/kT}}$$

  – Average number of particles in state (its occupancy)

$$\bar{n} = \sum_n nP(n) \qquad x \equiv (\varepsilon-\mu)/kT$$

$$= \sum_n \frac{ne^{-nx}}{\mathcal{Z}} = -\frac{1}{\mathcal{Z}}\sum_n \frac{\partial}{\partial x} e^{-nx} = -\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial x}$$

$$\bar{n}_{BE} = -\left(1-e^{-x}\right)\frac{\partial}{\partial x}\left(1-e^{-x}\right)^{-1}$$

$$= \frac{1}{e^{(\varepsilon-\mu)/kT}-1} \quad \text{(boson)}$$

$$\bar{n}_{FD} = \frac{1}{e^{(\varepsilon-\mu)/kT}+1} \quad \text{(fermion)}$$

compare forms of distributions...