

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

$$U(\omega, T) d\omega = \frac{\omega^2}{\pi^2 c^3} \cdot \hbar\omega \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1} d\omega \quad (33)$$

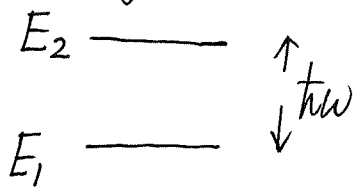
- Einstein wanted to find a way to derive Planck's formulae, i.e. an expression for $U(\omega, T)$

▪ Bohr (1913)

- Atom has discrete energies ("stationary states")
- Spectral lines come from transitions between stationary states

▪ Einstein (1917)

- Cavity's wall \Rightarrow Many Atoms (they absorb/emit; they vibrate)
- Capturing Bohr's key idea, assumed two-state systems

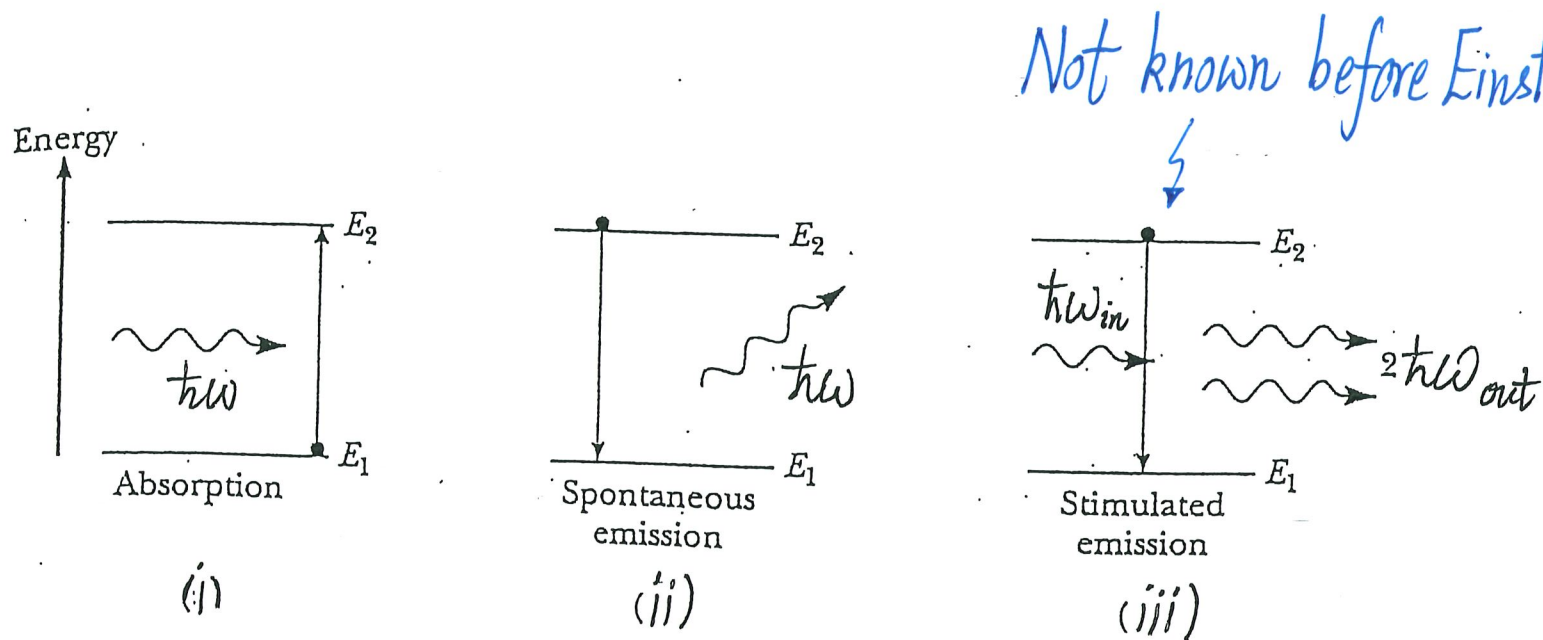
$$\omega = \frac{E_2 - E_1}{\hbar}$$


The diagram shows two horizontal lines representing energy levels. The upper line is labeled E_2 and the lower line is labeled E_1 . A vertical double-headed arrow connects the two lines, with the label $\hbar\omega$ next to it.

- 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 \Rightarrow equilibrium can be achieved

To get Planck's formula (especially "-1" in denominator),
Einstein needed to invoke 3 processes



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.(33)

(i) Stimulated Absorption (level 1 \rightarrow level 2)

"Stimulated" \Rightarrow 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
 $= B_{12} U(\omega, T)$ (34a)

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

Remark: We know from QM that (see Eq. (30))

$$\lambda_{1 \rightarrow 2} = \underbrace{\frac{\pi e^2}{3 \epsilon_0 \hbar^2} |\mathbf{r}_{21}|^2}_{B_{12} \text{ from QM}} U(\omega) \quad \left(\text{Einstein didn't know this in 1917} \right)$$

(ii) Spontaneous Emission (level 2 \rightarrow level 1)

"Spontaneous" \Rightarrow Prob. of spontaneous emission per atom per unit time

$$= A_{21} \quad (\text{Einstein's } A\text{-coefficient}) \quad (34b)$$

independent of $U(\omega, T)$ [\because spontaneous]

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

(iii) Stimulated Emission (level 2 \rightarrow level 1)

"Stimulated" \Rightarrow Prob. of stimulated emission per atom per unit time

$$= B_{21} U(\omega, T) \quad [\text{How is it related to } B_{12} ?] \quad (34c)$$

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

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

$N_1 + N_2$ atoms \rightarrow N_2 atoms in level 2 (higher energy)
 \searrow N_1 atoms in level 1 (lower energy)

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

$$\boxed{\frac{N_2}{N_1} = e^{-(E_2 - E_1)/kT} = e^{-\hbar\omega/kT}} \quad (35)$$

- $kT \ll E_2 - E_1$, $N_1 \gg N_2$; $kT \gg E_2 - E_1$, $N_1 \approx N_2$

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 .

So $\frac{N_2}{N_1} = e^{-(E_2-E_1)/kT}$

Eq. (35)

Meaning → $N_2 < N_1$
 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 $1 \rightarrow 2$ transitions AND $2 \rightarrow 1$ transitions

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

$$N_1 \cdot B_{12} U(\omega, T) = N_2 \cdot B_{21} U(\omega, T) + N_2 \cdot A_{21} \quad (36)$$

Eg. (36) \rightarrow $\frac{N_2}{N_1} = \frac{B_{12} U(\omega, T)}{B_{21} U(\omega, T) + A_{21}} = e^{-\frac{h\omega}{kT}}$ (statistical physics) (Eq. (35))

Solve for $U(\omega, T)$

$$U(\omega, T) = \frac{A_{21}}{B_{12} e^{\frac{h\omega}{kT}} - B_{21}} \quad (37) \quad [\text{started to look like (33)}]$$

Compare $U(\omega, T) = \frac{A_{21}}{B_{12} e^{\frac{\hbar\omega}{kT}} - B_{21}}$ with $U(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$ (33)

Important Results To get Planck's formula...

(a) $B_{12} = B_{21} = B$ (38) [same as obtained by QM $\lambda_{1 \rightarrow 2} = \lambda_{2 \rightarrow 1}$ (same $U(\omega_{12})$)]

(b) $U(\omega, T) = \frac{A_{21}}{B} \frac{1}{e^{\hbar\omega/kT} - 1} \Rightarrow \frac{A_{21}}{B} = \frac{A}{B} = \frac{\hbar\omega^3}{\pi^2 c^3} \propto \omega^3$ (39)

$A = \frac{\hbar\omega^3}{\pi^2 c^3} B$

[get A if we know B]

Yes, we do!
From QM
(Einstein didn't)

(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

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

By Eq. (34b), A has unit of $\frac{1}{\text{time}}$ or $\boxed{\frac{1}{A} \text{ is a time}}$

(f) [Optional]

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

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

$(\hbar \omega) \cdot \omega^2$
 \uparrow \uparrow
 an energy (quantum mechanics)

from counting number of modes
 with angular freq. $\omega \rightarrow \omega + d\omega$
 [which is $\sim \omega^2 d\omega$]