Lecture 9

Working on stat mech

$Q(N_1, N_2, \ldots) =$ # of states in configuration with N_n particles in level n, w/ energy E_n degeneracy d_n

Distinguishable: $Q = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}$

Fermions: $Q = \prod \frac{d_n!}{N_n!(d_n-N_n)!}$

Bosons: $Q = \prod \frac{(N_n+d_n-1)!}{N_n!(d_n-1)!}$

Configuration with largest value of Q is most probable... for large N, unlikely to be in config. much different from that.

So find $N_1^*, N_2^*, \ldots$ such that $Q(N^*s)$ is max

But require $\sum N_n = N$
$\sum_n E_n N_n = E$ as well

Use Lagrange multipliers:

To find max of $F(x)$, subject to $f(x) = c$,

maximize $G(x,\lambda) = F(x) + \lambda[f(x) - c]$

with respect to x and λ

For discussion, look up in your calc book.

Also, instead of maximizing Q itself, work with $\ln Q$: log is monotonic, so same thing
Nice because Πs $\to$ Σs

So we define

$$G(\alpha, \beta, N_1, N_2, \ldots) = \ln Q + \alpha[N - \Sigma N_n] + \beta[E - \sum_n N_n E_n]$$

Two constraints, so two Lagrange terms

Now maximize:

Distinguishable:

$$G = \ln N! + \sum_n [N_n \ln d_n - \ln N_n!] + \alpha[N - \Sigma N_n]$$
$$+ \beta[E - \Sigma N_n E_n]$$

Want: $\frac{\partial G}{\partial N_n}$

Use Stirling's approximation $\ln N_n! \approx N_n \ln N_n - N_n$ for large N_n

So $\frac{\partial}{\partial N_n} \ln N_n! = \ln N_n + N_n \frac{1}{N_n} - 1 = \ln N_n$

and $\frac{\partial G}{\partial N_n} = \ln d_n - \ln N_n - \alpha - \beta E_n = 0$

$$\ln \frac{N_n}{d_n} = -\alpha - \beta E_n$$

$$\Rightarrow \boxed{N_n^* = d_n e^{-(\alpha + \beta E_n)}}$$

Still need to set α & β from $\sum_n N_n^* = N$
$\sum_n N_n^* E_n = E$ ... come back

Fermions:

$$G = \sum_n \left[\ln d_n! - \ln N_n! - \ln (d_n - N_n)! \right]$$
$$+ \alpha \left[N - \sum N_n \right] + \beta \left[E - \sum_n N_n E_n \right]$$

Need $d_n \gg 1$ if $N_n \gg 1$. Also assume $d_n - N_n \gg 1$

(If $d_n = N_n$, Stirling still works, $\ln 0! = 0$

If $d_n > N_n$, probably $d_n - N_n \gg 1$ since d_n & N_n are huge)

Then $$\frac{\partial G}{\partial N_n} = -\ln N_n + \ln (d_n - N_n) - \alpha - \beta E_n = 0$$

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

$$\frac{d_n}{N_n} - 1 = e^{(\alpha + \beta E_n)}$$

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

Boson case works the same way, I'll let you do it for yourselves. Get

$$\boxed{N_n^* = \frac{d_n}{e^{(\alpha + \beta E_n)} - 1}}$$

To go further, need α & β. Consider a specific system: non-interacting particles in a box, volume V

Label states by $\vec{k} = \left(\frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z} \right)$

integers n_x, n_y, n_z

with $E_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$, $k = |\vec{k}|$

If we say N_k = # of particles between k and $k+dk$,

Then d_k = # of states between k & $k+dk$

Know from free electron gas: $d_k = \frac{1}{8} \frac{4\pi k^2 dk}{(\pi^3/V)}$

$$= \frac{V}{2\pi^2} k^2 dk$$

Then convert sums to integrals

For distinguishable particles,

$$N = \sum_k d_k \, e^{-(\alpha + \beta E_k)}$$

$$\to \int_0^\infty e^{-(\alpha+\beta E_k)} \frac{V}{2\pi^2} k^2 dk$$

$$= \frac{V}{2\pi^2} e^{-\alpha} \int_0^\infty e^{-\beta \frac{\hbar^2 k^2}{2m}} k^2 dk$$

$$u = \sqrt{\frac{\beta \hbar^2}{2m}} \, k$$

$$= \frac{V}{2\pi^2} e^{-\alpha} \left(\frac{2m}{\beta \hbar^2} \right)^{3/2} \int_0^\infty e^{-u^2} u^2 du$$

(look up, $= \frac{\sqrt{\pi}}{4}$)

Solve for $\boxed{e^{-\alpha} = \frac{N}{V} \left(\frac{2\pi \hbar^2 \beta}{m} \right)^{3/2}}$

Also $E = \frac{V}{2\pi^2} e^{-\alpha} \int_0^\infty e^{-\beta \frac{\hbar^2 k^2}{2m}} \left(\frac{\hbar^2 k^2}{2m}\right) k^2 \, dk$

solve, get

$$E = \frac{3V}{2\beta} e^{-\alpha} \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}$$

substitute for $e^{-\alpha}$, get

$$E = \frac{3N}{2\beta}, \quad \text{or} \quad \boxed{\beta = \frac{3}{2}\frac{N}{E}}$$

But now step back. We already know about non-interacting particles in a box... its an ideal gas.

From thermodynamics, know $\frac{E}{N} = \frac{3}{2} k_B T$, temperature T

Evidently, $\beta = \frac{1}{k_B T}$

We got thermodynamics result from counting quantum states... Stat Mech ties together microscopic & macroscopic models.

Also set $\alpha = -\frac{\mu}{k_B T}$, μ = chemical potential (less familiar thermodynamics)

Unfortunately, can't do integrals for bosons & fermions

Have $N = \int \frac{1}{\exp\left[\left(\frac{\hbar^2 k^2}{2m} - \mu\right)/k_B T\right] \pm 1} \frac{V}{2\pi^2} k^2 \, dk$

solve numerically.

But in limit $E_k - \mu \gg kT$, exp is large compared to 1

looks like distinguishable particles again

In that limit $\mu = -\alpha kT = kT \ln\left[\frac{N}{V}\left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2}\right]$

Call $\sqrt{\frac{mkT}{2\pi\hbar^2}} \equiv \Lambda$

"Thermal de Broglie wavelength"

Typical wavelength for particles with $E \approx kT$

So $\mu = kT \ln(\rho\Lambda^3)$ $\quad \rho = \frac{N}{V}$ density

So $\rho\Lambda^3 = \#$ of particles w/in one cubic wavelength

If $\rho\Lambda^3 \ll 1$, $\ln \rho\Lambda^3 < 0$, $|\ln \rho\Lambda^3| \sim 1$ since its a log

So $\mu \sim -kT$

So ignore exchange effects if $E_r - \mu > kT$

$\Rightarrow E_r + kT > kT$

$E_r > 0$, true for all states.

General rule: can ignore exchange effects if $\rho\Lambda^3 \ll 1$, otherwise, need integrals.