F. Einstein (1917): His A and B coefficients

- Einstein tried to obtain Planck's thermal (black-body) radiation formula by considering
    - Interaction between light (EM waves) in cavity and atoms in wall of cavity
    - thermal equilibrium (statistical physics)
- His work thus came as a result of efforts by
    - Boltzmann (~1900)
    - Planck (~1900)
    - Einstein (1905) (photon)
    - Bohr (~1913) (atom)

(but prior to quantum theory)

Planck (1900) Formula

$$U(f,T)\,df = \frac{8\pi f^2}{c^3}\cdot hf \cdot \frac{1}{e^{\frac{hf}{kT}}-1}\,df$$

= energy per unit volume inside cavity due to EM waves in freq. range f to $f+df$ at equilibrium at temperature T

For our purpose, write as

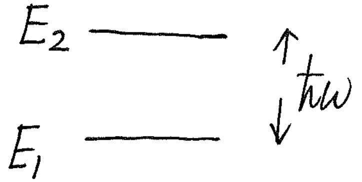
$$U(\omega,T)\,d\omega = \frac{\omega^2}{\pi^2 c^3}\cdot \hbar\omega\,\frac{1}{e^{\frac{\hbar\omega}{kT}}-1}\,d\omega \qquad (27)^{+}$$

- Einstein wanted to find a way to derive Planck's formula, i.e. an expression for $U(\omega,T)$

[+] $U(\omega,T)$ is the $U(\omega)$ in $\lambda_{1\to 2}$ and $\lambda_{2\to 1}$ for matter & EM waves in thermal equilibrium

- <u>Bohr</u> (1913)
  - Atom has discrete energies ("stationary states")
  - Spectral lines come from transitions between stationary states
- <u>Einstein (1917)</u>
  - Cavity's wall ⇒ <u>Many</u> <u>Atoms</u> (they absorb/emit; they vibrate)
  - Capturing Bohr's key idea, assumed <u>two-state</u> <u>systems</u> (many of them)

$$\omega = \frac{E_2 - E_1}{\hbar}$$



  - there could be various values of ω
  - this ω will be the "ω" in $U(\omega, T)$
  - Atoms absorb and emit radiation (exchange energies) from and to the radiation in cavity ⇒ <u>equilibrium</u> can be achieved

In terms of Statistical Physics, we have a system containing atoms and radiation, in thermal equilibrium at a temperature T

If N_1 = # atoms in state 1, N_2 = # atoms in state 2

there are transitions $1 \to 2$, $2 \to 1$

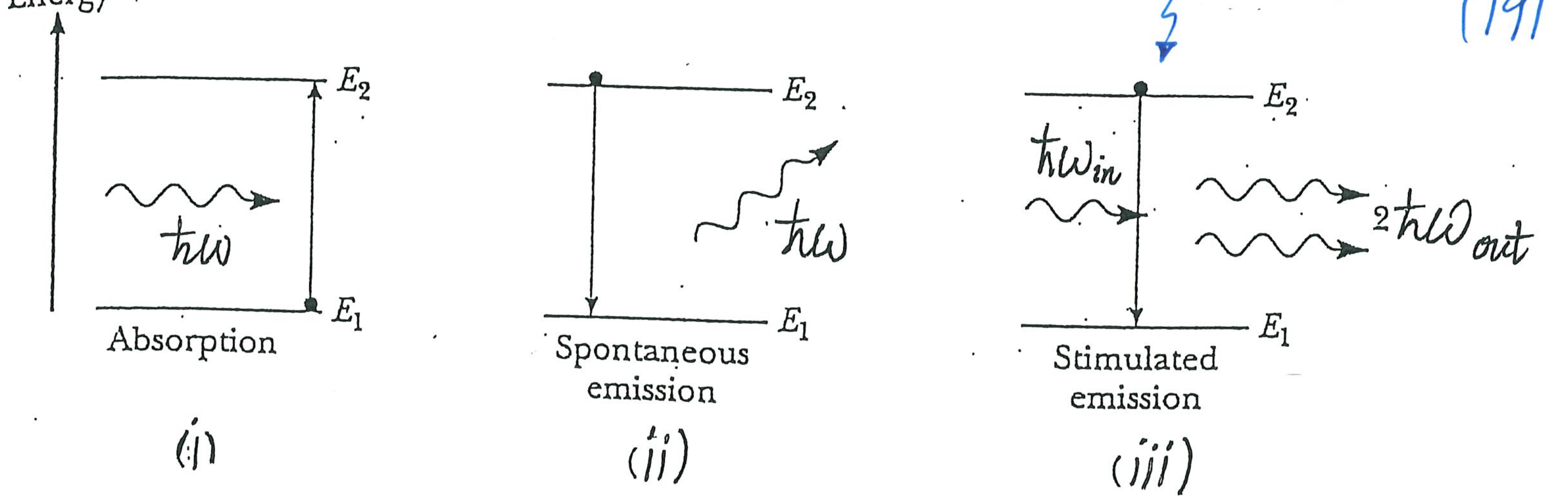
but when system is in thermal equilibrium at a temperature T,

$$\frac{N_2}{N_1} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = e^{-(E_2-E_1)/kT} = e^{-\hbar\omega/kT} \qquad (28)$$

- this is the piece of thermal physics that helps us out
- we assumed state 1 and state 2 are non-degenerate

To get Planck's formula (especially "−1" in denominator), <u>Einstein</u> <u>needed</u> to invoke <u>3</u> <u>processes</u>

Not known before Einstein's work (1917)



The processes of (i) absorption and (ii) spontaneous emission. The lifetime of the upper state is t_s, and the photon is emitted in a random direction. (iii) Stimulated emission. In this process, the emitted photons are in phase with the stimulating photon, and all have the same direction of travel.

- (i) and (ii) were regarded "common sense" processes
- Einstein needed (iii) to obtain Eq. (27)

(i) Stimulated Absorption (level 1 → level 2)

"Stimulated" ⇒ Probability of absorption per atom per unit time $\propto U(\omega,T)$ [this is what "stimulated" meant]

Write: Probability of absorption per atom per unit time

$$= B_{12}\, U(\omega,T) \qquad (29a)$$

[B_{12} = Einstein's B-coefficient = (simply) B]

Remark: We know from QM that (see Eq. (24))

$$\lambda_{1\to2} = \underbrace{\frac{\pi e^2}{3\varepsilon_0 \hbar^2}}_{B_{12} \text{ from QM}} |r_{21}|^2\, U(\omega)$$

(Einstein didn't know this in 1917)

(ii) Spontaneous Emission (level 2 → level 1)

"Spontaneous" ⇒ Prob. of spontaneous emission per atom per unit time

$$= \underbrace{A_{21}}_{\text{independent of } U(\omega,T)} \quad (\text{Einstein's A-coefficient}) \qquad (29b)$$

[∵ Spontaneous]

Remark: Hard to understand this process within Schrödinger's QM

(iii) Stimulated Emission (level 2 → level 1)

"Stimulated" ⇒ Prob. of stimulated emission per atom per unit time

$$= B_{21}\, U(\omega, T) \qquad [\text{How is it related to } B_{12}\,?] \quad (29c)$$

[Without this process, could not get Planck's formula]

Remark: We know from QM, $B_{21} = B_{12}$ $(\because \lambda_{1\to 2} = \lambda_{2\to 1})$

Einstein didn't know this in 1917

Take stock:

$$\text{Per atom per unit time}\begin{cases} B_{12}\cdot U(\omega,T) & \text{[stimulated absorption]} \\ A_{21} & \text{[spontaneous emission]} \\ B_{21}\cdot U(\omega,T) & \text{[stimulated emission]} \end{cases}$$

Temperature enters via equilibrium statistical physics

$$N_1 + N_2 \text{ atoms} \begin{array}{l} \nearrow N_2 \text{ atoms in level 2 (higher energy)} \\ \searrow N_1 \text{ atoms in level 1 (lower energy)} \end{array}$$

- Statistical Physics ⇒ At equilibrium $N_1 > N_2$ (any temperature)

$$\boxed{\frac{N_2}{N_1} = e^{-(E_2-E_1)/kT} = e^{-\hbar\omega/kT}} \qquad (28)$$

- $kT \ll E_2 - E_1$, $N_1 \gg N_2$; $kT \gg E_2 - E_1$, $N_1 \gtrsim N_2$ (still $N_1 > N_2$)

Aside:

- For a collection of N entities (independent ones), each one could be at energies E_1 or E_2 (say $E_2 > E_1$), then $N_2 \propto e^{-E_2/kT}$ and $N_1 \propto e^{-E_1/kT}$ when system is at thermal equilibrium at temperature T.

$$\text{So } \underbrace{\frac{N_2}{N_1} = e^{-(E_2-E_1)/kT}}_{\text{Eq. (28)}}$$

— Meaning

→ $N_2 < \underbrace{N_1}_{\text{more entities in lower state}}$

→ Can't use T to put more entities in higher state

→ When $N_2 > N_1$, the system is out of equilibrium

- Equilibrium is attained by balancing 1→2 transitions AND 2→1 transitions

$$\underbrace{\text{\# atoms going from 1 to 2 per unit time by absorption}} = \underbrace{\text{\# atoms going from 2 to 1 per unit time by \underline{stimulated emission}}} + \underbrace{\text{\# atoms going from 2 to 1 per unit time by \underline{spontaneous emission}}}$$

$$\boxed{N_1 \cdot B_{12}\, U(\omega,T) = N_2 \cdot B_{21}\, U(\omega,T) + N_2 \cdot A_{21}} \qquad (30)$$

Eq.(30) →

$$\frac{N_2}{N_1} = \frac{B_{12}\, U(\omega,T)}{\underbrace{B_{21}\, U(\omega,T) + A_{21}}_{\text{Solve for } U(\omega,T)}} \overset{\uparrow}{=} e^{-\frac{\hbar\omega}{kT}}$$

(statistical physics) (Eq.(28))

$$\boxed{U(\omega,T) = \frac{A_{21}}{B_{12}\, e^{\hbar\omega/kT} - B_{21}}} \qquad (31)$$

[started to look like Planck's formula]

Compare $U(\omega,T) = \dfrac{A_{21}}{B_{12}e^{\frac{\hbar\omega}{kT}} - B_{21}}$ with $U(\omega,T) = \dfrac{\hbar\omega^3}{\pi c^3}\dfrac{1}{e^{\frac{\hbar\omega}{kT}}-1}$ (27)

Important Results To get Planck's formula...

(a) $\boxed{B_{12} = B_{21} = B}$ (32) [same as obtained by QM $\lambda_{1\to 2} = \lambda_{2\to 1}$ (same $U(\omega_{12})$)]

(b) $U(\omega,T) = \dfrac{A_{21}}{B}\cdot\dfrac{1}{e^{\hbar\omega/kT}-1}$ $\Rightarrow$ $\boxed{\dfrac{A_{21}}{B} = \dfrac{A}{B} = \dfrac{\hbar\omega^3}{\pi^2c^3}}$ $\propto \omega^3$ (33)

$\Rightarrow$ $\boxed{A = \dfrac{\hbar\omega^3}{\pi^2c^3}B}$ (34) Yes, we do! From QM (Einstein didn't)

[get A if we know B]

(c) Need to introduce B_{21} (stimulated emission, not known in 1917) to get "-1" in Planck's formula

(d) $A_{21} \propto \omega^3 B$

- implies a state high in energy (so ω_{21} is big) will "decay" to state "1" much readily (in shorter time) than a state with energy closer (thus smaller ω_{21}) to state "1"
- thus, harder to "hold" an atom in a highly excited state (this is true) due to faster spontaneous emission
- OR a highly excited state has a shorter life time

(e) $A_{21} = \frac{\hbar\omega^3}{\pi^2 c^3} B \Rightarrow A_{21}$ & B have different units

By Eq. (29b), A has unit of $\frac{1}{\text{time}}$ OR $\boxed{\frac{1}{A} \text{ is a time}}$

(f) [Optional] (for those doing statistical physics)

$$A_{21} = \frac{\hbar\omega^3}{\pi^2 c^3} B = \frac{(\hbar\omega)\cdot\omega^2}{\pi^2 c^3} B$$

In statistical physics/statistical mechanics/solid state physics courses, we will see $(\hbar\omega^3)$ actually comes from

$$\underset{\substack{\uparrow \\ \text{an energy} \\ \text{(quantum mechanics)}}}{(\hbar\omega)} \cdot \underset{\substack{\nwarrow \\ \text{from counting number of modes} \\ \text{with angular freq. } \omega \to \omega + d\omega \\ [\text{which is} \sim \omega^2 d\omega] \text{ in 3D system}}}{\omega^2}$$

G. Spontaneous Emission

Einstein: $A_{21} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{21}$; Schrödinger's QM $\lambda_{1\to2} = \underbrace{\frac{\pi e^2}{3\varepsilon_0\hbar^2}|r_{21}|^2}_{B_{21}} \cdot U(\omega_{21})$

↑ Schrödinger's QM can't treat vacuum

↑ Einstein didn't know

Putting the results together

$$\boxed{A_{21} = \frac{\omega^3}{3\pi\varepsilon_0 c^3\hbar} e^2|r_{21}|^2} \qquad (35)$$

a QM result (without effort!)

↪ Units: $\frac{1}{\text{time}}$

$\frac{1}{A}$ is a time $\qquad \tau = \frac{1}{A}$ = life time of an excited state

$$= \frac{3\pi\varepsilon_0 c^3\hbar}{\omega^3} \frac{1}{e^2|r_{21}|^2}$$

- Let $N_2(t)$ be number of excited atoms (at state "2") at time t

$N_2(t)$ drops due to spontaneous emission (No stimulation)

Recall: $A_{(21)}$ OR A is prob. per atom per unit time to decay to a lower state "1"

$$\therefore \frac{dN_2(t)}{dt} = -A N_2(t)$$

↖ Einstein's A coefficient

$$\Rightarrow N_2(t) = N_2(0)\, e^{-At} \equiv N_2(0)\, e^{-t/\tau} \quad (\tau = \text{life time})$$

$$\therefore \boxed{\tau = \frac{1}{A}} \quad (36)$$

Einstein's A-coefficient inversed is excited state's lifetime

(really getting many things from nothing!)

For state "2" having <u>only</u> state "1" to decay to, A_{21} is given by (35)

Thus
$$\boxed{\tau = \frac{3\pi\varepsilon_0 c^3 \hbar}{\omega^3}\,\frac{1}{e^2|r_{21}|^2}} \qquad (37) \qquad \text{(Magical!)}$$

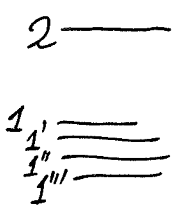
Appreciation: QM provides a formula to calculate τ through evaluating an integral r_{21} (recall $\omega = \frac{E_2 - E_1}{\hbar}$)

- $\sim \frac{1}{\omega^3} \Rightarrow$ highly excited states have short τ

  Very hard to study! (A hot research topic, see "Rydberg Atoms")
- state with lower state (allowed) to go $\Rightarrow |r_{21}|^2$ not small

  $\Rightarrow$ short τ
- state with no lower state to go $\Rightarrow$ long τ (meta stable state)

What if State "2" has <u>many</u> <u>lower states</u> to go?



$$\frac{dN_2(t)}{dt} = -A_{21}N_2(t) - A_{21'}N_2(t) - A_{21''}N_2(t) \cdots$$

$$\therefore \tau_2 = \frac{1}{A_{21} + A_{21'} + A_{21''} + A_{21'''} + \cdots}$$

this is τ of state 2

- More states to go $\Rightarrow$ shorter τ
- Biggest A dominates

OR

$$\frac{1}{\tau_2} = A_{21} + A_{21'} + A_{21''} + A_{21'''} + \cdots$$

$$= \frac{1}{\tau_{21}} + \frac{1}{\tau_{21'}} + \frac{1}{\tau_{21''}} + \frac{1}{\tau_{21'''}} + \cdots$$

due to 2→1   due to 2→1'   due to 2→1''' (each can be handled by QM)

<u>Key Point</u>: life time is related to spontaneous emission through <u>the A-coefficient(s)</u>

Lifetime of Excited States τ

- Excited state could have short lifetime τ because
  - there is (are) lower state(s) with allowed transitions ($\because |r_{21}|^2$)
  - excited state is high in energy ($\because \omega^3$)
  - many lower states to go to

Short lifetime	Long Life time
$\tau \sim 10^{-9}\,s - 10^{-8}\,s$	$\tau \sim 10^{-3}\,s$
H-atom: $2p \rightarrow 1s$ ($\sim 10^{-9}\,s$)	[Metastable state] (important for operation of LASER)

Life time is related to spontaneous emission