Chapter 11: Quantum Statistics

Multi-particle systems are complex. They can contain huge number of particles (e.g. a gas at standard conditions can contain 10^{22} particles). These systems are usually described on a statistical basis.

Consider the classical picture of a gas:

- The particle density distribution is distributed according to the **Boltzmann distribution**:

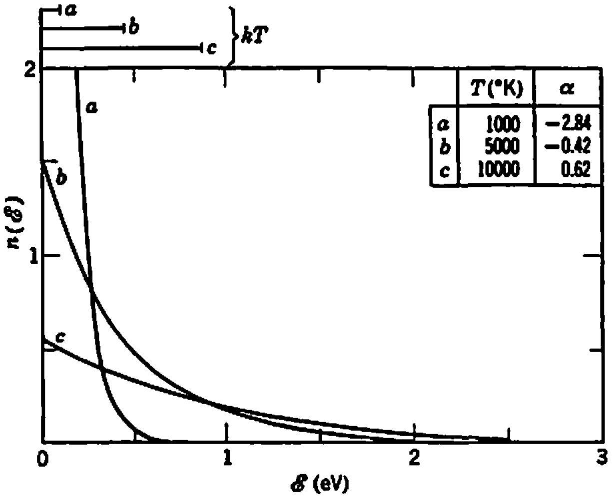
$$n(\varepsilon) = Ae^{-\varepsilon/kT}$$

- The Boltzmann distribution can be used to obtain the Maxwell velocity distribution that describes the distribution of the speed of the gas molecules.
- Statistical arguments can be used to describe the behavior of systems with as little as 100 particles.

To obtain the Boltzmann distribution, the following assumptions are made:

- All possible configurations occur with equal probability.
- Identical entities are treated as if they are distinguishable when counting the number of configurations.

The Figure on the right shows the Boltzmann distribution for a system of constant density at various temperatures.



Quantum mechanics is responsible for the following changes to the classical model:

- If there is an overlap of the wavefunctions of the particles, we have to assume that the particles are indistinguishable.
- If there is no overlap in the wavefunctions of the particles, we have to assume that they are distinguishable and the Boltzmann distribution is valid.
- The results of any calculation cannot depend on the assignment of labels to the particles.
- If the particles are **fermions** (spin 1/2, 3/2, …) the total wavefunction must be anti-symmetric.

- If the particles are **bosons** (spin 0, 1, 2, …) the total wavefunction must be symmetric.

Consider the following examples:

- Two bosons in states α and β:
  The wavefunction of these two bosons must be symmetric and given by the following expressions:

$$\psi_s = \frac{1}{2}\sqrt{2}\left\{\psi_\alpha(1)\psi_\beta(2)+\psi_\beta(1)\psi_\alpha(2)\right\} = \psi_{12}$$

It is easy to see that this wavefunction is symmetric under the exchange of particles 1 and 2:

$$\psi_{12} = \frac{1}{2}\sqrt{2}\left\{\psi_\alpha(1)\psi_\beta(2)+\psi_\beta(1)\psi_\alpha(2)\right\} = \frac{1}{2}\sqrt{2}\left\{\psi_\beta(2)\psi_\alpha(1)+\psi_\alpha(2)\psi_\beta(1)\right\} = \psi_{21}$$

The probability density distribution of the wavefunction is given by

$$\psi_s^*\psi_s = \frac{1}{2}\left\{\psi_\alpha^*(1)\psi_\beta^*(2)+\psi_\beta^*(1)\psi_\alpha^*(2)\right\}\left\{\psi_\alpha(1)\psi_\beta(2)+\psi_\beta(1)\psi_\alpha(2)\right\}$$

If both boson are in the same state, $\alpha = \beta$, and the probability density distributions becomes

$$\begin{aligned}\psi_s^*\psi_s &= \frac{1}{2}\left\{\psi_\beta^*(1)\psi_\beta^*(2)+\psi_\beta^*(1)\psi_\beta^*(2)\right\}\left\{\psi_\beta(1)\psi_\beta(2)+\psi_\beta(1)\psi_\beta(2)\right\} = \\ &= \frac{1}{2}\left\{2\psi_\beta^*(1)\psi_\beta^*(2)\right\}\left\{2\psi_\beta(1)\psi_\beta(2)\right\} = 2\psi_\beta^*(1)\psi_\beta^*(2)\psi_\beta(1)\psi_\beta(2)\end{aligned}$$

Compare this to the classical model:

$$\psi_{classical} = \psi_\beta(1)\psi_\beta(2)$$

and

$$\psi_{classical}^*\psi_{classical} = \psi_\beta^*(1)\psi_\beta^*(2)\psi_\beta(1)\psi_\beta(2) = \frac{1}{2}\left(\psi_s^*\psi_s\right)_{quantum}$$

This last relation can be rewritten as

$$\left(\psi_s^*\psi_s\right)_{quantum} = 2\left(\psi_{classical}^*\psi_{classical}\right)$$

The presence of one boson in the β state thus increases the possibility to find another boson in the β state. For 2 particles, the enhancement factor is 2.

- Consider what happens when we have 3 bosons. In this case, the wavefunction is

$$\psi_s = \frac{1}{\sqrt{6}}\left\{\begin{matrix}\psi_\alpha(1)\psi_\beta(2)\psi_\gamma(3)+\psi_\alpha(1)\psi_\beta(3)\psi_\gamma(2)+\psi_\alpha(2)\psi_\beta(3)\psi_\gamma(1)+ \\ \psi_\alpha(2)\psi_\beta(1)\psi_\gamma(3)+\psi_\alpha(3)\psi_\beta(1)\psi_\gamma(2)+\psi_\alpha(3)\psi_\beta(2)\psi_\gamma(1)\end{matrix}\right\}$$

This wavefunction is symmetric under the exchange of any two particles. If the three particles in the same state the wavefunction is equal to

$$\begin{aligned}\psi_s &= \frac{1}{\sqrt{6}}\left\{\begin{matrix}\psi_\beta(1)\psi_\beta(2)\psi_\beta(3)+\psi_\beta(1)\psi_\beta(3)\psi_\beta(2)+\psi_\beta(2)\psi_\beta(3)\psi_\beta(1)+ \\ \psi_\beta(2)\psi_\beta(1)\psi_\beta(3)+\psi_\beta(3)\psi_\beta(1)\psi_\beta(2)+\psi_\beta(3)\psi_\beta(2)\psi_\beta(1)\end{matrix}\right\} = \\ &= \frac{6}{\sqrt{6}}\psi_\beta(1)\psi_\beta(2)\psi_\beta(3)\end{aligned}$$

The probability density distribution for this wavefunction is given by

$$\left(\psi_s^*\psi_s\right)_{quantum} = 6\left\{\psi_\beta^*(1)\psi_\beta^*(2)\psi_\beta^*(3)\psi_\beta(1)\psi_\beta(2)\psi_\beta(3)\right\} = 3\times 2\times\left(\psi_s^*\psi_s\right)_{classical}$$

- For *n* particles, the following relation can be derived:

$$\left(\psi_s^*\psi_s\right)_{quantum} = n!\left(\psi_s^*\psi_s\right)_{classical}$$

To summarize what we have learned from these examples, define the probability to find the first Boson in a state to be P_1. Now consider the probability to find *n* bosons in this state:

- In the classical model, the probability will be equal to

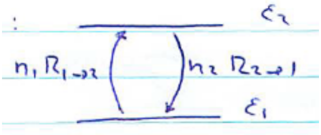
$$P_{n,classical} = \left(P_1\right)^n \quad \Rightarrow \quad P_{n+1,classical} = \left(P_1\right)^{n+1} = P_1\left(P_1\right)^n = P_1 P_{n,classical}$$

- In the quantum model, the probability will be equal to

$$P_{n,quantum} = n!\left(P_1\right)^n \quad \Rightarrow \quad P_{n+1,quantum} = (n+1)!\left(P_1\right)^{n+1} = (n+1)P_1 n!\left(P_1\right)^n = (n+1)P_1 P_{n,quantum}$$

Since the probability distributions are different, we do not expect that the Boltzmann distribution can describe a quantum system. What distribution will be use to describe a quantum system?

Consider a system with two energy levels, as shown in the diagram on the right. The transition rates between the two states are:



$R_{1\to 2}$: probability per second per particle to make a transition from state 1 to state 2.

$R_{2\to 1}$: probability per second per particle to make a transition from state 2 to state 1.

If the system is in equilibrium, the number of particles making a transition from state 1 to state 2 must be equal to the number of particles making a transition from state 2 to state 1:

$$n_1 R_{1\to 2} = n_2 R_{2\to 1} \quad \Rightarrow \quad \frac{n_1}{n_2} = \frac{R_{2\to 1}}{R_{1\to 2}}$$

If we are considering a classical system the number of particles in each state is distributed according to the Boltzmann distribution:

$$\left.\begin{array}{l} n_1 = Ae^{-\varepsilon_1/kT} \\ n_2 = Ae^{-\varepsilon_2/kT} \end{array}\right\} \quad \Rightarrow \quad \frac{R_{2\to 1}}{R_{1\to 2}} = \frac{e^{-\varepsilon_1/kT}}{e^{-\varepsilon_2/kT}}$$

For a quantum system with boson, the transition probabilities will change but the requirement for equilibrium will not change:

$$n_1 R_{1\to 2}^{bosons} = n_2 R_{2\to 1}^{bosons} \quad \Rightarrow \quad \frac{n_1}{n_2} = \frac{R_{2\to 1}^{bosons}}{R_{1\to 2}^{bosons}}$$

If there are n_1 bosons in state 1 and n_2 bosons in state 2, the transition probabilities for bosons will be modified in the following way:

$$R_{1\to 2}^{bosons} = \left(1 + n_2\right) R_{1\to 2}^{classical}$$
$$R_{2\to 1}^{bosons} = \left(1 + n_1\right) R_{2\to 1}^{classical}$$

The requirement for equilibrium can now be rewritten as

$$\frac{n_1}{n_2}=\frac{\left(1+n_1\right)R_{2\to 1}^{classical}}{\left(1+n_2\right)R_{2\to 1}^{classical}}=\frac{\left(1+n_1\right)\,e^{-\varepsilon_1/kT}}{\left(1+n_2\right)\,e^{-\varepsilon_2/kT}}\quad\Rightarrow\quad\frac{n_1}{1+n_1}e^{\varepsilon_1/kT}=\frac{n_2}{1+n_2}e^{\varepsilon_2/kT}$$

The left-hand side of the last equation only depends on the properties of state 1 while the right-hand side of the equation only depends on the properties of state 2. The equation can only be satisfied if both sides are equal to a constant that does not depend on the properties of states 1 and 2, but may depend on the temperature of the system:

$$\frac{n_1}{1+n_1}e^{\varepsilon_1/kT}=\frac{n_2}{1+n_2}e^{\varepsilon_2/kT}=e^{-\alpha}=\text{constant (may be a function of } T\text{)}$$

Consider first state 1. Using the previous equation we can obtain the following expression for the number of bosons in state 1:

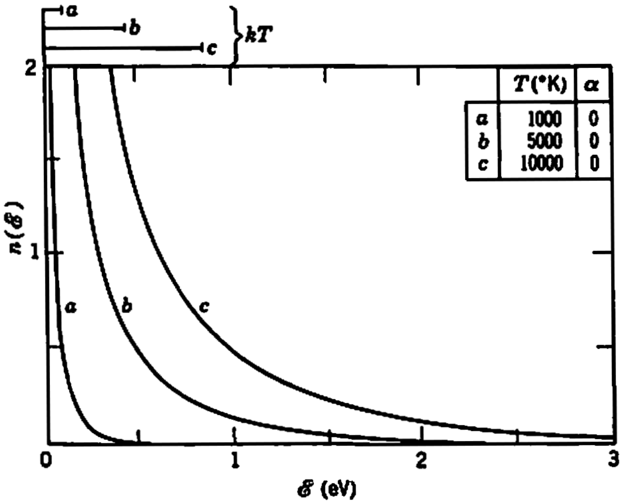
$$\frac{n_1}{1+n_1}e^{\varepsilon_1/kT}=e^{-\alpha}\quad\Rightarrow\quad n_1=e^{-\left(\alpha+\varepsilon_1/kT\right)}+n_1e^{-\left(\alpha+\varepsilon_1/kT\right)}\quad\Rightarrow$$

$$n_1\left(1-e^{-\left(\alpha+\varepsilon_1/kT\right)}\right)=e^{-\left(\alpha+\varepsilon_1/kT\right)}\quad\Rightarrow\quad\boxed{n_1=\frac{e^{-\left(\alpha+\varepsilon_1/kT\right)}}{1-e^{-\left(\alpha+\varepsilon_1/kT\right)}}=\frac{1}{e^{\alpha}e^{\varepsilon_1/kT}-1}}$$

The general expression for the number of bosons in a given state is the following:

$$n\left(\varepsilon\right)=\frac{1}{e^{\alpha}e^{\varepsilon/kT}-1}$$

This distribution is called the **Bose distribution** and is schematically shown in the Figure on the right for three different temperatures.



When the energy is well below *kT* the Bose distribution exceeds the Boltzmann distribution since

$$n_{Bose}\left(\varepsilon\right)=\frac{1}{e^{\alpha}e^{\varepsilon/kT}-1}>\frac{1}{e^{\alpha}e^{\varepsilon/kT}}=n_{Boltzmann}\left(\varepsilon\right)$$

At large energies, the distribution approaches the shape of the Boltzmann distribution.

Now consider that the particles we are dealing with are fermions. Due to the Pauli exclusion principle, the number of particles in a given state can only be 0 or 1. The transition probabilities for fermions are related to the classical transition probabilities in the following way:

$$R_{1\to 2}^{fermions} = \left(1-n_2\right)R_{1\to 2}^{classical}$$
$$R_{2\to 1}^{fermions} = \left(1-n_1\right)R_{2\to 1}^{classical}$$

When state 1 is occupied, transitions from state 2 to state 1 are not allowed; when state 2 is occupied, transitions from state 1 to state 2 are not allowed. The requirement for equilibrium can now be rewritten as

$$\frac{n_1}{n_2} = \frac{\left(1-n_1\right)R_{2\to 1}^{classical}}{\left(1-n_2\right)R_{2\to 1}^{classical}} = \frac{\left(1-n_1\right)}{\left(1-n_2\right)}\frac{e^{-\varepsilon_1/kT}}{e^{-\varepsilon_2/kT}} \quad \Rightarrow \quad \frac{n_1}{1-n_1}e^{\varepsilon_1/kT} = \frac{n_2}{1-n_2}e^{\varepsilon_2/kT}$$

The left-hand side of the last equation only depends on the properties of state 1 while the right-hand side of the equation only depends on the properties of state 2. The equation can only be satisfied if both sides are equal to a constant that does not depend on the properties of states 1 and 2, but may depend on the temperature of the system:

$$\frac{n_1}{1-n_1}e^{\varepsilon_1/kT} = \frac{n_2}{1-n_2}e^{\varepsilon_2/kT} = e^{-\alpha} = \text{constant (may be a function of } T\text{)}$$

Consider first state 1. Using the previous equation we can obtain the following expression for the number of fermions in state 1:

$$\frac{n_1}{1-n_1}e^{\varepsilon_1/kT} = e^{-\alpha} \quad \Rightarrow \quad n_1 = e^{-\left(\alpha+\varepsilon_1/kT\right)} - n_1 e^{-\left(\alpha+\varepsilon_1/kT\right)} \quad \Rightarrow$$

$$n_1\left(1+e^{-\left(\alpha+\varepsilon_1/kT\right)}\right) = e^{-\left(\alpha+\varepsilon_1/kT\right)} \quad \Rightarrow \quad \boxed{n_1 = \frac{e^{-\left(\alpha+\varepsilon_1/kT\right)}}{1+e^{-\left(\alpha+\varepsilon_1/kT\right)}} = \frac{1}{e^{\alpha}e^{\varepsilon_1/kT}+1}}$$

The general expression for the number of fermions in a given state is the following:

$$n\left(\varepsilon\right) = \frac{1}{e^{\alpha}e^{\varepsilon/kT}+1}$$

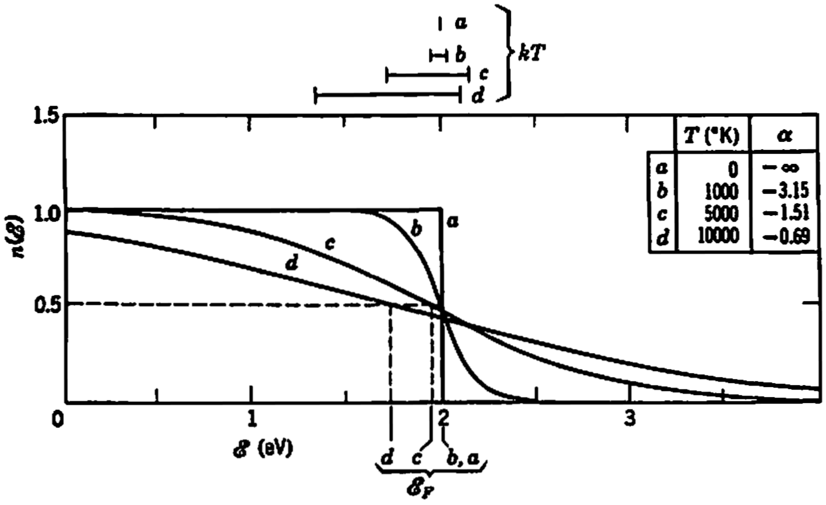
This distribution is called the **Fermi distribution**. The constant α is usually replaced by another constant call the **Fermi energy**. The Fermi energy is defined as

$$\varepsilon_f = -\alpha kT$$

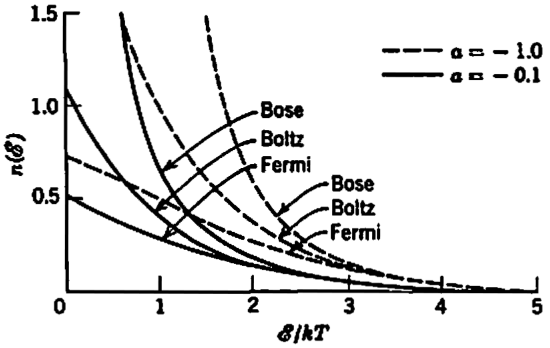
Using the Fermi energy, we can rewrite the Fermi distribution as

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_f)/kT} + 1}$$

The Fermi distribution is schematically shown in the Figure on the right for four different temperatures. At large energies, the Fermi distribution approaches the Boltzmann distribution. At low energies, the density approaches 1, well below the density associated with the Boltzmann distribution.



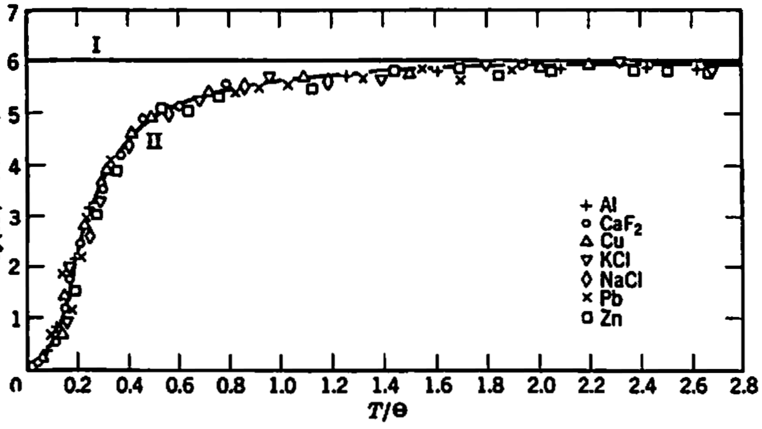
A comparison between the three distributions discussed so far is shown in the Figure at the right. We note the following:



- All curves converge when n becomes small. This is not a surprise since when the Boltzmann occupancy of states is small, the Pauli exclusion principle does not play a critical role.
- When the Boltzmann occupancy of states is large, the Pauli exclusion principle will have a significant impact and the three distributions diverge. The Fermi occupancy will always be less than the Boltzmann occupancy; the Bose occupancy will always be larger than the Boltzmann occupancy.
- Curves for different αs are shifted in ε/kT space. The α parameter is related to some characteristic energy scale.

Specific Heat and Quantum Effects

The concept of **specific heat**, relates the change in energy of a system to the change in its temperature. It was found that the specific heat for solids at room temperature was similar for most materials and equal to



$$C_V = \frac{dE}{dT} = 3R \simeq 6 \text{ cal/mole/K}$$

and consistent with the expected value for ideal gases. The observed behavior can be understood if the system is assumed to consist out of N atoms, vibrating independently in three dimensions and assuming that the average kinetic energy is kT.

At low temperatures the specific heat behaves differently:

- At low temperatures, C_V varies for different materials.
- At low temperatures, C_V varies with temperature as T^3.

Einstein tried to account for these observations by proposing that the average kinetic energy of the particles is not kT but $h\nu / \left(e^{h\nu/kT} - 1\right)$. There were several problems with this proposal:

- In order to provide reasonable agreement with the data, a different characteristic frequency is required for each material.
- The proposal cannot account for the observed T^3 dependence at low temperatures.

The solution to the problem was found by Debye. His solution involved the following steps:

- Assume that the system consists of $3N$ coupled vibrators. In this model the particles are distinguishable and we can use the Boltzmann distribution function; however, the particles are strongly interaction, which was not one of the basic assumption that was made in the derivation of the Boltzmann distribution function.
- For longitudinal vibrations the following relation can be used to determine the number of states in a small frequency range:

$$N(\nu)d\nu = \frac{4\pi \overbrace{V}^{\text{volume}}}{\underbrace{v^3}_{\text{velocity}}} \underbrace{\nu^2}_{\text{frequency}} d\nu$$

- Debye assumed that there are $3N_0$ vibrators per mole (N_0 is Avogadro's constant). This requires that there is a limiting frequency. This limiting frequency is defined by the following requirement:

$$\int_0^{\nu_{\max}} N(\nu)\,d\nu = 3N_0$$

Using the expression for N from the previous bullet, we can rewrite this expression as

$$\int_0^{\nu_{\max}} \frac{4\pi V}{v^3}\nu^2\,d\nu = \frac{4\pi V}{3v^3}\nu_{\max}^3 = 3N_0 \quad\Rightarrow\quad \nu_{\max} = v\left(\frac{9N_0}{4\pi V}\right)^{1/3}$$

- Assuming that the average energy of an oscillator is equal to $h\nu/\left(e^{h\nu/kT}-1\right)$ and that all frequencies between 0 and the maximum frequency are occupied, we can determine the energy contained within the system being considered:

$$E = \int_0^{\nu_{\max}} \varepsilon N(\nu)\,d\nu = \int_0^{\nu_{\max}} \frac{h\nu}{e^{h\nu/kT}-1}\frac{4\pi V}{v^3}\nu^2\,d\nu = \frac{4\pi V}{v^3}h\int_0^{\nu_{\max}} \frac{1}{e^{h\nu/kT}-1}\nu^3\,d\nu$$

In order to solve this integral we introduce the variable x where

$$x = \frac{h\nu}{kT} \quad\Rightarrow\quad \nu = \frac{kT}{h}x \quad\Rightarrow\quad d\nu = \frac{kT}{h}dx$$

The energy of the system can be rewritten in terms of x:

$$E = \frac{4\pi V}{v^3}h\int_0^{x_{\max}} \frac{1}{e^x-1}\left(\frac{kT}{h}x\right)^3\frac{kT}{h}dx = \frac{4\pi V}{v^3}h\left(\frac{kT}{h}\right)^4\int_0^{x_{\max}} \frac{x^3}{e^x-1}dx$$

where

$$x_{\max} = \frac{h}{kT}\nu_{\max} = \frac{h}{kT}v\left(\frac{9N_0}{4\pi V}\right)^{1/3} \quad\Rightarrow\quad \begin{cases} \dfrac{kT}{h} = \dfrac{\nu_{\max}}{x_{\max}} \\ \nu_{\max}^3 = v^3\left(\dfrac{9N_0}{4\pi V}\right) \quad\Rightarrow\quad \dfrac{4\pi V}{v^3} = \dfrac{9N_0}{\nu_{\max}^3} \end{cases}$$

The energy can thus be rewritten as

$$\begin{aligned} E &= \frac{9N_0}{\nu_{\max}^3} h \left(\frac{\nu_{\max}}{x_{\max}} \right)^4 \int_0^{x_{\max}} \frac{x^3}{e^x - 1} dx = 9N_0 \left(\frac{\nu_{\max}}{x_{\max}} \right) h \left(\frac{1}{x_{\max}} \right)^3 \int_0^{x_{\max}} \frac{x^3}{e^x - 1} dx = \\ &= 9N_0 \left(\frac{kT}{h} \right) h \frac{1}{x_{\max}^3} \int_0^{x_{\max}} \frac{x^3}{e^x - 1} dx = 9RT \frac{1}{x_{\max}^3} \int_0^{x_{\max}} \frac{x^3}{e^x - 1} dx \end{aligned}$$

The **characteristic temperature** of the system is defined as

$$\theta = \frac{h\nu_{\max}}{k} \quad \Rightarrow \quad x_{\max} = \frac{h}{kT} \nu_{\max} = \frac{h}{kT} \frac{k}{h} \theta = \frac{\theta}{T}$$

In terms of this temperature, we can rewrite the energy of the system as

$$E = 9R \left(\frac{T^4}{\theta^3} \right) \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx$$

- The system energy we just calculated can be used to determine the heat capacity by differentiating it with respect to *T*:

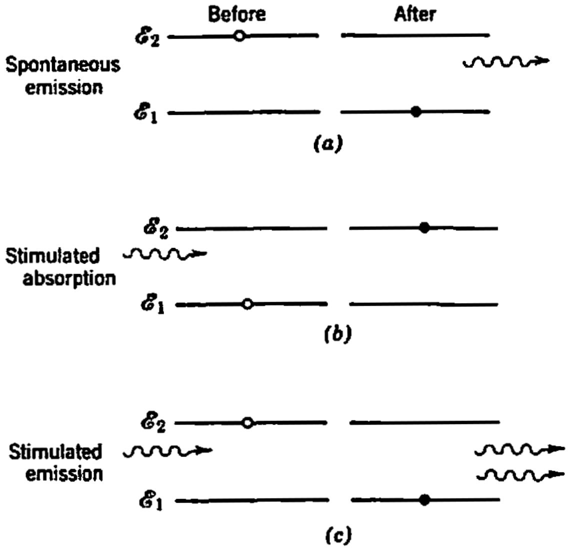
$$\begin{aligned} C_V = \frac{dE}{dT} &= 9R \left\{ \left[\frac{d}{dT} \left(\frac{T^4}{\theta^3} \right) \right] \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx + \left(\frac{T^4}{\theta^3} \right) \frac{(\theta / T)^3}{e^{\theta/T} - 1} \left(-\frac{\theta}{T^2} \right) \right\} = \\ &= 9R \left\{ 4 \left(\frac{T^3}{\theta^3} \right) \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx - \frac{\theta}{T} \frac{1}{e^{\theta/T} - 1} \right\} \end{aligned}$$

At low *T* the integral approaches $\pi^4/15$ and the first term provides the observed T^3 dependence of the heat capacity.

An important application of quantum statistics is **the laser**. To understand the operation of a laser, we need to understand the process of emission and absorption. The emission process is a quantum effect; fluctuations are required to produce the emission since "pure" eigenfunctions do not overlap. The mean lifetime of excited states in atoms is about 10^{-8} seconds. Some states, the so-called **metastable states**, have a much longer lifetime.

Consider an atom with two states: the ground state and a first excited state. If we examine a collection of atoms at a given temperature we find that a number of atoms will be in the first excited state. If the system is in equilibrium, the number of atoms that emits a photon is the same as the number of atoms that absorb a photon. For the **absorption process** we note the following:

- The absorbed photon must have the correct energy $h\nu$.
- The number of transitions is proportional to the energy density $\rho(\nu)$.
- The transition rate for absorption is equal to $R_{1\to 2} = B_{12}\rho(\nu)$ where B_{12} is the matrix element that includes information on the properties of the states involved in the transition.



The **emission process** involves two processes: **spontaneous emission** and **stimulated emission**. The rate of spontaneous emission only depends on a matrix element connecting the two states. The rate of spontaneous emission depends on both a matrix element that includes information on the properties of the states involved in the transition and on the energy density. The total emission rate is equal to

$$R_{2\to 1} = A_{21} + B_{21}\rho(\nu)$$

If the system is in equilibrium we must require that

$$n_1R_{1\to 2} = n_2R_{2\to 1} \quad \Rightarrow \quad n_1B_{12}\rho(\nu) = n_2A_{21} + n_2B_{21}\rho(\nu)$$

This equation can be used to determine the energy density $\rho(\nu)$:

$$\rho(\nu) = \frac{n_2A_{21}}{n_1B_{12} - n_2B_{21}} = \frac{A_{21}}{\frac{n_1}{n_2}B_{12} - B_{21}} = \frac{A_{21}/B_{21}}{\frac{n_1}{n_2}\left(B_{12}/B_{21}\right) - 1} =$$

$$= \frac{A_{21}/B_{21}}{\left(B_{12}/B_{21}\right)\frac{e^{-\varepsilon_1/kT}}{e^{-\varepsilon_2/kT}} - 1} = \frac{A_{21}/B_{21}}{\left(B_{12}/B_{21}\right)e^{(\varepsilon_2-\varepsilon_1)/kT} - 1} = \frac{A_{21}/B_{21}}{\left(B_{12}/B_{21}\right)e^{h\nu/kT} - 1}$$

But the energy density associated with the external radiation field must be consistent with black-body radiation. We thus must require that

$$\rho(\nu) = \frac{A_{21}/B_{21}}{(B_{12}/B_{21})e^{h\nu/kT}-1} = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}$$

This requires that

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}$$
$$\frac{B_{12}}{B_{21}} = 1$$

We can now estimate the ratio of spontaneous emission to stimulated emission. This ratio is equal to

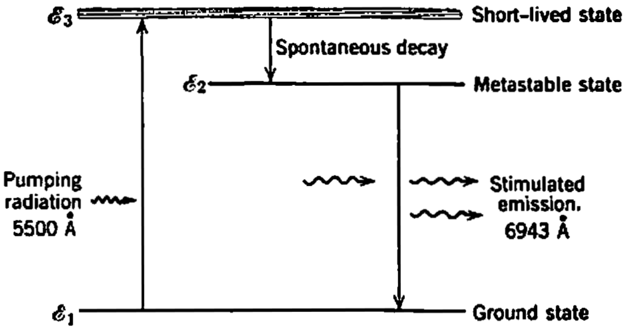
$$\frac{A_{21}}{B_{21}\rho(\nu)} = \frac{A_{21}}{B_{21}\left(\dfrac{A_{21}/B_{21}}{(B_{12}/B_{21})e^{h\nu/kT}-1}\right)} = (B_{12}/B_{21})e^{h\nu/kT}-1 = e^{h\nu/kT}-1$$

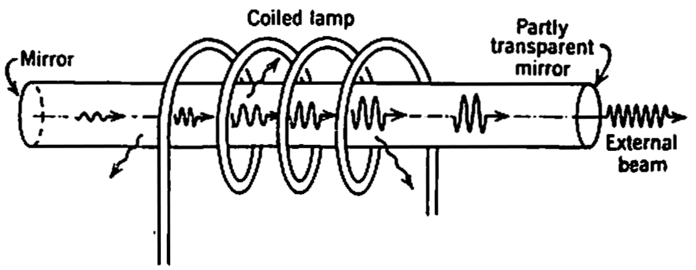
This equation shows that stimulated emission becomes important when $h\nu \approx kT$. Stimulated emission dominates when $h\nu \ll kT$.

The ratio of emission to absorption is equal to

$$\frac{n_2A_{21}+n_2B_{21}\rho(\nu)}{n_1B_{12}\rho(\nu)} = \left(\frac{n_2}{n_1}\right)\left\{\frac{A_{21}}{B_{12}\rho(\nu)}+\frac{B_{21}}{B_{12}}\right\} = \left(\frac{n_2}{n_1}\right)\left\{e^{h\nu/kT}-1+1\right\} = \frac{n_2}{n_1}e^{h\nu/kT} \underset{h\nu\ll kT}{\cong} \frac{n_2}{n_1}$$

This relation shows that if we can create a **population inversion** ($n_2 >> n_1$) then emission will dominate absorption. In a laser, a population inversion is created by optical pumping of atoms to a state that is short lived and decays to a metastable state. This is schematically shown in the energy diagram on the right-hand side.





The black-body frequency distribution is consistent with viewing the photons as a **photon gas**. Since photons have spin 1, they are bosons and their properties are governed by the Bose distribution:

$$n(\varepsilon) = \frac{1}{e^{\alpha} e^{\varepsilon/kT} - 1}$$

Since photons can be created and destroyed, the energy integral of the Bose distribution can change. Since the constant α is related to the total number of particles the system contains, we must conclude that for a photon gas, there can be no dependence of n on α. The number of photons in a state of energy $\varepsilon = h\nu$ is thus equal to

$$n(\varepsilon) = \frac{1}{e^{\varepsilon/kT} - 1}$$

If $N(\varepsilon)d\varepsilon$ is the number of quantum states with an energy between ε and $d\varepsilon$, the number of photons with an energy between ε and $d\varepsilon$ is equal to $n(\varepsilon)N(\varepsilon)d\varepsilon$. Since each photon carries an energy ε, the total photon energy between ε and $d\varepsilon$ is equal to $\varepsilon n(\varepsilon)N(\varepsilon)d\varepsilon$. Using the expression we obtained in Chapter 1 for $N(\varepsilon)d\varepsilon$ we can now determine the energy density of the photon gas per unit volume:

$$\rho(\varepsilon)d\varepsilon = \frac{\varepsilon n(\varepsilon)N(\varepsilon)d\varepsilon}{V} = \frac{\varepsilon\left(\frac{1}{e^{\varepsilon/kT} - 1}\right)\left(\frac{8\pi V}{c^3}\frac{\varepsilon^2 d\varepsilon}{h^3}\right)}{V} = \frac{8\pi}{c^3 h^3}\frac{\varepsilon^3 d\varepsilon}{e^{\varepsilon/kT} - 1}$$

Since $\varepsilon = h\nu$, we can convert the energy density from the function of energy to a function of frequency:

$$\rho(\nu)d\nu = \rho(\varepsilon)\frac{d\varepsilon}{h} = \frac{8\pi}{c^3 h^3}\frac{h^3\nu^3 h d\nu}{e^{h\nu/kT} - 1} = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT} - 1}d\nu$$

The frequency distribution of the photon gas is thus given by

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT} - 1}$$

which is the black-body distribution.

A **Bose condensate** is system consisting out of bosons for which the total number of particles is constant. This requirement differentiates a Bose condensate from the photon gas. If we have a Bose condensate with N particles, we can write the energy distribution of these particles as

$$n(\varepsilon) = \frac{1}{e^{\alpha} e^{\varepsilon/kT} - 1}$$

The constant α is fixed by requiring that

$$N = \int_0^\infty n(\varepsilon) N(\varepsilon) d\varepsilon = \int_0^\infty \frac{1}{e^{\alpha} e^{\varepsilon/kT} - 1} \underbrace{\frac{4\pi V}{h^3} \left(2m^3\right)^{1/2} \varepsilon^{1/2} d\varepsilon}_{\text{Density of states in sqaure well}} = \underbrace{\frac{\left(2\pi mkT\right)^{3/2}}{h^3} V e^{-\alpha}}_{\substack{\text{Classical distribution for} \\ \text{classical oscillators.}}} \left\{ 1 + \underbrace{\frac{1}{2^{3/2}} e^{-\alpha}}_{\text{Correction}} + \ldots \right\}$$

The factor $e^{-\alpha}$ is thus proportional to *N*. To first approximation:

$$e^{-\alpha} = \frac{Nh^3}{\left(2\pi mkT\right)^{3/2} V} \quad \Rightarrow \quad n(\varepsilon) = \frac{1}{\frac{\left(2\pi mkT\right)^{3/2} V}{Nh^3} e^{\varepsilon/kT} - 1}$$

The average energy per boson is equal to

$$\bar{\varepsilon} = \frac{\int_0^\infty \varepsilon n(\varepsilon) N(\varepsilon) d\varepsilon}{N} = \frac{\int_0^\infty \varepsilon n(\varepsilon) N(\varepsilon) d\varepsilon}{\int_0^\infty n(\varepsilon) N(\varepsilon) d\varepsilon} = \frac{\int_0^\infty \frac{1}{e^{\alpha} e^{\varepsilon/kT} - 1} \frac{4\pi V}{h^3} \left(2m^3\right)^{1/2} \varepsilon^{3/2} d\varepsilon}{\frac{\left(2\pi mkT\right)^{3/2}}{h^3} V e^{-\alpha} \left\{ 1 + \frac{1}{2^{3/2}} e^{-\alpha} + \ldots \right\}} =$$

$$= \frac{\frac{\left(2\pi mkT\right)^{3/2}}{h^3} V e^{-\alpha} \left(\frac{3}{2} kT\right) \left\{ 1 + \frac{1}{2^{5/2}} e^{-\alpha} + \ldots \right\}}{\frac{\left(2\pi mkT\right)^{3/2}}{h^3} V e^{-\alpha} \left\{ 1 + \frac{1}{2^{3/2}} e^{-\alpha} + \ldots \right\}} \approx \frac{3}{2} kT \left(1 + \frac{1}{2^{5/2}} e^{-\alpha} \right) \left(1 - \frac{1}{2^{3/2}} e^{-\alpha} \right) =$$

$$= \frac{3}{2} kT \left(1 + \left(\frac{1}{2^{5/2}} - \frac{1}{2^{3/2}} \right) e^{-\alpha} - \frac{1}{2^4} e^{-2\alpha} \right) \approx \frac{3}{2} kT \left(1 - \underbrace{\frac{1}{2^{5/2}} e^{-\alpha}}_{\substack{\text{Deviation from} \\ \text{the classical gas}}} \right)$$

We thus conclude that the average energy of a boson is less than the energy of a classical gas molecule. The pressure of a boson gas is thus lower than the corresponding pressure of a classical gas. The effect of the correction (the second term in the expression of the average energy) shows up for low *m*, low *T*, and high *N*/*V*.

If instead of dealing with bosons we deal with fermions, we can use a similar calculation to the one calculation of the boson gas to determine the average energy of the fermions in the Fermi gas. For the Fermi gas we find

$$\overline{\varepsilon} = \frac{3}{2}kT\left(1 + \underbrace{\frac{1}{2^{5/2}}e^{-\alpha}}_{\substack{\text{Deviation from}\\ \text{the classical gas}}}\right)$$

We note that for a Fermi gas the average energy exceeds the average energy of a classical gas. As a result, the pressure of a Fermi gas is higher than that of a classical gas.

An example of a Fermi gas is a **free-electron gas**. A free-electron gas shows up in solids in the form of conduction electrons. The Fermi energy of these electrons is

$$\varepsilon_{fermi} = -\alpha kT = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}$$

The Fermi energy of a silver atom is about 5.5 eV. At a temperature of 4×10^4 K, the Fermi energy is equal to *kT*. At temperatures below 10^4 K, *kT* is much less than the Fermi energy and the electron occupancy distribution can be described by a step function. At temperatures above 10^5 K, the distribution function can be described by an exponential fall off.