Lecture 25

Intro to Quantum Stat Mech, pt 2

Ideal Gas Distinguishable Particles (Neglect spin)

$$Q(N,V,T) = q^N = \left(\sum_n e^{-\beta\epsilon_n}\right)^N$$ "Boltzmann particles"

w/ Occupation #s,

$$Q(N,V,T) = \sum_f g(\{f\}) e^{-\beta \sum_n \epsilon_n f_n}$$

$$g(\{f\}) = \frac{N!}{\prod_n f_n!}$$ ← new state, distinguishable same occupation #s

eg, 2 states, $f = f_1 + f_2$ $\quad g(f_1, f_2) = \frac{N!}{f_1! f_2!} = \frac{N!}{f_1!(N-f_1)!}$

$$Q(N,V,T) = \sum_{\{f\}} \frac{N!}{\prod_n f_n!} \prod_n e^{-\beta f_n \epsilon_n} = \left(\sum_n e^{-\beta\epsilon_n}\right)^N \quad !!$$

multinomial expansion

So, 1 particle $\sum_n e^{-\beta\epsilon_n} = \sum_n e^{-2\pi^2\beta\hbar^2|n|^2/mL^2}$

when $L \to \infty$, spacing becomes continuous, almost

$$\Rightarrow \int dn\, e^{-2\pi^2\beta\hbar^2|n|^2/mL^2} = 4\pi\int_0^\infty dn\, n^2 e^{-2\pi^2\beta\hbar^2 n^2/mL^2}$$

$$\overset{\text{result}}{=} V\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} = V/\Lambda^3$$ ← same as classical ideal gas

All QM must be in spin interactions

Identical fermions / bosons

Exchanging particles is same physical state, so

$g(\{f_{\vec{n}m}\}) = 1$, but

$f_{\vec{n}m} = 0, 1$ for fermions

$$Q(N,V,T) = \sum_{\{f_{\vec{n}m}\}} e^{-\beta \sum_m \sum_n f_{nm} \varepsilon_n} = \sum_{\{f_{\vec{n}m}\}}{}' \prod_n \prod_m e^{-\beta f_{nm} \varepsilon_n}$$

w/ restriction $\sum_m \sum_n f_{nm} = N$

which is hard to keep track of

Instead better to use $\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} \xi^N Q(N,V,T)$

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_f{}' \prod_m \prod_n e^{-\beta f_{nm} \varepsilon_n}$$, Same results in thermo limit

still subject to occupation #, but outer sum relieves restriction as all things will be relaxed

ie $$\mathcal{Z}(\mu, V, T) = \sum_{f_{nm}} \prod_m \prod_n e^{+\beta(\mu - \varepsilon_n) f_{nm}}$$

has all values of N taken into account

B/c $$\sum_{f_1} \sum_{f_2} \sum_{f_3} \cdots e^{+\beta(\mu-\varepsilon_1) f_1} e^{+\beta(\mu - \varepsilon_2) f_2} \cdots$$

$$= \left(\sum_{f_1} e^{+\beta(\mu-\varepsilon_1) f_1} \sum_{f_2} e^{+\beta(\mu-\varepsilon_2) f_2} \cdots \right)$$

$$\Rightarrow \mathcal{Z} = \prod_m \prod_n \sum_{\{f_{nm}\}} e^{\beta(\mu-\varepsilon_n) f_{nm}}$$

for fermions $f_{nm} = 0$ or 1

$$\star\ \mathcal{Z} = \prod_m \prod_n \left(1 + e^{\beta(\mu-\varepsilon_n)}\right) \qquad \text{(fermions)}$$

For bosons, $f_{nm} = 0 \to \infty$, like last time

$$\mathcal{Z} = \prod_m \prod_n \frac{1}{1 - e^{\beta(\mu-\varepsilon_n)}} \qquad \text{(bosons)}$$

Product over $m = 0 \ldots 2s+1 = g$

$$\mathcal{Z} = \prod_n \left(1 + a\, e^{\beta(\mu-\varepsilon_n)}\right)^{g \cdot a}$$

$a = 1$ for fermions, -1 for bosons

$$PV/k_BT = \ln \mathcal{Z} = g a \sum_n \ln\left(1 + a\, e^{\beta(\mu-\varepsilon_n)}\right)$$

$$= g a \sum_n \ln\left(1 + a\, \xi\, e^{-\beta\varepsilon_n}\right)$$

$\xi = e^{\beta\mu}$, fugacity

$$\langle N \rangle = \xi \frac{\partial}{\partial \xi} \ln \mathcal{Z} = \xi\, g\, a \sum_n \frac{a\, e^{-\beta\varepsilon_n}}{1 + a\, \xi\, e^{-\beta\varepsilon_n}} = g \sum_n \frac{e^{\beta(\mu-\varepsilon_n)}}{1 + a\, e^{\beta(\mu-\varepsilon_n)}}$$

Now, comparing to a fixed N situation

$$N = \sum_m \sum_n f_{nm}$$

$$\Rightarrow \langle N \rangle = \sum_m \sum_n \langle f_{nm} \rangle$$

$\Rightarrow$ we can associate $\langle f_{nm} \rangle = \dfrac{e^{\beta(\mu-\varepsilon)}}{1+e^{\beta(\mu-\varepsilon_n)}}$ for fermions

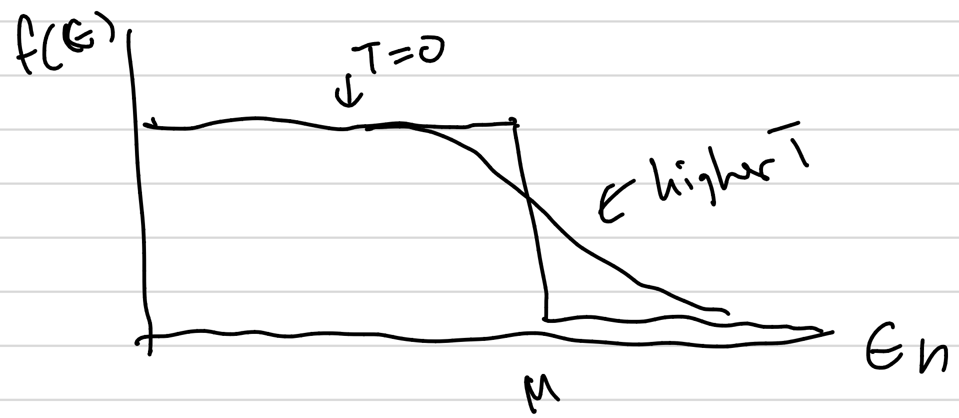
$$\Rightarrow \frac{1}{1+e^{-\beta(\mu-\varepsilon_n)}} = \frac{1}{1+e^{\beta(\varepsilon_n-\mu)}}$$ (fermi-dirac distribution)

consider low temp, high β,

for $\varepsilon_n - \mu > 0$, $\langle f \rangle \to 0$

$\varepsilon_n - \mu < 0$ $\langle f \rangle \to 1$

$$\langle f_{nm} \rangle^{T=0} = \begin{cases} 0 & \varepsilon_n > \mu \\ 1 & \varepsilon_n < \mu \end{cases} = \Theta(\mu - \varepsilon_n)$$



The energy where states above are unoccupied is the "fermi energy"

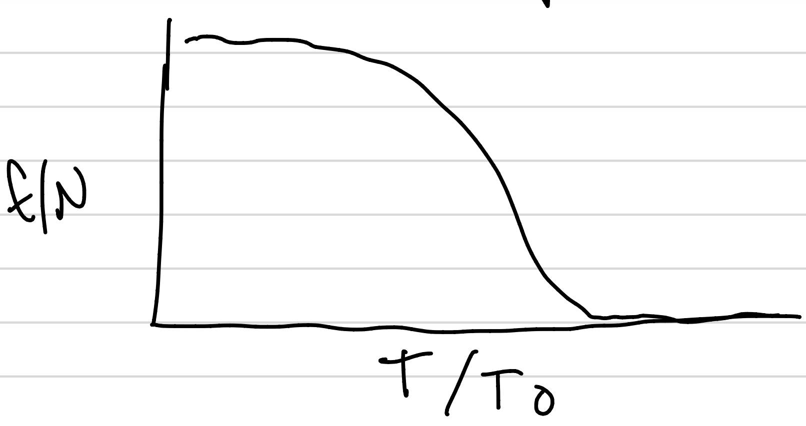
Ideal boson gas

Don't have time to go into details, but boson gas can undergo bose einstein condensation where at low T all particles go into the same state

$$\langle f_{nm} \rangle = \frac{1}{e^{\beta(E_n - \mu)} - 1}$$

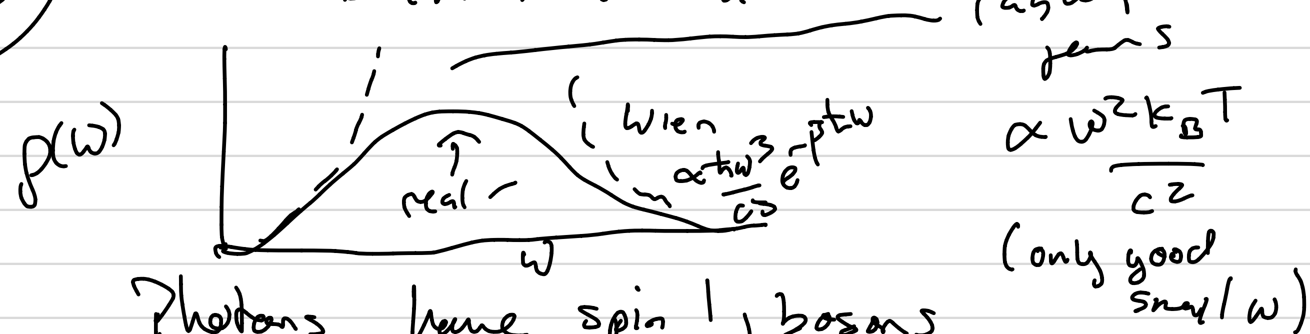
$$\langle f_{0m} \rangle = \frac{e^{\beta\mu}}{1 - e^{\beta\mu}}$$

at some temp, can show



Black-body radiation

← heat insulating object, will absorb & emit radiation



Photons have spin 1, bosons

also emitting & absorbing photons, so just like our grand canonical treatment

Only standing waves commensurate w/ the size of the cavity are allowed, kind of like particle in a box

Hence only $\vec{k} = \frac{\pi}{L}\vec{n}$ $\quad n_x, n_y, n_z = 1, 2, \ldots$

$\varepsilon = \hbar c |\vec{k}| = \hbar c k$

momentum $= \hbar|\vec{k}| = \hbar k$

$k^2 = \pi^2/L^2 (n_x^2 + n_y^2 + n_z^2)$

Number of waves w/ momentum $< |k|$ is volume of sphere upper quadrant (all pos n's)

$\Phi(k) = \frac{4}{3}\pi \text{"}R\text{"}^3/8 = \frac{1}{6}\pi\left(\frac{Lk^3}{\pi}\right) = Vk^3/6\pi^2$

btwn k & dk

$w(k)\,dk \quad = \frac{d\Phi}{dk}dk = \frac{Vk^2}{2\pi^2}dk$

$\times 2$ for 2 polarizations

One can show (no time here)
that $\mu = 0$ for an ideal Gas of photons

In this case we know

$$\langle f_\varepsilon \rangle = \frac{1}{e^{\beta\varepsilon} - 1}$$

$$\Rightarrow \langle \mathcal{E} \rangle = \sum_{\varepsilon} \varepsilon f_\varepsilon = \sum_{k} \frac{\hbar c k}{e^{\beta\hbar c k} - 1}$$

if k's close together, can convert to integral w/ DOS

$$\langle \mathcal{E} \rangle \to \int_0^\infty dk\, w(k) \frac{\hbar c k}{e^{\beta\hbar c k} - 1}$$

$$= \frac{V\hbar c}{\pi^2} \int_0^\infty dk \frac{k^3}{e^{\beta\hbar c k} - 1} \qquad \omega = ck$$

$$= \frac{V\hbar}{c^3\pi^2} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta\omega\hbar} - 1}$$

$$E/V \equiv \int_0^\infty \rho(\omega, T)\, d\omega$$

$$\Rightarrow \rho(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$ ← planck formula

@ low ω, $e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega$

$$\Rightarrow \rho(\hbar\omega \ll k_BT, T) \approx \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\beta\hbar\omega}$$

$$\propto \frac{\omega^2 k_B T}{c^3}$$

& @ high freq $\rho(\omega, T) \propto \frac{\hbar\omega^3}{c^3} e^{-\beta\hbar\omega}$

Summary: in stat mech, we consider averages over many particles & it gives us powerful tools & can derive sim methods to solve problems where exact solutions seem impossible!

- we also connect microsopic quantities to bulk observable measurements
- but more importantly can predict flucs in small # experiments & heterogeneous environments
- and maybe even out of eq
- Hopefully you can apply these ideas in your own work!