Lecture 9

Working on stat mech.

\[ Q(N_1, N_2, \ldots) = \text{# of states in configuration} \]

with \( N_a \) particles in level \( n \), w/ energy \( E_n \)

Distinguishable:

\[ Q = N! \frac{d_n^{N_n}}{N_a!} \]

Fermions:

\[ Q = \prod N_a! (d_n - N_a)_1 \]

Bosons:

\[ Q = \prod \frac{(N_0 + \cdots + d_n)_1}{N_a! (d_n - 1)_1} \]

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 \( Q(N^*) \) is max.

But require \( \sum N_a = N \)

\[ \sum E_a N_a = E \quad \text{as well} \]

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 \( \lambda \).

For discussion, look up in your calc book.
Also, instead of maximizing $Q$ itself, work with $\log Q$; $\log$ is monotonic, so some thing nice because $T \rightarrow \Sigma$

So we define

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

Two constraints, so two Lagrange terms

Now maximize:

Distinguishable:

$$G = \ln N_1 + \sum \left[ \ln N_n \ln \frac{d_n}{N_n} - \ln N_n! \right] + \alpha \left[ N - \sum N_n \right] + \beta \left[ E - \sum N_n E_n \right]$$

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

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

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

$$\ln d_n = -\alpha - \beta E_n$$

$$\Rightarrow \left[ N_n^* = d_n e^{-(\alpha + \beta E_n)} \right]$$

Still need to get $\alpha \& \beta$ from $\sum N_n^* = N$

$$\sum N_n^* E_n = E \ldots \text{come back}$$
Fermions:

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

Need \( d_n \gg 1 \) if \( N_n \gg 1 \). Also assume \( d_n-N_n \gg 1 \)

(If \( \phi = N_n \), Stirling still works, \( \ln 0! = 0 \)
If \( \phi > N_n \), possibly \( d_n-N_n \gg 1 \) since \( d_n \) is huge)

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

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

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

\[ N_n = N_0 e^{d_n \left[ \frac{1}{e^{(\alpha + \beta E_n)} - 1} \right]} \]

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

\[ N^\star_r = \frac{d_n}{e^{(\alpha + \beta E_n)} - 1} \]

To go further, need \( \alpha \neq \beta \). Consider a specific system: non-interacting particles in a box, volume \( V \).
Level states by $k = \left( \frac{\pi \alpha}{a}, \frac{\pi \beta}{b}, \frac{\pi \gamma}{c} \right)$

with $E_k = \frac{\hbar^2 k^2}{2m}$, $k = |k|$.

If we say $N_k = \# \text{ of particles between } k \text{ and } k + dk$,

Then $d_k = \# \text{ of states between } k \text{ and } k + dk$.

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

Then convert sums to integrals.

For distinguishable particles,

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

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

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

$$= \frac{V}{2\pi^2} e^{-\alpha} \left( \frac{2\alpha}{\beta^{3/2}} \right)^{3/2} \int_0^\infty \frac{e^{\frac{-k^2}{2m}}}{m^{1/2}} dk$$

Look up $\int_0^\infty \frac{e^{-k^2}}{m^{1/2}} dk = \frac{\sqrt{\pi}}{2}$. 

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

$$e = \frac{N}{V} \left( \frac{2\pi^{3/2} \hbar}{m} \right)^{3/2}$$
Also \( E = \frac{V}{2 \pi^2} \int_0^\infty e^{-\beta \frac{V}{k_b T} \left( \frac{k^3}{2m} \right)} k^2 \, dk \)

Solve, get

\[ E = \frac{3V}{2 \beta} e^{-\alpha} \left( \frac{m}{2\pi k_b T^3} \right)^{3/2} \]

Substitute for \( e^{-\alpha} \), get

\[ E = \frac{3N}{2 \beta}, \quad \text{or} \quad \beta = \frac{3}{2} \frac{N}{E} \]

But now step back. We already know about non-interacting particles in a box... it's 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 get thermodynamics result from counting quantum states... Stat mech ties together microscopic and macroscopic models.

Also get \( \alpha = -\frac{\frac{3}{2} k_b T}{k_b T} \), \( \mu \) = chemical potential.

(less familiar thermodynamics)

Unfortunately, can't do integrals for bosons & fermions.

Have \( N = \int \exp \left[ \frac{\frac{3}{2} k_b T}{k_b T} k^3 \right] / k_b T \) \( \approx 1 \)

\[ \frac{V}{2 \pi^2 k^2 \, dk} \]

solve numerically.
But in limit $E_r - \mu > \kappa T$, exp is large compared to 1

looks like distinguishable particles again

In that limit $\mu = -\omega \kappa T = \kappa T \ln \left[ \frac{N}{V} \left( \frac{2\pi m}{\hbar^2} \right)^{3/2} \right]$.

Call $\sqrt[3]{m \kappa T} = \Lambda$

"Thermal de Broglie wavelength"

Typical wavelength for particles with $E_r > \kappa T$

So $\mu = \kappa T \ln (\rho \Lambda^3)$, $\rho > \frac{N}{V}$ density.

So $\rho \Lambda^3 \approx 1$ of particles with one cubic wavelength.

If $\rho \Lambda^3 \ll 1$, $\ln \rho \Lambda^3 < 0$, $100 \rho \Lambda^3 \approx 1$

since it's a log

So $\mu \approx -\kappa T$

So ignore exchange effects if $E_r - \mu > \kappa T$

$\Rightarrow E_r + \kappa T > \kappa T$

$E_r > 0$, fine for all states.

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