Bose-Einstein Statistics

Any number of particles can exist in one quantum state.

Distribution function can be given by

$$f_{B.E.}(\varepsilon) = \frac{1}{e^{\alpha} e^{\varepsilon/kT} - 1}$$

where α may be a function of temperature, T.

For Photon gas $\alpha = 0 \Rightarrow e^{\alpha} = 1$

Bose-Einstein Condensation

If the temperature of any gas is reduced, the wave packets grow larger as the atoms lose momentum according to uncertainty principle.

When the gas becomes very cold, the dimensions of the wave packets exceeds the average atomic spacing resulting into overlapping of the wave packets. If the atoms are bosons, eventually, all the atoms fall into the lowest possible energy state resulting into a single wave packet. This is called Bose-Einstein condensation.

The atoms in such a Bose-Einstein condensate are barely moving, are indistinguishable, and form one entity – a superatom.

Fermi-Dirac Statistics

Obey Pauli's exclusion Principle

Distribution function can be given by

$$f_{F.D.}(\varepsilon) = \frac{1}{e^{\alpha} e^{\varepsilon/kT} + 1}$$

f (ϵ) can never exceed 1, whatever be the value of α, ϵ and T. So only one particle can exist in one quantum state.

α is given by

$$\alpha = -\frac{\varepsilon_F}{kT}$$

where ε_F is the Fermi Energy

then

$$f_{F.D.}(\varepsilon) = \frac{1}{e^{(\varepsilon-\varepsilon_F)/kT} + 1}$$

Case I:

T = 0

$$(\varepsilon - \varepsilon_F)/kT = -\infty \qquad \text{For } \epsilon < \epsilon_F$$

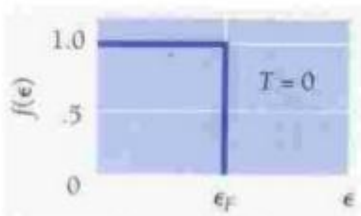
$$(\varepsilon - \varepsilon_F)/kT = +\infty \qquad \text{For } \epsilon > \epsilon_F$$

For $\epsilon < \epsilon_F$

$$f_{F.D.}(\varepsilon) = \frac{1}{e^{-\infty} + 1} = 1$$

For $\epsilon > \epsilon_F$

$$f_{F.D.}(\varepsilon) = \frac{1}{e^{+\infty} + 1} = 0$$



Thus at T = 0, For $\epsilon < \epsilon_F$ all energy states from $\epsilon = 0$ to ϵ_F are occupied as

$$f_{F.D.}(\varepsilon) = 1$$

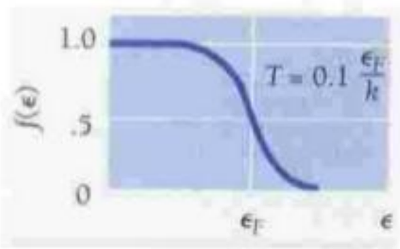
Thus at T = 0, all energy states for which $\epsilon > \epsilon_F$ are vacant.

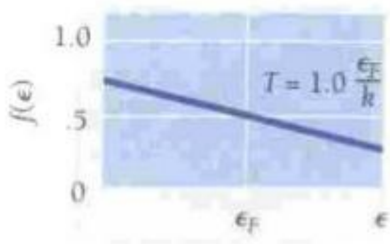
$$f_{F.D.}(\varepsilon) = 0$$

Case II:

T > 0

Some of the filled states just below ϵ_F becomes vacant while some just above ϵ_F become occupied.



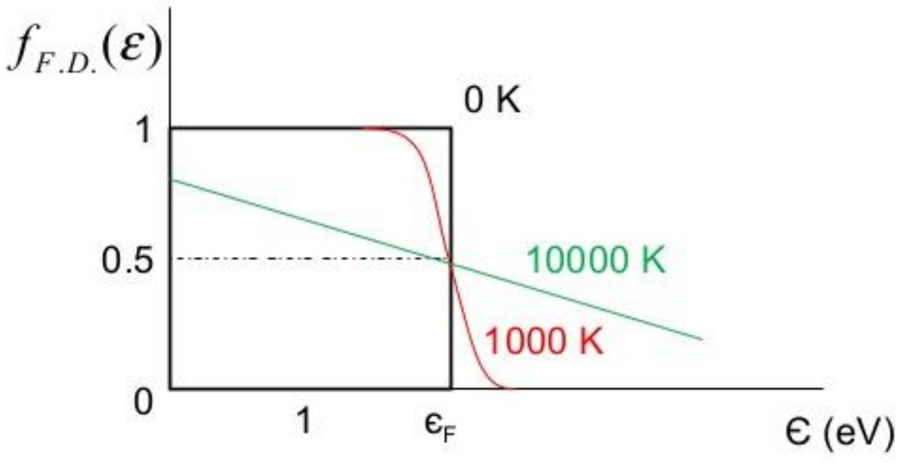


Case III:

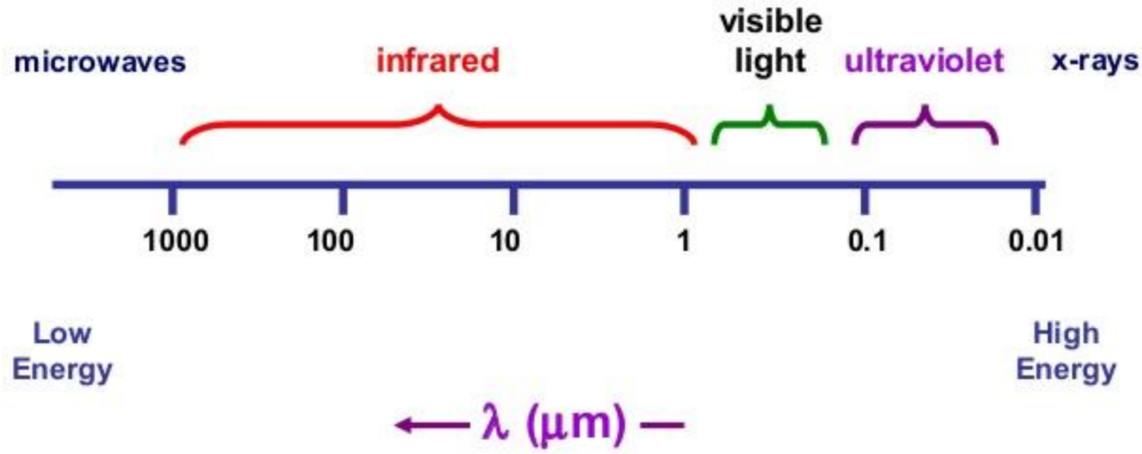
At $\epsilon = \epsilon_F$

$$f_{F.D.}(\varepsilon) = \frac{1}{e^0 + 1} = \frac{1}{2} \quad \text{For all T}$$

Probability of finding a fermion (i.e. electron in metal) having energy equal to fermi energy (ϵ_F) is ½ at any temperature.



Electromagnetic Spectrum



Black Body Radiation

All objects radiate electromagnetic energy continuously regardless of their temperatures.

Though which frequencies predominate depends on the temperature.

At room temperature most of the radiation is in infrared part of the spectrum and hence is invisible.

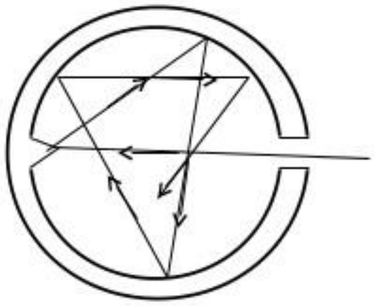
The ability of a body to radiate is closely related to its ability to absorb radiation.

A body at a constant temperature is in thermal equilibrium with its surroundings and must absorb energy from them at the same rate as it emits energy.

A perfectly **black body** is the one which absorbs completely all the radiation, of whatever wavelength, incident on it.

Since it neither transmits any radiation, it appears black whatever the color of the incident radiation may be.

There is no surface available in practice which will absorb all the radiation falling on it.



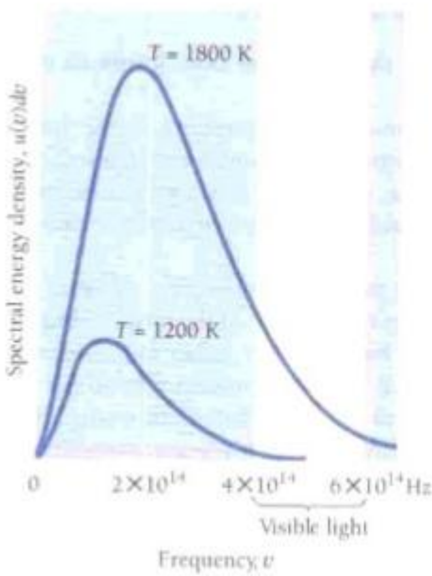
The cavity walls are constantly emitting and absorbing radiation, and this radiation is known as black body radiation.

Characteristics of Black Body Radiation

(i) The total energy emitted per second per unit area (radiancy E or area under curve) increases rapidly with increasing temperature.

(ii) At a particular temperature, the spectral radiancy is maximum at a particular frequency.

(iii) The frequency (or wavelength, λ_m) for maximum spectral radiancy decreases in direct proportion to the increase in temperature. This is called "Wien's displacement law"



$$\lambda_m \times T = \text{constant } (2.898 \times 10^{-3} \text{ m.K})$$

Planck's Radiation Law

Planck assumed that the atoms of the walls of cavity radiator behave as oscillators with energy

$$\varepsilon_n = nh\nu \qquad n = 0,1,2,3....$$

The average energy of an oscillator is

$$\bar{\varepsilon} = \frac{\varepsilon}{N} \qquad \text{N is total no. of Oscillators}$$

$$\bar{\varepsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} \qquad \text{(i)}$$

Thus the energy density (u_ν) of radiation in the frequency range ν to ν + dν is

$$u_\nu d\nu = \frac{8\pi\nu^2 d\nu}{c^3} \times \bar{\varepsilon}$$

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

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1}$$

This is Planck's Radiation formula in terms of frequency.

In terms of wavelength

$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda kT} - 1}$$

This is Planck's Radiation formula in terms of wavelength.

Case I : (Rayleigh-Jeans Law)

$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{hc/\lambda kT}-1}$$

When λ is large then $e^{hc/\lambda kT} \approx 1 + \frac{hc}{\lambda kT}$

$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5\left(1+\frac{hc}{\lambda kT}-1\right)}d\lambda$$

$$u_\lambda d\lambda = \frac{8\pi kT}{\lambda^4}d\lambda$$

This is Rayleigh-Jeans Law for longer λ's.

Case II : (Wein's Law)

$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{hc/\lambda kT}-1}$$

When λ is very small then $e^{hc/\lambda kT} >> 1$

$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}e^{-hc/\lambda kT}d\lambda$$

This is Wein's Law for small λ's.

$$u_\lambda d\lambda = \frac{A}{\lambda^5}e^{B/\lambda kT}d\lambda$$

This is another form of Wein's Law..

Here A and B are constants.

Stefan's Law

Planck's Radiation formula in terms of frequency is

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3}\frac{d\nu}{e^{h\nu/kT}-1}$$

$$\frac{c}{4}u_\nu d\nu = \frac{2\pi h\nu^3}{c^2}\frac{d\nu}{e^{h\nu/kT}-1}$$

The spectral radiancy E_v is related to the energy density u_v by

$$E_\nu = \frac{c}{4}u_\nu$$

$$E_\nu d\nu = \frac{2\pi h}{c^2}\frac{\nu^3 d\nu}{e^{h\nu/kT}-1}$$

$$E = \int_0^\infty E_\nu d\nu = \frac{2\pi h}{c^2}\int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/kT}-1}$$

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

$$E = \frac{2\pi k^4 T^4}{h^3 c^2}\int_0^\infty \frac{x^3 dx}{e^x - 1}$$

But $\int_0^\infty \frac{x^3 dx}{e^x-1} = \frac{\pi^4}{15}$

$$E = \frac{2\pi^5 k^4}{15h^3c^2} T^4$$

Let $\frac{2\pi^5 k^4}{15h^3c^2} = \sigma$ (Stefan's constant)

$$E = \sigma T^4$$

This is Stefan's Law.

Here $\sigma = \frac{2\pi^5 k^4}{15h^3c^2}$ = 5.67 x 10^{-5} erg/(cm^2.sec.K^4)

= 5.67 x 10^{-8} W/(m^2.K^4)

Wein's Displacement Law

Planck's Radiation formula in terms of frequency is

$$u_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

Using $\frac{d(u_\lambda)}{d\lambda} = 0$ for $\lambda = \lambda_{\max}$

$$\frac{hc}{kT\lambda_{\max}} = \text{Constant}$$

$\lambda_m \times T =$ constant (2.898 x 10^{-3} m.K)

Peaks in Black Body radiation shifts to shorter wavelength with increase in temperature.

Specific Heat of Solids

Atoms in solid behave as oscillators.

In case of solids total average energy per atom per degree of freedom is kT (0.5kT from K.E. and 0.5kT from P.E.).

Each atom in the solid should have total energy = 3kT (3 degrees of freedom).

For one mole of solid, total energy, E = $3N_o kT$ (classically)

Here N_o is the Avogadro number.

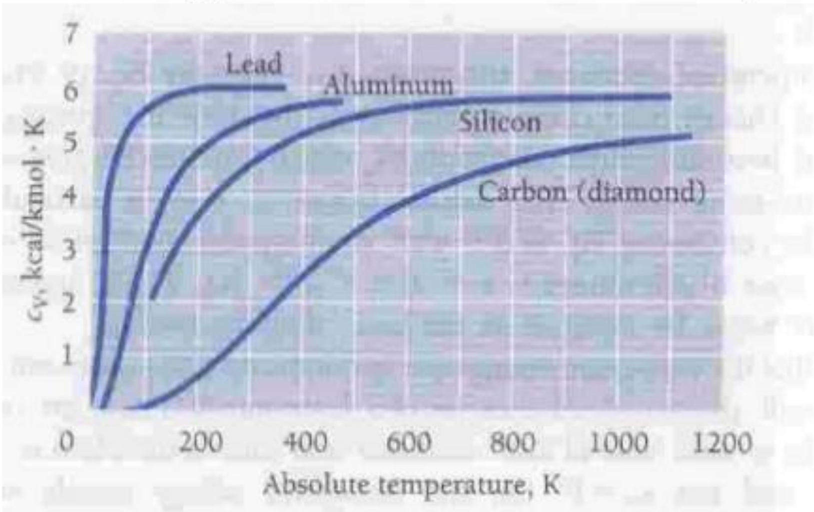
$$E = 3RT$$

Specific heat at constant volume is

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = 3R \quad \sim 6 \text{ kcal/kmol.K}$$

This is Dulong & Petit's Law.

This means that atomic specific heat (at constant volume) for all solids is approx 6 kcal/kmol.K and is independent of T.



Dulong and Petit's Law fails for light elements such as B, Be and C.

Also it is not applicable at low temperatures for all solids.

Einstein's theory of Specific Heat of Solids

According to it the motion of the atoms in a solid is oscillatory.

The average energy per oscillator atom) is

$$\bar{\varepsilon} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

The total energy for one mole of solid in three degrees of freedom.

$$E = 3N_o \frac{h\nu}{e^{h\nu/kT} - 1}$$

The molar specific heat of solid is $C_v = \left(\frac{\partial E}{\partial T} \right)_V$

$$C_v = 3N_o h\nu \left(\frac{h\nu}{kT^2} \right) \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} = 3N_o k \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

$$C_v = 3R \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

This is Einstein's specific heat formula.

Case I:

At high T, kT >> hv then

$$e^{h\nu/kT} \approx 1 + \frac{h\nu}{kT}$$

$$C_v \approx 3R\left(\frac{hv}{kT}\right)^2 \frac{\left(1+\frac{hv}{kT}\right)}{\left(1+\frac{hv}{kT}-1\right)^2}$$

$$C_v \approx 3R\left(1+\frac{hv}{kT}\right)$$

$$C_v \approx 3R \qquad (\therefore kT >> hv)$$

This is in agreement with Dulong & Petit's Law at high T.

Case II: At low T, hv >> kT then $e^{hv/kT} >> 1$

$$C_v \approx 3R\left(\frac{hv}{kT}\right)^2 e^{-hv/kT}$$

This implies that as $T \to 0, C_v \to 0$

i.e. is in agreement with experimental results at low T.

Free electrons in a metal

Typically, one metal atom gives one electron.

One mole atoms gives one mole of free electrons, (N_o)

If each free electron can behave like molecules of an ideal gas. Then

Average K.E. for 1 mole of electron gas, $E_e = \frac{3}{2} N_o kT = \frac{3}{2} RT$

Molar specific heat of electron gas, $\left(C_v\right)_e = \left(\frac{\partial E_e}{\partial T}\right)_V = \frac{3}{2} R$

Then total specific heat in metals at high T should be

$$C_v = 3R + \frac{3}{2} R = \frac{9}{2} R$$

But experimentally at high T $\quad C_v \approx 3R$

$\Rightarrow$ Free electrons don't contribute in specific heat,

Why?

Electrons are fermions and have upper limit on the occupancy of the quantum state.

By definition highest state of energy to be filled by a free electron at T = 0 is obtained at $\epsilon = \epsilon_F$

The no. of electrons having energy ϵ is

$$N = \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon \quad \text{where} \quad g(\varepsilon) d\varepsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \sqrt{\varepsilon}\, d\varepsilon$$

Here V is the volume of the metal

$$N = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3}\int_0^{\varepsilon_F}\sqrt{\varepsilon}\,d\varepsilon \qquad = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3}\varepsilon_F{}^{3/2}$$

$$\Rightarrow \varepsilon_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{3/2} \qquad \text{(i)}$$

where N/V is the density of free electrons.

Electron energy distribution

No. of electrons in the electron gas having energy between ϵ and ϵ + dϵ is

$$n(\varepsilon)d\varepsilon = g(\varepsilon)f(\varepsilon)d\varepsilon$$

$$n(\varepsilon)d\varepsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3}\frac{\varepsilon^{3/2}\sqrt{\varepsilon}}{e^{(\varepsilon-\varepsilon_F)/kT}+1}d\varepsilon$$

using (i)

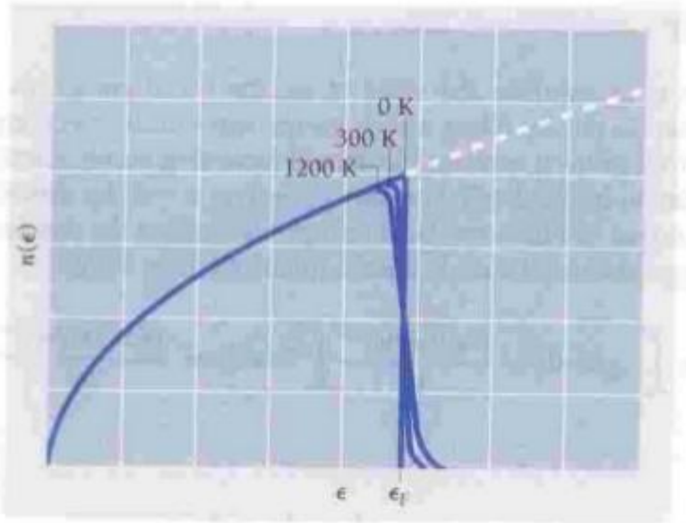
$$n(\varepsilon)d\varepsilon = \left(\frac{3N}{2}\right)\frac{\varepsilon^{-3/2}\sqrt{\varepsilon}}{e^{(\varepsilon-\varepsilon_F)/kT}+1}d\varepsilon$$

This is electron energy distribution formula, according to which distribution of electrons can be found at different temperatures.

When a metal is heated then only those electrons which are near the top of the fermi level (kT of the Fermi energy) are excited to higher vacant energy states.

kT = 0.0025 eV at 300K

kT = 0.043 eV at 500K



The electrons in lower energy states cannot absorb more energy because the states above them are already filled.

This is why the free electrons contribution in specific heat is negligible even at high T.

Average electron energy at 0K

Total energy at 0K is

$$E_o = \int_0^{\varepsilon_F} \varepsilon n(\varepsilon) d\varepsilon$$

Since at 0K all electrons have energy less than or equal to ϵ_F

$$e^{(\varepsilon-\varepsilon_F)/kT} = e^{-\infty} = 0$$

$$E_o = \frac{3N}{2}\varepsilon_F^{-3/2}\int_0^{\varepsilon_F}\varepsilon^{3/2}d\varepsilon \quad = \frac{3N}{5}\varepsilon_F$$

Then average electron energy

$$\left(\bar{\varepsilon}_o\right) = \frac{E_o}{N} = \frac{3}{5}\varepsilon_F \quad \text{at 0K.}$$