

Thermodynamics vignette

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxwell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- Number of states accessible at an energy E is $g_{\mathcal{R}}(E)$
- $g_{\mathcal{R}}(E)$ is a big number. It's more convenient to talk of the entropy which is the natural logarithm of the number of states:
 $\sigma_{\mathcal{R}}(E) = \ln g_{\mathcal{R}}(E)$.
- Thermodynamic temperature τ measures the energy required to produce a certain increase in the number of available states. The Boltzmann constant k_B lets us scale τ to “thermometer” temperature: $\tau = k_B T$. Putting these together gives

$$\frac{1}{k_B T} = \frac{1}{\tau} \equiv \left(\frac{\partial \sigma}{\partial U} \right)_N \quad \text{with} \quad k_B = 1.381 \times 10^{-23} \text{ Joule/Kelvin.} \quad (1)$$

- For large systems, the relative likelihood of a system choosing one particular state with energy E is given by the Maxwell-Boltzmann distribution function: $f_{MB} = \exp[-E/k_B T]$.

Quantum statistics

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxwell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- We will want to look at distributions of the number of particles n as a function of energy E , or $n(E)$.
- Think back to our discussion of the Planck blackbody radiation distribution result: the number of photons having a particular energy $n(E)$ was given by the product of:
 - Density of available states $g(E)$
 - Probability of occupying available states $f(E)$, which we will also call a *distribution function*.
- Thus we'll want to calculate (see Serway Eq. 10.6)

$$n(E) dE = g(E)f(E) dE \quad (2)$$

An example

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxwell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- Consider a hydrogen atom with $E_1 = -13.6$ eV equal to its ground state energy with no external field, and ignoring hyperfine splitting. There are two states ($n = 1, \ell = 0, m_s = [-1/2, 1/2]$) so $g(E_1) = 2$.
- For energy $E_2 = -3.4$ eV, we have the following possibilities: ($n = 2, \ell = 0, m_\ell = 0, m_s = [-1/2, 1/2]$) gives 2 states ($n = 2, \ell = 1, m_\ell = [-1, 0, 1],$ and $m_s = [-1/2, 1/2]$) gives 6 states
So $g(E_2) = 8$.
- Then consider the relative population of states at the temperature at the surface of the sun or $T = 4150$ K where $k_B T = 0.36$ eV:

$$\frac{N(n=1)}{N(n=2)} = \frac{G(E_1)}{G(E_2)} \frac{\exp[-\frac{E_1}{k_B T}]}{\exp[-\frac{E_2}{k_B T}]} = \frac{2 \exp[-\frac{13.6}{0.36}]}{8 \exp[-\frac{3.4}{0.36}]} = 1.7 \times 10^{-12}$$

Almost all atoms are excited!!!

Maxwell velocity distribution I

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxwell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- Consider the distribution of speeds of atoms in an ideal (non-interacting) gas. That is, we want $n(v) = g(v)f(v)$ as a function of speed v rather than energy E .
- To find the density of available states $g(v)$, we realize that in principle all velocities in 3D are possible, so $g(v) dv$ is the volume of a spherical shell of thickness dv at v :

$$g(v) = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_v^{v+dv} r dr = 4\pi v^2 dv \quad (3)$$

- The relative distribution function for occupying a state is given by $\exp[-E/k_B T]$. The energy associated with a state of velocity v is $(1/2)mv^2$, and if we allow for a normalization factor A to get the absolute probability, we have

$$f(v) = A \exp\left[-\frac{mv^2}{2k_B T}\right] \quad (4)$$

Maxwell velocity distribution II

- Normalize the number distribution with velocity $n(v)$ according to the total number of particles N :

$$\int_0^{\infty} n(v) dv = \int_0^{\infty} g(v)f(v) dv = \int_0^{\infty} 4\pi v^2 A \exp\left[-\frac{mv^2}{2k_B T}\right] dv = N$$

- Let's do the integral:

$$\int_0^{\infty} 4\pi v^2 A \exp\left[-\frac{mv^2}{2k_B T}\right] dv$$

Defining $a \equiv m/(2k_B T)$ puts the integral to

$$4\pi A \int_0^{\infty} v^2 \exp[-av^2] dv = 4\pi A \frac{\sqrt{\pi}}{4a^{3/2}} = N$$

so we find $N = 4\pi^{3/2}A/(4a^{3/2})$ which, using $a \equiv m/(2k_B T)$, gives

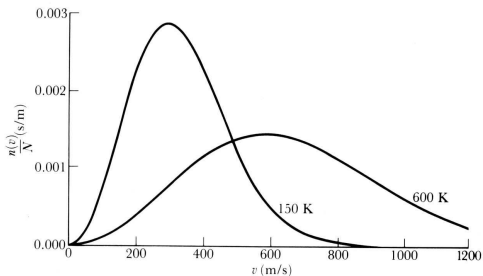
$$A = N \left(\frac{m}{2\pi k_B T} \right)^{3/2}$$

Maxwell velocity distribution III

Now that we know A we can go back to Eqs. 3 and 4 to find

$$\begin{aligned}n(v) dv &= g(v)f(v) dv = [4\pi v^2 dv][A \exp[-\frac{mv^2}{2k_B T}]] \\ &= 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp[-\frac{mv^2}{2k_B T}]\end{aligned}\quad (5)$$

which reproduces Serway Eq. 10.8. Here's a plot for N_2 gas from Fig. 22.3 of Sandin, *Essentials of Modern Physics*:



Maxwell velocity distribution IV

- The most common speed is found from taking the derivative of $n(v)$ and setting it to zero.

This gives $v_p = \sqrt{2k_B T/m}$.

- The average speed \bar{v} is found from $\bar{v} = \int_0^\infty v n(v) dv$.

This gives $\bar{v} = \sqrt{8k_B T/(\pi m)}$ (see Serway Eq. 10.12)

- The root-mean-square or RMS speed is found from

$$v_{\text{rms}} = \sqrt{\int_0^\infty v^2 n(v) dv}$$

This gives $v_{\text{rms}} = \sqrt{3k_B T/m}$ from which we find $(1/2)mv_{\text{rms}}^2 = (3/2)k_B T$ (see Serway Eq. 10.13).

- Gravitational escape velocity: $(1/2)mv^2 = GmM_{\text{earth}}/r_{\text{earth}}$ gives

$$v_{\text{escape}} = \sqrt{\frac{2GM_{\text{earth}}}{r_{\text{earth}}}} = \sqrt{8\pi G\rho_{\text{earth}}r_{\text{earth}}^2}$$

or $v_{\text{escape}} = 11.2 \text{ km/sec}$ or about 25,000 mph.

- We leak a very small fraction of our atmosphere out to space!
Especially helium. Smaller planets have a lower escape velocity and thus leak more.

Leaking Helium

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxwell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- Helium is formed by radioactive decay (α particles are helium nuclei). This happens at the earth's surface, and also subsurface; subsurface-generated helium is brought to the surface in natural gas wells. This sheds light on controversies between [creationists](#) and [scientific debunkers](#).
- Rather than simply vent this helium and eventually lose it from the planet, a program was begun to capture and store it: the National Helium Reserve. However, its \$25M annual cost became a poster child of government waste in the eyes of some after the 1996 congressional elections: “We don't have a fleet of dirigibles, do we?”
- The [alarm was sounded by scientists](#), and a [National Academies study](#) was ordered. Sure enough, problems in helium supply [are now being reported](#). . .

Maxwell-Boltzman redeux

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- In the derivation of the Maxwell-Boltzman distribution we had probability ratios which looked like

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{\exp[\sigma_{\mathcal{R}}(U_0 - \epsilon_1)]}{\exp[\sigma_{\mathcal{R}}(U_0 - \epsilon_2)]}$$

upon which we did a Taylor expansion like

$$\sigma(U_0 - \epsilon) = \sigma_{\mathcal{R}}(U_0) - \epsilon \frac{\partial \sigma_{\mathcal{R}}}{\partial U} \Big|_{V,N} + \dots = \sigma_{\mathcal{R}}(U_0) - \frac{\epsilon}{k_B T} + \dots$$

- We then said the Maxwell-Boltzman relative probability distribution for filling available states as we add energy ϵ goes like

$$f_{\text{MB}}(\epsilon) = A \exp[-\epsilon/(k_B T)] \quad (6)$$

where we have to find the normalization factor A .

Partition function

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- We now want a way of turning the *relative* probability of the Maxwell-Boltzmann distribution function into an *absolute* probability.
- For a system S , the *absolute* probability can be found by the relative probability for one particular configuration with energy ϵ_S divided by the sum of all particular configurations:

$$P(\epsilon_S) = \frac{\exp[-\epsilon_S/(k_B T)]}{\sum_S \exp[-\epsilon_S/(k_B T)]} = \frac{\exp[-\epsilon_S/(k_B T)]}{Z} \quad (7)$$

where

$$Z \equiv \sum_S \exp[-\epsilon_S/(k_B T)] \quad (8)$$

is known as the *partition function*, and we can write $A = 1/Z$ in Eq. 6.

Gibbs free energy

- Now let's consider a system with a number of particles N and a potential energy μ which affects the energy of the particles. An expansion similar to Eq. 9 of how the log of the number of states changes as N and μ are allowed to change goes as

$$\sigma(N_0 - N, U_0 - \mu) = \sigma(N_0, U_0) - N \left. \frac{\partial \sigma}{\partial N_0} \right|_{U_0} - \epsilon \left. \frac{\partial \sigma}{\partial U_0} \right|_{N_0} + \dots \quad (9)$$

- Once again, we define temperature in terms of how the log of the number of states σ increases as we add energy U_0 for a fixed number of particles N_0 :

$$\frac{1}{k_B T} \equiv \left. \frac{\partial \sigma}{\partial U_0} \right|_{N_0} \quad (10)$$

- 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_0 for a fixed energy U_0 :

$$-\frac{\mu}{k_B T} \equiv \left. \frac{\partial \sigma}{\partial N_0} \right|_{U_0} \quad (11)$$

Gibbs free energy II

- Inserting Eqs. 10 and 15 into the expansion of Eq. 9 gives relative probabilities of

$$\frac{P(N_1, \epsilon_1)}{P(N_2, \epsilon_2)} = \frac{\exp[(N_1\mu - \epsilon_1)/(k_B T)]}{\exp[(N_2\mu - \epsilon_2)/(k_B T)]}. \quad (12)$$

- The probability term $\exp[(N_1\mu - \epsilon_1)/(k_B T)]$ is called a Gibbs factor (Gibbs was one of the first Americans to make a significant contribution to physics).
- Let's do like we did with the partition function Z , except what we'll now have is a Gibbs sum or the grand partition function

$$\mathcal{Z}(\mu, k_B T) = \sum \exp[(N\mu - \epsilon)/k_B T]$$

It then turns out that the Gibbs sum can be simplified to

$$\mathcal{Z}(\mu, k_B T) = 1 + \lambda \exp[-\epsilon/(k_B T)] \quad (13)$$

where $\lambda \equiv \exp[\mu/(k_B T)]$ is called the *absolute activity* (though it really looks like just another Boltzmann factor).

Quantum statistics: main parts

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxwell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- $g(E)$ 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):

$$n(E) dE = g(E)f(E) dE$$

- 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 : $\frac{1}{k_B T} = \frac{1}{\tau} \equiv \left(\frac{\partial \sigma}{\partial U}\right)_N$ 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

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxwell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- Again, temperature is defined from $\frac{1}{k_B T} = \left. \frac{\partial \sigma}{\partial U} \right|_N$
- 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)

$$f_{\text{MB}} = \exp[-E/k_B T] \quad (14)$$

- 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 :

$$-\frac{\mu}{k_B T} \equiv \left. \frac{\partial \sigma}{\partial N} \right|_U \quad (15)$$

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 $f_{MB}(E) = \exp[-E/k_B T]$ 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-interacting 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?

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxwell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

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) $f_{FD}(E)$

$$\begin{aligned} &= \frac{1}{E} \frac{\sum_n n E \exp[n(\mu - E)/k_B T]}{\sum_n \exp[n(\mu - E)/k_B T]} \\ &= \frac{1}{E} \frac{0 \cdot \exp[0 \cdot (\mu - E)/k_B T] + (1E) \cdot \exp[1 \cdot (\mu - E)/k_B T]}{\exp[0 \cdot (\mu - E)/k_B T] + \exp[1 \cdot (\mu - E)/k_B T]} \\ &= \frac{1}{E} \frac{E \exp[(\mu - E)/k_B T]}{1 + \exp[(\mu - E)/k_B T]} = \frac{1}{E} \frac{E}{\exp[(E - \mu)/k_B T] + 1} \\ \Rightarrow f_{FD}(E) &= \frac{1}{\exp[(E - E_f)/k_B T] + 1} \end{aligned} \quad (16)$$

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): we have $f_{\text{BE}}(E)$

$$\begin{aligned} &= \frac{1}{E} \frac{\sum_n nE \exp[n(\mu - E)/k_B T]}{\sum_n \exp[n(\mu - E)/k_B T]} \\ &= \frac{1}{E} \frac{0 + E \exp[1(\mu - E)/k_B T] + 2E \exp[2(\mu - E)/k_B T] + \dots}{1 + \exp[1(\mu - E)/k_B T] + \exp[2(\mu - E)/k_B T] + \dots} \end{aligned}$$

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

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

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

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

Bose-Einstein II

The ratio is

$$\begin{aligned}\frac{A}{B} &= \frac{1 + y + y^2 + y^3 + \dots + (y + 2y^2 + 3y^3 + \dots)}{1 + y + y^2 + y^3 + \dots} \\ &= \frac{B + yA}{B} = 1 + y\frac{A}{B}\end{aligned}$$

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

$$f_{\text{BE}}(E) = \frac{y}{(1 - y)} = \frac{1}{1/y - 1} = \frac{1}{\exp[(E - \mu)/k_B T] - 1} \quad (17)$$

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)

$$f_{\text{BE}}(E) = \frac{1}{\exp[E/k_B T] - 1} \quad (18)$$

Blackbody revisited

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

$$g(E) = \frac{1}{8} \frac{4\pi n^2 dn}{V} 2 \quad (19)$$

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

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

We then have

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

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.
- See the October 2006 issue of *Physics Today*.



Satyendra Nath
Bose in 1925
(1894–1974)

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxwell-Boltzmann

Fermi-Dirac

Bose-Einstein

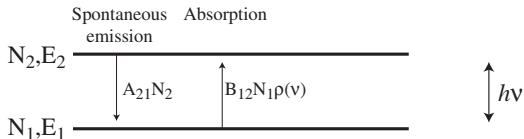
Blackbody
revisited

Bose

Einstein and
radiation

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:

$$\left(\frac{dN_2}{dt}\right)_{\text{spont}} = -A_{21}N_2 \quad (20)$$

- 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 $\rho(\nu)$:

$$\left(\frac{dN_1}{dt}\right)_{\text{abs}} = -\left(\frac{dN_2}{dt}\right)_{\text{abs}} = -B_{12}N_1\rho(\nu) \quad (21)$$

Einstein and radiation II

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxell-Boltzmann

Fermi-Dirac

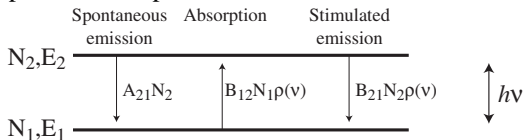
Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- Einstein proposed a third process:



- 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 $\rho(\nu)$:

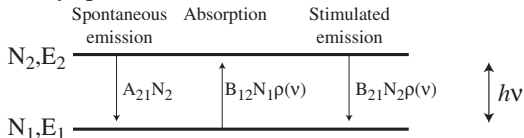
$$\left(\frac{dN_2}{dt}\right)_{\text{stim}} = -B_{21}N_2\rho(\nu) \quad (22)$$

- And remember our other two processes:

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

Einstein and radiation III

- Assume thermodynamic equilibrium, 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,

$$\frac{dN_2}{dt} = 0 = -N_2A_{21} - N_2B_{21}\rho(\nu) + N_1B_{12}\rho(\nu) \quad (23)$$

which gives

$$\begin{aligned}(N_1B_{12} - N_2B_{21})\rho(\nu) &= N_2A_{21} \\ \rho(\nu) &= \frac{N_2A_{21}}{N_1B_{12} - N_2B_{21}} = \frac{A_{21}}{B_{12}(N_1/N_2) - B_{21}}\end{aligned}$$

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

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

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

Einstein and radiation V

Thermodynamics
review

Quantum statistics

Maxwell velocity
distribution

Helium

Partition and Gibbs

Quantum statistics:
the basics (again)

Chemical potential

Distribution I:
Maxwell-Boltzmann

Fermi-Dirac

Bose-Einstein

Blackbody
revisited

Bose

Einstein and
radiation

- Pick the right hand term:

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

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 $2 \rightarrow 1$.