P423 – Lecture 17 : Chemical potential for ideal gases, blackbody radiation, time-dependent perturbation theory. ①

Last class: $$\langle n \rangle = \begin{cases} e^{-\frac{\varepsilon-\mu}{k_BT}} & \text{for distinguishable particles (Maxwell-Boltzmann distribution)} \\ \dfrac{1}{e^{\frac{\varepsilon-\mu}{k_BT}}-1} & \text{for Bosons (Bose-Einstein dist.)} \\ \dfrac{1}{e^{\frac{\varepsilon-\mu}{k_BT}}+1} & \text{for Fermions (Fermi-Dirac Dist)} \end{cases}$$

where μ is chemical potential Calculated from

$$N = \sum_\varepsilon \underbrace{n_\varepsilon}_{\text{fnc of } T \text{ and } \mu} d_\varepsilon$$

$$\Rightarrow N = f(T,\mu)$$

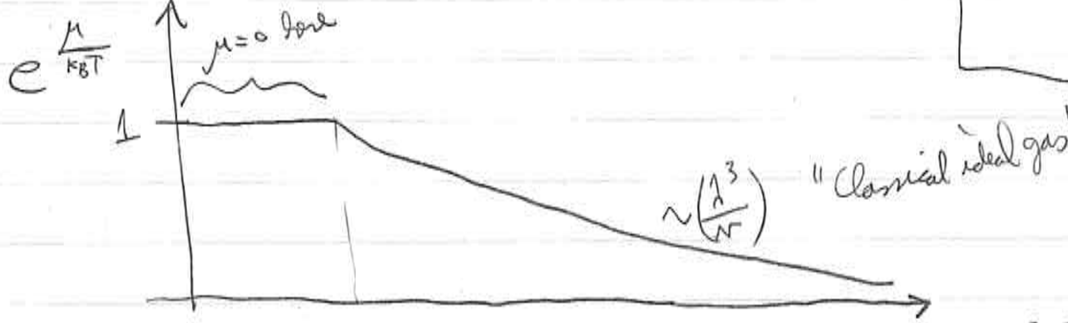
$$\Rightarrow \mu = \mu(T,N)$$

$$N = \int dk \underbrace{\left(\frac{1}{8}\frac{4\pi k^2}{\frac{\pi^3}{V}}\times(2s+1)\right)}_{d_k} n\left(\varepsilon = \frac{\hbar^2k^2}{2m}\right)$$

For ideal Fermi gas: $$\mu(T,N) = E_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_BT}{E_F}\right)^2 + \sigma(T^4)\right]$$

So to a very good approximation $\mu \approx E_F$ when $T \ll T_F$.

For a Bose gas, $\mu(T,N)$ shows critical Behavior:



$$\left(\frac{1}{2.612}\right)$$

↑

Transition to a Bose-Einstein Condensate

$$\frac{v}{\lambda^3} = \left[\underbrace{\left(\frac{V}{N}\right)}_{v}\underbrace{\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}}_{\frac{1}{\lambda^3}}\right]$$

When $$\frac{v}{\lambda^3} < \frac{1}{2.612} \Rightarrow \frac{V}{N}\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2} < \frac{1}{2.612}$$

$$\Rightarrow T < T_c = \left(\frac{N}{V}\right)^{\frac{2}{3}} \frac{1}{(2.612)^{2/3}} \frac{h^2}{2\pi m k_B}$$ we get a Bose-Einstein Condensate:

All the particles collapse into the lowest energy state, i.e. $N_{i=\text{ground}} = N$ and all other N_i are zero.

Blackbody radiation

- Photons are Bosons: They have spin 1 (but only $m_s = \pm 1$ is observable).
- Their energy is $E_k = \hbar\omega = \hbar c k$.
- Also, their number is not conserved $\Rightarrow \mu = 0$ (μ is the Lagrange multiplier for keeping N constant).

Based on this, let's calculate the photon energy density in a gas of photons (Blackbody):

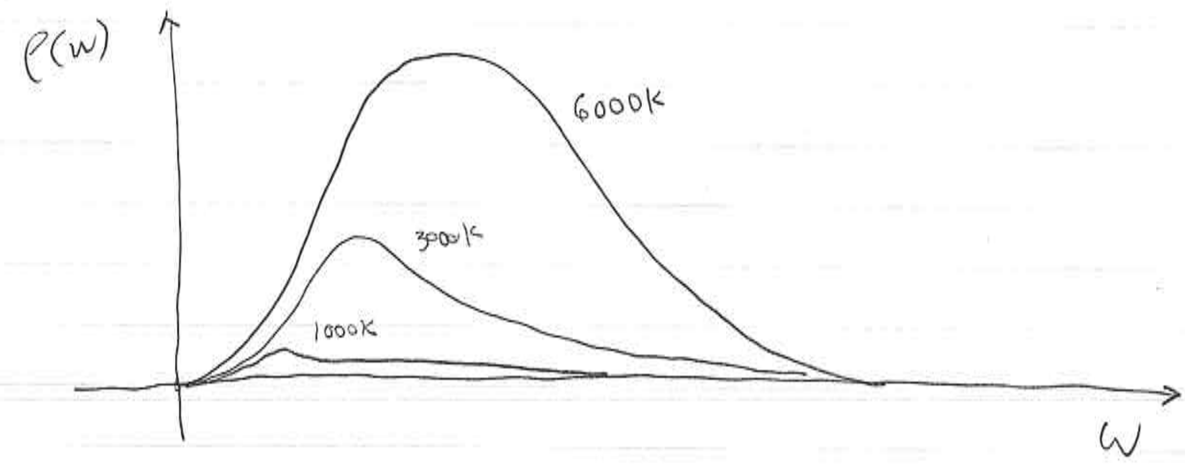
$$d_k = \underbrace{2}_{\text{spin}} \cdot \frac{1}{8} \frac{4\pi k^2 dk}{\frac{\pi^3}{V}} = \frac{V}{\pi^2} k^2 dk \underset{\uparrow\, \omega = ck}{=} \frac{V}{\pi^2} \frac{1}{c^3} \omega^2 d\omega$$

The energy density within $d\omega$ is: $\rho(\omega)d\omega = \frac{E_k d_k}{V} n(\epsilon_k) = \frac{\hbar\omega}{\cancel{V}} \frac{\cancel{V}}{\pi^3 c^3} \omega^2 d\omega \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$

$$\Rightarrow \boxed{\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\frac{\hbar\omega}{k_B T}} - 1}}$$

"Universal",
Depends only on Temprature T
(apart from fundamental constants $\hbar$ and c)

Energy per unit volume, per unit freq. of the Electromagnetic field at thermal Equilibrium with temperature T.



Now you know how to read the specifications of an LED light bulb (It's given as a temperature that refers to the Blackbody spectra).

Time dependent perturbation theory

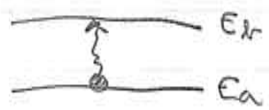
Quantum statics: $V(\vec{r})$ does <u>not</u> depend on time

$$\mathcal{H}\psi = i\hbar\frac{\partial\psi}{\partial t} \Rightarrow \psi(\vec{r},t) = e^{-\frac{it}{\hbar}\hat{\mathcal{H}}}\,\psi(\vec{r})$$

When ψ is an energy eigenstate $\mathcal{H}\psi = E\psi$: $\psi(\vec{r},t) = e^{-\frac{it}{\hbar}E}\psi(\vec{r})$

What happens when V depends on time?

If time dependence of V is "weak" we can think of it as leading to transitions between levels, or "quantum jumps":



Small collisions between particles in gas  $(11,11,11) \xrightarrow{\Gamma \text{ transition rate}} (5,7,17)$.

Time dependent pert. theory allows you to compute transition rates Γ for quantum jumps.
"Fermi's golden rule" formula.

<u>Two level system subject to a time dependent perturbation</u>

$$\mathcal{H} = \underset{\text{indep of time}}{\mathcal{H}_0} + \underset{\text{"small"}}{\mathcal{H}'(t)}$$

$$\begin{cases} \mathcal{H}_0\psi_a = \epsilon_a\psi_a \\ \mathcal{H}_0\psi_b = \epsilon_b\psi_b \end{cases}$$

$$\langle\psi_a|\psi_b\rangle = \delta_{a,b}$$

$\psi(t=0) = c_a\psi_a + c_b\psi_b$, under $\mathcal{H}_0$ evolution:

$$\psi(t) = c_a e^{-\frac{i\epsilon_a t}{\hbar}}\psi_a + c_b e^{-\frac{i\epsilon_b t}{\hbar}}\psi_b, \text{ with } |c_a|^2 + |c_b|^2 = 1.$$

④

Now suppose we turn on $H'(t)$. $\{\psi_a, \psi_b\}$ are a complete set, so the wave fnc can be written as:

$$\Psi(t) = c_a(t)\, e^{-i\frac{E_a t}{\hbar}}\psi_a + c_b(t)\, e^{-i\frac{E_b t}{\hbar}}\psi_b$$

Plug this into Schrödinger's eqn: $H\Psi = i\hbar\frac{\partial\Psi}{\partial t}$, where $H = H_0 + H'(t)$:

$$\cancel{c_a e^{-i\frac{E_a t}{\hbar}} \underbrace{H_0\psi_a}_{=E_a\psi_a}} + \cancel{c_b e^{-i\frac{E_b t}{\hbar}} H_0\psi_b} + c_a e^{-i\frac{E_a t}{\hbar}} H'\psi_a + c_b e^{-i\frac{E_b t}{\hbar}} H'\psi_b =$$

$$= i\hbar\Big[\cancel{-\frac{iE_a}{\hbar} c_a e^{-i\frac{E_a t}{\hbar}}\psi_a} \cancel{- i\frac{E_b}{\hbar} c_b e^{-i\frac{E_b t}{\hbar}}\psi_b} + \dot{c}_a e^{-i\frac{E_a t}{\hbar}}\psi_a + \dot{c}_b e^{-i\frac{E_b t}{\hbar}}\psi_b\Big]$$

Take $\langle\psi_a|$:

$$c_a e^{-i\frac{E_a t}{\hbar}} \underbrace{\langle\psi_a|H'|\psi_a\rangle}_{\equiv H'_{aa}} + c_b e^{-i\frac{E_b t}{\hbar}} \underbrace{\langle\psi_a|H'|\psi_b\rangle}_{H'_{ab}} = i\hbar e^{-i\frac{E_a t}{\hbar}}\dot{c}_a \underbrace{\langle\psi_a|\psi_a\rangle}_{=1} + (\ldots)\underbrace{\langle\psi_a|\psi_b\rangle}_{0}$$

$\times\left(-\frac{i}{\hbar}\right)e^{i\frac{E_a t}{\hbar}}$:

$$\boxed{\dot{c}_a = -\frac{i}{\hbar}\left[c_a H'_{aa} + c_b e^{-i(E_b - E_a)\frac{t}{\hbar}} H'_{ab}\right]}$$

Similarly, $\langle\psi_b|$ on eqn:

$$c_a e^{-i\frac{E_a t}{\hbar}} H'_{ba} + c_b e^{-i\frac{E_b t}{\hbar}} H'_{bb} = i\hbar\dot{c}_b e^{-i\frac{E_b t}{\hbar}}$$

$$\boxed{\dot{c}_b = -\frac{i}{\hbar}\left[c_b H'_{bb} + c_a e^{+i(E_b - E_a)\frac{t}{\hbar}} H'_{ba}\right]}$$

For simplicity assume $H'_{aa} = H'_{bb} = 0$ (diagonals vanish – actually when H' is "weak", they do not make much of a difference).

and $\boxed{\omega_0 \equiv \frac{E_b - E_a}{\hbar}}$ $(E_b \geq E_a)$
$\omega_0 \geq 0$

$$\Rightarrow \boxed{\begin{aligned} \dot{c}_a &= -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \\ \dot{c}_b &= -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \end{aligned}}$$

These are exact.

Time dependent perturbation theory

Suppose particle starts in the lower state:

$$c_a(\overset{t=0}{0}) = 1 \quad , \quad c_b(0) = 0$$

Zeroth order: $(H' = 0)$:

$$c_a^{(0)} = 1 \qquad c_b^{(0)} = 0$$

First order: plug zeroth order into diff eqns:

$$\dot{c}_a^{(1)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} \underbrace{c_b^{(0)}}_{=0} = 0 \Longrightarrow c_a^{(1)}(t) = \text{Const} \quad \boxed{= 1}$$

$$\dot{c}_b^{(1)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} \underbrace{c_a^{(0)}}_{=1} \Longrightarrow \boxed{c_b^{(1)}(t) = -\frac{i}{\hbar} \int_0^t dt' \, H'_{ba}(t') e^{i\omega_0 t'}} \text{, first order in } H'.$$

Since $c_a^{(1)}(t) = \sqrt{1 - [c_b^{(1)}(t)]^2} = \underbrace{1}_{c_a^{(0)}} + \mathcal{O}(H'^2) = 1$

2nd order:

$$\frac{dc_a^{(2)}}{dt} = -\frac{i}{\hbar} H'_{ab}\, e^{-i\omega_0 t} \underbrace{\left(-\frac{i}{\hbar}\right)\int_0^t dt''\, H'_{ba}(t'')\, e^{i\omega_0 t''}}_{c_b^{(1)}}$$

$$\Rightarrow c_a^{(2)}(t) = 1 + \left(-\frac{i}{\hbar}\right)\int_0^t dt'\, H'_{ab}(t')\, e^{-i\omega_0 t'} \left(-\frac{i}{\hbar}\right)\int_0^{t'} dt''\, H'_{ba}(t'')\, e^{i\omega_0 t''}$$

$$\frac{dc_b^{(2)}}{dt} = -\frac{i}{\hbar} H'_{ba}(t')\, e^{i\omega_0 t'} \underbrace{c_a^{(1)}}_{=1} \Rightarrow c_b^{(2)}(t) = c_b^{(1)}(t).$$

General result:

$$c_a^{(2n)}(t) = c_a(t=0)\left[1 + \sum_{j=1}^{n} \left(-\frac{i}{\hbar}\right)^{2j}\left(\int_0^t dt_1\, H'_{ab}(t_1)\, e^{-i\omega_0 t_1}\int_0^{t_1} dt_2\, H'_{ba}(t_2)\, e^{i\omega_0 t_2}\cdots \int_0^{t_{2j-1}} dt_{2j}\, H'_{ba}(t_{2j})\, e^{i\omega_0 t_{2j}}\right)\right]$$

$$+ c_b(t=0)\sum_{j=1}^{n} \left(-\frac{i}{\hbar}\right)^{2j-1}\left(\int_0^t dt_1\, H'_{ab}(t_1)\, e^{-i\omega_0 t_1}\int_0 dt_2\, H'_{ba}(t_2)\, e^{+i\omega_0 t_2}\cdots \int_0^{t_{2j-2}} dt_{2j-1}\, H'_{ab}(t_{2j-1})\, e^{-i\omega_0 t_{2j-1}}\right)$$

$$c_b^{(2n)}(t) = c_a(t=0)\sum_{j=1}^{n} \left(-\frac{i}{\hbar}\right)^{2j-1}\left(\int_0^t dt_1\, H'_{ba}(t_1)\, e^{i\omega_0 t_1}\int_0^{t_1} dt_2\, H'_{ab}(t_2)\, e^{-i\omega_0 t_2}\cdots \int_0^{t_{2j-2}} dt_{2j-1}\, H'_{ba}(t_{2j-1}) \times e^{i\omega_0 t_{2j-1}}\right)$$

$$+ c_b(t=0)\left[1 + \sum_{j=1}^{n} \left(-\frac{i}{\hbar}\right)^{2j}\left(\int_0^t dt_1\, H'_{ba}(t_1)\, e^{i\omega_0 t_1}\int_0^{t_1} dt_2\, H'_{ab}(t_2)\, e^{-i\omega_0 t_2}\cdots \int_0^{t_{2j-1}} dt_{2j}\, H'_{ab}(t_{2j}) \times e^{-i\omega_0 t_{2j}}\right)\right]$$

Sinusoidal perturbation

Suppose $H'(\vec{r},t) = V(\vec{r})\cos(\omega t)$

$$\Rightarrow H'_{ab} = V_{ab}\cos(\omega t)\ ,\ \text{where } V_{ab} = \langle \psi_a | V | \psi_b \rangle \quad \left(\text{and } V_{aa} = V_{bb} = 0 \text{ for simplicity.}\right)$$

To 1^{st} order:

$$C_b(t) \approx -\frac{i}{\hbar} V_{ba} \int_0^t dt'\, e^{i\omega_0 t'} \cos(\omega t') = -\frac{i}{\hbar}\frac{V_{ba}}{2}\int_0^t dt' \left[e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'}\right]$$

$$= -\frac{i}{2\hbar} V_{ba}\left[\frac{e^{i(\omega_0+\omega)t}-1}{i(\omega_0+\omega)} + \frac{e^{i(\omega_0-\omega)t}-1}{i(\omega_0-\omega)}\right]$$

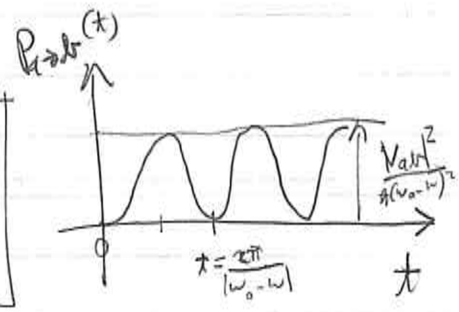
Assume: $\omega_0+\omega \gg |\omega_0-\omega|$ i.e. ω is close to ω_0:

$$C_b(t) \approx -\frac{V_{ba}}{2\hbar}\frac{e^{i\frac{(\omega_0-\omega)t}{2}}}{(\omega_0-\omega)}\left[+e^{i\frac{(\omega_0-\omega)t}{2}} - e^{-i\frac{(\omega_0-\omega)t}{2}}\right]$$

$$= -i\frac{V_{ba}}{\hbar}\frac{\sin\left[(\omega_0-\omega)\frac{t}{2}\right]}{(\omega_0-\omega)} e^{i\frac{(\omega_0-\omega)t}{2}}$$

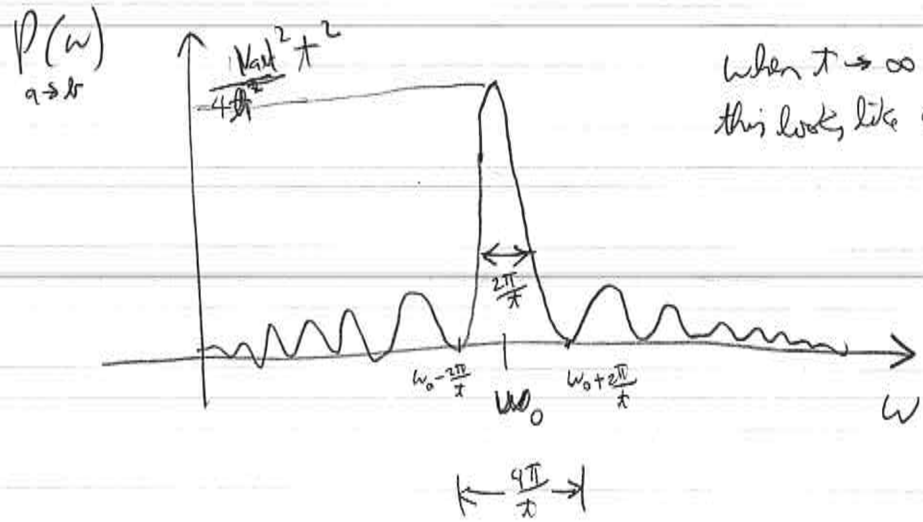
Transition probability:

$$\boxed{P_{a\to b}(t) = |C_b(t)|^2 = \frac{|V_{ab}|^2}{\hbar^2}\frac{\sin^2\left[(\omega_0-\omega)t/2\right]}{(\omega_0-\omega)^2}}$$



Interpretation of oscillatory $P_{a\to b}$: Atom "borrows" an energy equal to $\Delta E = \hbar|\omega_0-\omega|$ during a time $\Delta t \approx \frac{2\pi}{|\omega_0-\omega|}$ so that $\Delta E\,\Delta t = 2\pi\hbar$ (This is greater than $\hbar$, so it respects the energy-time uncertainty relation $\Delta E\,\Delta t \gtrsim \hbar$)

As a fnc of ω:



when $t \to \infty$, this looks like a delta fnc!

we must have $P(\omega) < 1$ or $\frac{|V_{ab}|^2 t^2}{4\hbar^2} < 1$ for pert to remain valid

But note that when $t \to \infty$ transition is only allowed if $\omega \to \omega_0$. This is just a statement of energy conservation: The EM field supplies $\hbar\omega$ of energy (the photon) so when $\omega < \omega_0$ that energy is not enough to induce a "Real transition" (one that lasts for $\Delta t >> \frac{\hbar}{\Delta E}$). Only virtual transitions are induced (the ones that last $\Delta t \sim \frac{\hbar}{\Delta E}$). On the other hand, when $\omega = \omega_0$ a real transition does happen.

Similar argument for $\omega > \omega_0$ because energy conservation can not be satisfied with just one photon and one atom (no photon with energy $\hbar(\omega - \omega_0)$ in the problem).