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Lecture #34 Quantum Statistical Mechanics

Statistical mechanics assumes that in thermal equilibrium every distinct state with the same total energy E is equally probable.

Note classical and quantum statistical mechanics very close. You have so many particles that a statistical or probabilistic discreption is the only thing that makes sense even in classical mech.

Only difference between Q and C is how you count the states.

In QM particles are identical so you dont count configurations with particles interchanged as different states.

I.E. $\phi_A(r_1)\, \phi_B(r_2)$ is same as $\phi_A(r_2)\, \phi_B(r_1)$

Also have Pauli exclusion principle only (at most) one Fermion to a given orbital.

Problem given $N_{tot} = \sum_i N_i$ Fermions and total energy $E_{tot} = \sum_i N_i E_i$

how to determine the N_i to maximize the total # of possible states?

Here i is an energy level which we assume has degeneracy d_i

Example free fermions: Label states with wave vector k $\quad i \to k \quad E_i = \frac{\hbar^2 k^2}{2m}$

Last time $\sum_{n_x n_y n_z} \Rightarrow V \int \frac{d^3k}{(2\pi)^3}$

$= \frac{V}{2\pi^2} \int k^2 \, dk$ after doing angular integrals $= 4\pi$

So $\boxed{d_i = \frac{V}{2\pi^2} k^2 \, dk}$

This is # of states with wave vector between k and $k + dk$.

For a large system $d_i \gg 1$

How many ways to put N_i particles in d_i states (all of energy $E_i = \hbar^2 k^2/2m$)

d_i chose N_i $= \frac{d_i!}{N_i!\,(d_i - N_i)!} = \binom{d_i}{N_i}$

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This is for Fermions: clearly $N_i < d_i$
Each of the d_i states is either full (with one and only one particle in it) or empty. It does not matter which of the N_i particles is in a given state since the particles are identical.

Total # of states of system

$$Q = \prod_{i=1}^{\infty} \binom{d_i}{N_i}$$

To find the most probable configuration we want to chose the N_i to maximize Q subject to

$$\sum_i N_i = N_{tot}$$

and

$$\sum_i N_i E_i = E_{tot}$$

Trick use Lagrange multipliers α, β
Maximize

$$G = \ln Q + \alpha\left(N_{tot} - \sum_i N_i\right) + \beta\left(E_{tot} - \sum_i N_i E_i\right)$$

ie $\frac{\partial G}{\partial \alpha} = 0 = \frac{\partial G}{\partial \beta} = \frac{\partial G}{\partial N_i}$

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$$\ln \binom{d_n}{N_n} = \ln d_n! - \ln(N_n!) - \ln(d_n - N_n)!$$

Stirling's approx to factorials

$$\ln z! \cong z \ln z - z \qquad \text{for} \quad z \gg 1$$

$$\ln \binom{d_n}{N_n} \cong d_n \ln d_n - \cancel{d_n} - N_n \ln N_n + \cancel{N_n}$$
$$- (d_n - N_n) \ln (d_n - N_n) + \cancel{d_n} - N_n$$

$$G \cong \sum_n \Big\{ d_n \ln d_n - N_n \ln N_n - (d_n - N_n) \ln (d_n - N_n)$$
$$- \alpha N_n - \beta E_n N_n \Big\} + \alpha N_{tot} + \beta E_{tot}$$

$$\frac{\partial G}{\partial N_n} = - \ln N_n + \ln (d_n - N_n) - \alpha - \beta E_n$$

Set $\frac{\partial G}{\partial N_n} = 0$ and solve for N_n

$$\ln \left(\frac{d_n - N_n}{N_n} \right) = \alpha + \beta E_n$$

$$\frac{d_n - N_n}{N_n} = e^{\alpha + \beta E_n}$$

$$\Rightarrow \boxed{N_n = d_n \frac{1}{1 + e^{\alpha + \beta E_n}}}$$

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It turns out β can be defined as the inverse temperature

$$\beta = 1/k_B T$$

Boltzman const.

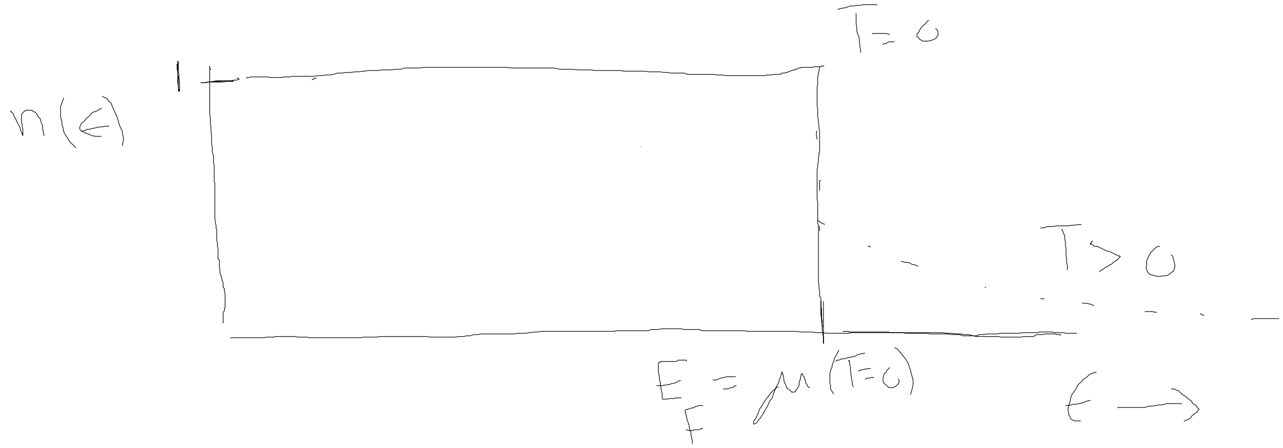
While α is adjusted to get the correct # of particles. By convention people define the 'chemical' pot. μ

$$\mu \equiv -\alpha\, k_B T$$

So

$$\boxed{n(\epsilon) = \frac{N_n}{d_n} = \frac{1}{1 + e^{(\epsilon - \mu)/k_B T}}}$$

Fermi Dirac distribution



For Bosons the counting is different because you can put more then one particle in a given state.

\# of ways to put N_n fermions in d_n states $= \begin{pmatrix} d_n \\ N_n \end{pmatrix}$

\# of ways to put N_n bosons in d_n states $= \begin{pmatrix} N_n + d_n - 1 \\ N_n \end{pmatrix}$

See text. Boson choices are greate then Fermion. This gives

so $$\boxed{n(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_\beta T} - 1}}$$ Bosons

Bose - einstein distribution