Quantum statistics: main parts

- $g(E)$ describes the number of accessible states
- $\sigma(E) = \log g(E)$ describes the entropy of a system (log of the number of accessible states)
- $f(E)$ describes the probability of occupying different accessible states
- $n(E)$ describes the net number of particles at a particular energy (see Serway Eq. 10.6):

$$n(E)\, dE = g(E) f(E)\, dE \tag{1}$$

- Temperature T is related through Boltzmann's constant k_B to the thermodynamic temperature τ which describes how much energy it takes to open up more accessible states with fixed number of particles N:

$$\frac{1}{k_B T} = \frac{1}{\tau} \equiv \left(\frac{\partial \sigma}{\partial U}\right)_N . \tag{2}$$

with $k_B = 1.381 \times 10^{-23}$ Joules/Kelvin. Room temperature is at $k_B T \simeq 1/40$ eV.

Probability functions, temperature, and chemical potential

- Again, temperature is defined from $\frac{1}{k_B T} = \frac{\partial \sigma}{\partial U}|_N$
- The *relative* likelihood of a system with temperature T choosing one particular state with energy E is given by the Maxwell-Boltzmann distribution function (c.f., Serway Eq. 10.3)

$$f_{\text{MB}} = \exp[-E/k_B T] \tag{3}$$

- We also have a definition of the chemical potential μ in terms of how the log of the number of states σ increases as we add particles N for a fixed energy-per-particle U:

$$-\frac{\mu}{k_B T} \equiv \frac{\partial \sigma}{\partial N}|_U \tag{4}$$

This chemical potential μ gives an additional term in the probability function called a Gibbs factor: $\exp[(\mu - E)/(k_B T)]$

Applicability of the Maxwell-Boltzmann distribution

- The derivation of the Maxwell-Boltzmann distribution function relied upon a Taylor series expansion, which is implicitly built upon continuous occupancies. Therefore it is really a classical theory.
- But we applied it to calculate the probability of atoms being in various states, which involves quantum phenomena! Aren't we being inconsistent there? Answer: no, because we were talking about the average population in various states over many non-interacting atoms.
- Take-home message: Maxwell-Boltzmann statistics work for sparse collections of non-iteracting atoms. Ideal gasses certainly satisfy this property.
- But what happens when we get into situations where we really have to worry about quantum states having integer occupancies?

Fermi-Dirac statistics

- What's the distribution function $f(E)$ for things where we can have only 0 or 1 occupancy to a state? Consider a chemical potential μ which represents the classical occupancy of the state, and the energy of the state to be E.
- For states with $N = 0$ or 1, we have (see Serway Eq. 10.25)

$$\begin{aligned} f_{\mathrm{FD}}(E) &= \frac{1}{E}\frac{\sum_n nE\exp[n(\mu-E)/k_BT]}{\sum_n \exp[n(\mu-E)/k_BT]} \\ &= \frac{1}{E}\frac{0\cdot\exp[0\cdot(\mu-E)/k_BT]+(1E)\cdot\exp[1\cdot(\mu-E)/k_BT]}{\exp[0\cdot(\mu-E)/k_BT]+\exp[1\cdot(\mu-E)/k_BT]} \\ &= \frac{1}{E}\frac{E\exp[(\mu-E)/k_BT]}{1+\exp[(\mu-E)/k_BT]} = \frac{1}{E}\frac{E}{\exp[(E-\mu)/k_BT]+1} \\ (5) \quad f_{\mathrm{FD}}(E) &= \frac{1}{\exp[(E-E_f)/k_BT]+1} \end{aligned}$$

where E_F is called the Fermi energy.

- We will come back to Fermi-Dirac statistics in much more detail. But first. . .

Bose-Einstein statistics

- Now consider the case when we can put any number of particles in the same state (*e.g.*, photons):

$$\begin{aligned} f_{\mathrm{BE}}(E) &= \frac{1}{E}\frac{\sum_n nE\exp[n(\mu-E)/k_BT]}{\sum_n \exp[n(\mu-E)/k_BT]} \\ &= \frac{1}{E}\frac{0+E\exp[1(\mu-E)/k_BT]+2E\exp[2(\mu-E)/k_BT]+\ldots}{1+\exp[1(\mu-E)/k_BT]+\exp[2(\mu-E)/k_BT]+\ldots} \end{aligned}$$

- Let $y \equiv \exp[(\mu-E)/k_BT]$. We then have

$$f_{\mathrm{BE}}(E) = \frac{1}{E}E\frac{y+2y^2+3y^3+\ldots}{1+y+y^2+\ldots} = y\frac{1+2y+3y^2+\ldots}{1+y+y^2+\ldots}$$

- Now let $A \equiv 1+2y+3y^2+\ldots$ and $B \equiv 1+y+y^2+\ldots$ We then have

$$\frac{1+2y+3y^2+\ldots}{1+y+y^2+\ldots} = \frac{A}{B}$$

Bose-Einstein II

- The ratio is

$$\frac{A}{B} = \frac{1 + y + y^2 + y^3 + \ldots + (y + 2y^2 + 3y^3 + \ldots)}{1 + y + y^2 + y^3 + \ldots} = \frac{B + yA}{B} = 1 + y\frac{A}{B}$$

or $(1 - y)(A/B) = 1$ or $A/B = 1/(1 - y)$. As a result,

$$f_{\text{BE}}(E) = \frac{y}{(1 - y)} = \frac{1}{1/y - 1} = \frac{1}{\exp[(E - \mu)/k_B T] - 1} \quad (6)$$

- In this case since we can put as many particles as we want into any state, the chemical potential μ for shifting particles into different states doesn't have a physically sensible non-zero value, so we end up with (Serway Eq. 10.19)

$$f_{\text{BE}}(E) = \frac{1}{\exp[E/k_B T] - 1} \quad (7)$$

Blackbody revisited

- Return to blackbody radiation. The density of available states $g(E)$ is given by

$$g(E) = \frac{1}{8}\,\frac{4\pi n^2\,dn}{V}\,2 \tag{8}$$

  where the $1/8$ is for the positive octant of a sphere ($[n_x, n_y, n_z]$ are all positive), $4\pi n^2\,dn$ represents the shell of a sphere of available states, and the factor 2 at the end allows for two orthogonal polarization states.

- For wavelengths fitting in a cavity of length L, we require $n\lambda/2 = L$ or since $c = \lambda\nu$ we have

$$n\frac{c}{2\nu} = L \qquad n = 2\frac{L}{c}\nu \qquad dn = 2\frac{L}{c}\,d\nu$$

  We then have

$$g(\nu) = \frac{1}{8}\,\frac{4\pi n^2\,dn}{V}\,2 \qquad \rightarrow \qquad g(\nu) = \frac{8\pi}{c^3}\nu^2\,d\nu$$

Blackbody revisited II

- Again, we have $g(\nu) = \frac{8\pi}{c^3}\nu^2\,d\nu$
- Using the Bose-Einstein distribution function with $E = h\nu$, we have

$$f(\nu) = \frac{1}{\exp[h\nu/k_B T] - 1}$$

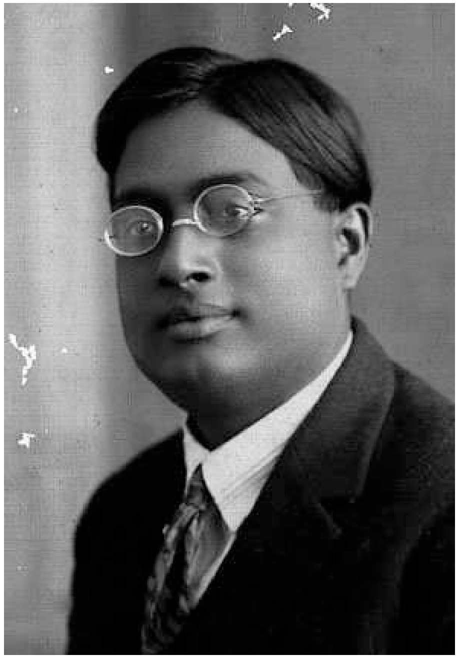
- The product is the photon number distribution $n(\nu) = g(\nu)f(\nu)\,d\nu$. The energy distribution involves an energy $h\nu$ per photon, or $n(E) = h\nu\,g(\nu)f(\nu)$ which gives

$$n(E) = \frac{8\pi h\nu^3}{c^3}\frac{1}{\exp[h\nu/k_B T] - 1}\,d\nu$$

which is the Planck blackbody radiation formula!

Satyendra Nath Bose

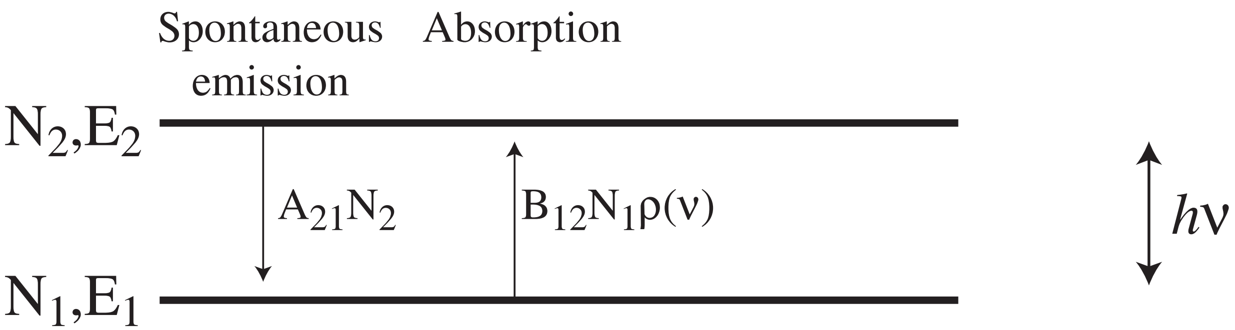
- Born in Calcutta, son of a railway engineer. By age 22 he was a lecturer in Physics at Calcutta University; moved to Dacca/Dhaka University in what is now Bangladesh in 1921.
- In 1924, used quantum statistics to derive Planck's formula as we've just described. Could not get his paper published. In desperation, he sent his paper to Einstein who recognized its worth, arranged for it to get published, and added to it in a companion publication.
- Bose then made two trips to Europe in the 1924–1926 period, visiting de Broglie, Einstein, and Marie Curie, among others. Upon Einstein's recommendation, became a professor at Calcutta University in 1926 despite not having a PhD.
- For more on the story, see the October 2006 issue of *Physics Today*.



Satyendra Nath Bose in 1925 (1894–1974)

Einstein and radiation

- This is done in Serway Sec. 12.7. Consider a two-level system, with energies $E_2 - E_1 = h\nu$, and populations N_1 and N_2:



- **Spontaneous emission**: the rate at which we lose electrons from state N_2 is proportional to the number of electrons in that state:

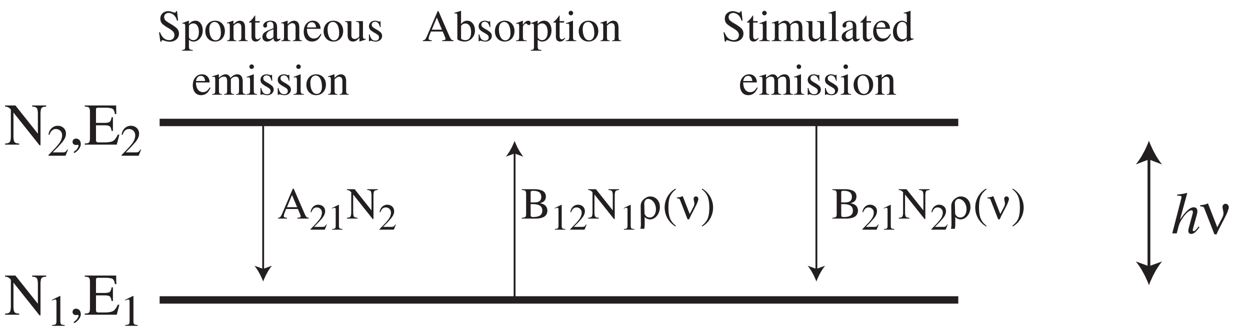
$$\left(\frac{dN_2}{dt}\right)_{\text{spont}} = -A_{21}N_2 \tag{9}$$

- **Absorption**: the rate at which we pump electrons up to state N_2 is proportional to the number of electrons in state N_1 and the photon density $\rho(\nu)$:

$$\left(\frac{dN_1}{dt}\right)_{\text{abs}} = -\left(\frac{dN_2}{dt}\right)_{\text{abs}} = -B_{12}N_1\rho(\nu) \tag{10}$$

Einstein and radiation II

- Einstein proposed a third process:



Spontaneous emission

Absorption

Stimulated emission

N_2, E_2

N_1, E_1

$A_{21}N_2$

$B_{12}N_1\rho(\nu)$

$B_{21}N_2\rho(\nu)$

$h\nu$

- **Stimulated emission**: we can also drive transitions from state 2 to state 1 in proportion to the population of state 2 and the photon density $\rho(\nu)$:

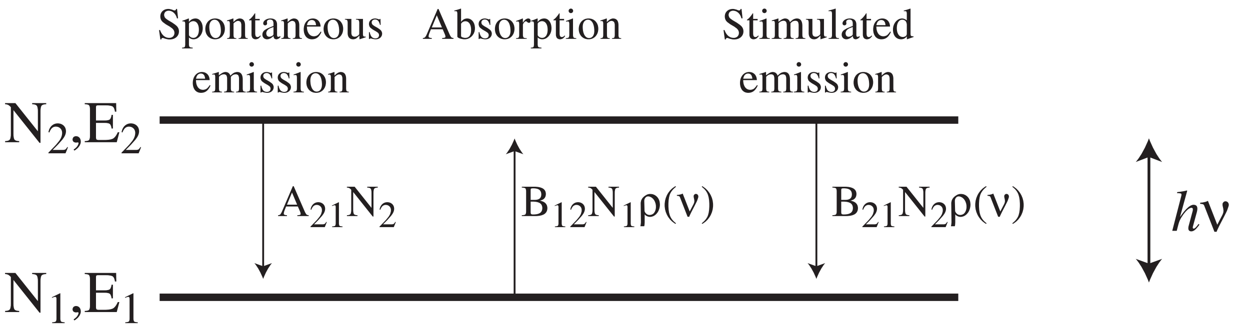
$$\left(\frac{dN_2}{dt}\right)_{\text{stim}} = -B_{21}N_2\rho(\nu) \tag{11}$$

- And remember our other two processes:

$$\left(\frac{dN_2}{dt}\right)_{\text{spont}} = -A_{21}N_2 \qquad \text{and} \qquad \left(\frac{dN_2}{dt}\right)_{\text{abs}} = B_{12}N_1\rho(\nu)$$

Einstein and radiation III

- Assume thermodynamic equillibrium, and assume $\rho(\nu)$ is the Planck blackbody spectrum.



- With the system in equilibrium, N_1 and N_2 evolve towards constant values. As a result,

$$\frac{dN_2}{dt} = 0 = -N_2 A_{21} - N_2 B_{21}\rho(\nu) + N_1 B_{12}\rho(\nu) \tag{12}$$

which gives

$$\begin{aligned} (N_1 B_{12} - N_2 B_{21})\rho(\nu) &= N_2 A_{21} \\ \rho(\nu) &= \frac{N_2 A_{21}}{N_1 B_{12} - N_2 B_{21}} = \frac{A_{21}}{B_{12}(N_1/N_2) - B_{21}} \end{aligned}$$

Einstein and radiation IV

- Again,

$$\rho(\nu) = \frac{A_{21}}{B_{12}(N_1/N_2) - B_{21}}$$

- Now use $\rho(\nu)$ as provided by a Planck blackbody spectrum, and realize that $N_1/N_2 = \exp[h\nu/k_B T]$. This gives

$$\begin{aligned}
\frac{8\pi h\nu^3}{c^3}\frac{1}{\exp[h\nu/k_BT]-1} &= \frac{A_{21}}{B_{12}\exp[h\nu/k_BT]-B_{21}} \\
\frac{8\pi h\nu^3}{c^3}B_{12}\exp[h\nu/k_BT] - \frac{8\pi h\nu^3}{c^3}B_{21} &= A_{21}\exp[h\nu/k_BT] - A_{21} \\
\left(\frac{8\pi h\nu^3}{c^3}B_{12} - A_{21}\right)\exp[h\nu/k_BT] &= \left(\frac{8\pi h\nu^3}{c^3}B_{21} - A_{21}\right) \\
\left(\frac{8\pi h\nu^3}{c^3}\frac{B_{12}}{B_{21}} - \frac{A_{21}}{B_{21}}\right)\exp[h\nu/k_BT] &= \left(\frac{8\pi h\nu^3}{c^3} - \frac{A_{21}}{B_{21}}\right)
\end{aligned}$$

- This must be true for any temperature T! The only way that can be so is for the quantities inside $\Big(\Big)$ to be zero on either side of the equation!

Einstein and radiation V

- Pick the right hand term:

$$\left(\frac{8\pi h\nu^3}{c^3} - \frac{A_{21}}{B_{21}}\right) = 0 \qquad \rightarrow \qquad \frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}$$

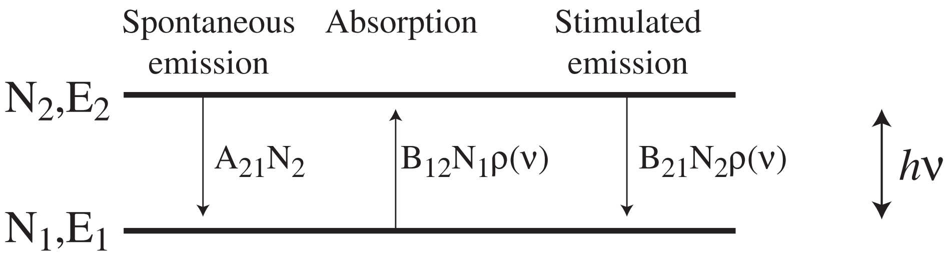
  That is, the spontaneous emission coefficient A_{21} divided by the stimulated emission coefficient B_{21} scales like ν^3. Stimulated emission declines like ν^{-3} or λ^3 relative to spontaneous emission, so it's easier to get stimulated emission with microwaves than it is with x rays.

- Now use the above result in the left hand term:

$$\left(\frac{8\pi h\nu^3}{c^3}\frac{B_{12}}{B_{21}} - \frac{A_{21}}{B_{21}}\right) = 0 \quad \rightarrow \quad \frac{8\pi h\nu^3}{c^3}\left(\frac{B_{12}}{B_{21}} - 1\right) = 0 \quad \rightarrow \quad B_{12} = B_{21}$$

  That is, the stimulated emission and absorption coefficients are one and the same! Recall Fermi's golden rule for transition rates: the rate is the same for $1 \rightarrow 2$ as for $2 \rightarrow 1$.

Review of transitions



- We have $B_{12} = B_{21}$: the stimulated emission and absorption coefficients are one and the same.
- We have $\dfrac{A_{21}}{B_{21}} = \dfrac{8\pi h\nu^3}{c^3}$ for the ratio between spontaneous emission A_{21} and stimulated emission B_{21}.
- Our processes then become

$$\left(\frac{dN_2}{dt}\right)_{\mathrm{stim}} = -BN_2\rho(\nu) \qquad \left(\frac{dN_2}{dt}\right)_{\mathrm{spont}} = -AN_2 \qquad \left(\frac{dN_2}{dt}\right)_{\mathrm{abs}} = +BN_1\rho(\nu)$$

- If we can put lots of atoms into state N_2 and have high photon density $\rho(\nu)$, we can have stimulated emission dominate. Since the electric field of one photon stimulates the emission of another, they are in phase with each other.