Degrees of freedom, Equipartition of Energy and Black Body Radiation

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Recapitulate

Classical Physics

Physics before 20^{th} century, i.e., physics before the birth of Quantum Mechanics

- **Mechanics**
- **Electrodynamics**
- **Thermodynamics**

Mechanics

Newton's first law:

Law of inertia

Newton's second law:

Introduces force ($\vec{F}$) as responsible for the change in linear momentum ($\vec{p} = m\vec{\mathrm{v}}$)

$$\vec{F} = m\vec{a}$$

$$\vec{F} = d\vec{p}/dt$$

Newton's second law:

Law of action and reaction

$$\overrightarrow{F_{21}} = -\overrightarrow{F_{12}}$$

Newton's law of gravitation:

$$\vec{F} = -G\frac{m_1 m_2}{r^2}\hat{r}$$

Electrodynamics

Maxwell's Equations

Gauss's law (Electric field) $$\vec{\nabla} \bullet \vec{E} = \rho / \varepsilon_0$$

Gauss's law (Magnetic field) $$\vec{\nabla} \bullet \vec{B} = 0$$

Faraday's law $$\vec{\nabla} \times \vec{E} = -\partial \vec{B} / \partial t$$

Ampere's law $$\vec{\nabla} \times \vec{B} = \mu_0 \varepsilon_0 \partial \vec{E} / \partial t$$

Wave equation $$\nabla^2 E = \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2}$$

Light is an electromagnetic wave with velocity $c = \dfrac{1}{\sqrt{\varepsilon_0 \mu_0}}$

Thermodynamics

Zeroth Law: This is the game

Two systems in thermal equilibrium with a third system are in thermal equilibrium with each other.

First Law: You cannot win

You cannot get something out of nothing, because matter and energy are conserved. $\Delta E=Q+W$

Second Law: You cannot break even

Any transfer of energy will result in some wastage (disorder) unless temperature of absolute zero is achieved.

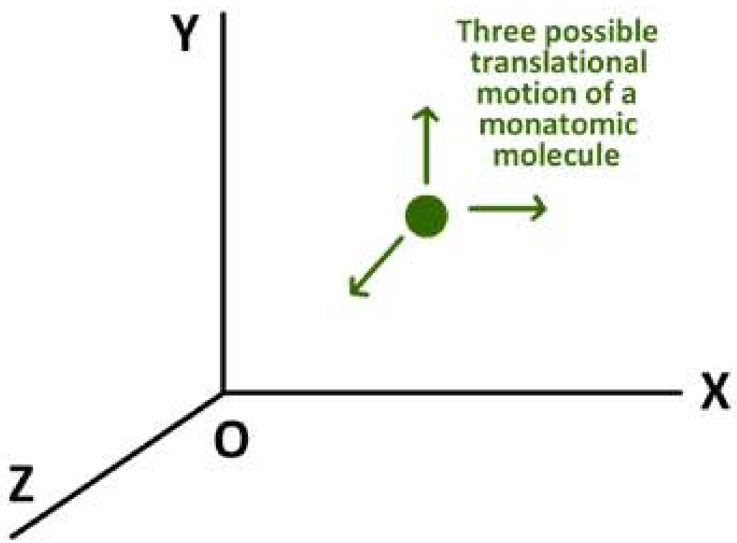
$\Delta S_{total} = \Delta S_{surrounding} + \Delta S_{system}$

Third Law: You cannot get out of the game

Absolute zero is unattainable.

Law of Equipartition of Energy

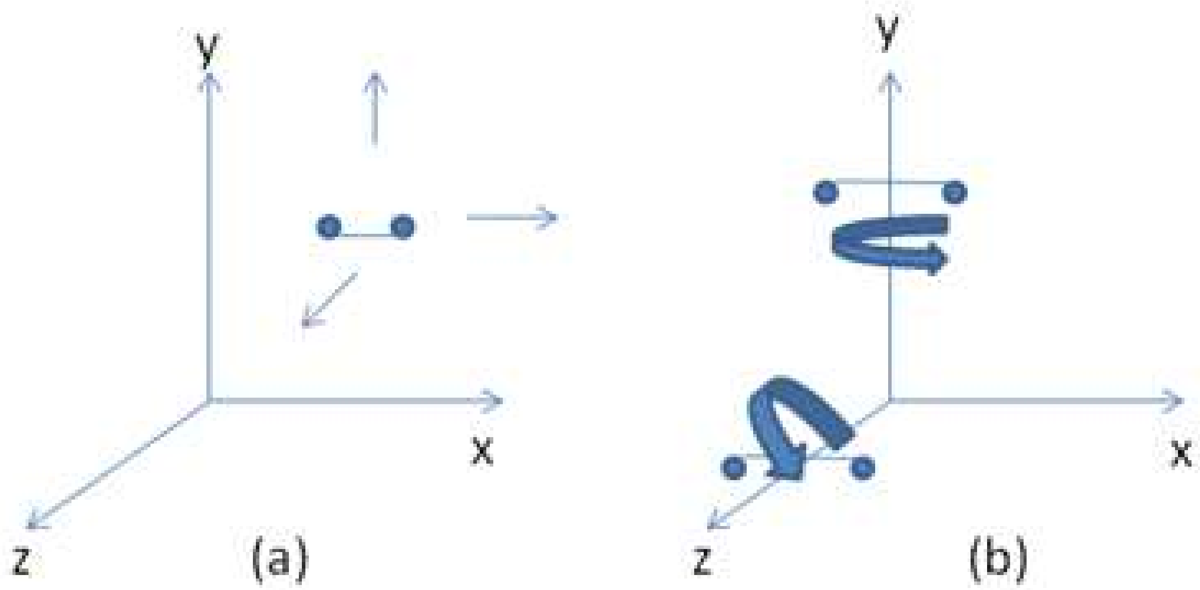
Degrees of freedom (DF): The minimum number of independent variables required for complete description of the state of a physical system.



Monoatomic molecule:

3 translational DF

Diatomic rigid molecule

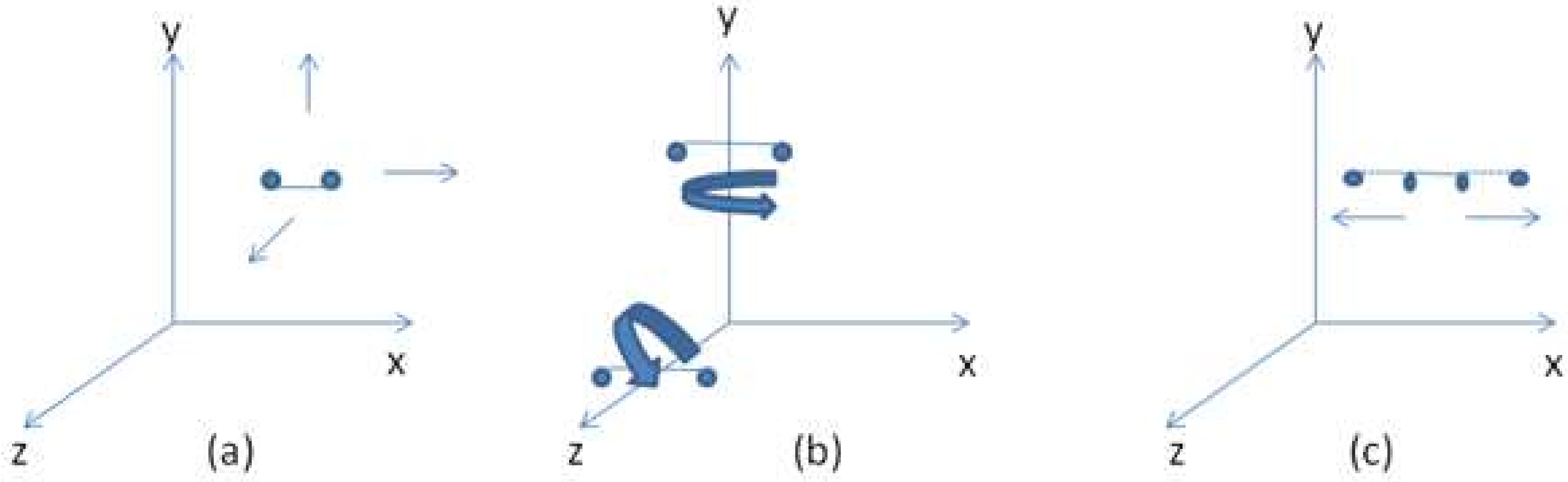


(a) Translational motion (of centre of mass) along three ⊥ axes

(b) Rotational motion along two axes ⊥ to the line joining the two atoms.

Total degrees of freedom: 3 translational, 2 rotational

Diatomic weakly bonded molecule



(a) **Translational motion** (of centre of mass) along three ⊥ axes

(b) **Rotational motion** along two axes ⊥ to the line joining the two atoms.

(c) **Vibrational motion** along the line joining the two atoms.

Total DF: 3 translational, 2 rotational, 1 vibrational

Generalization: N-atom Molecule

Linear Molecules

Translational DF : 3
Rotational DF : 2
Vibarional DF : 3N-5

Non Linear Molecules

Translational DF : 3
Rotational DF : 3
Vibarional DF : 3N-6

Summary:

	Translation*	Rotation	Vibration	Total DF
Monatomic	3	0	0	3
Diatomic	3	2	1	6
Linear polyatomic (N>2)	3	2	3N-5	3N
Nonlinear polyatomic (N>2)	3	3	3N-6	3N

* Centre of Mass

Law of Equipartition of Energy

At finite temperature (*T*), the energy is distributed as:

$$\frac{1}{2}kT$$ **For each Translational and Rotational DF**

$$kT$$ **For each vibrational DF**

($kT/2$ each for KE and PE)

k is the Boltzmann constant $= 1.38 \times 10^{-23}\, J.K^{-1}$

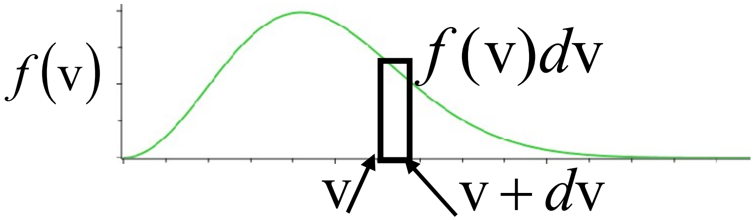
Supporting Material

Boltzmann distribution

$$f(E) = Ae^{-\frac{E}{kT}}$$

1-D translational motion (x-direction)

$KE = m\mathrm{v}_{\mathrm{x}}^2/2 \qquad E = m\mathrm{v}_{\mathrm{x}}^2/2$



Average Energy

$$\langle E \rangle = \frac{\int_{-\infty}^{\infty} Ef(E)d\mathrm{v}_{\mathrm{x}}}{\int_{-\infty}^{\infty} f(E)d\mathrm{v}_{\mathrm{x}}} = \frac{\frac{m}{2}\int_{-\infty}^{\infty} \mathrm{v}_{\mathrm{x}}^2 e^{-\frac{m\mathrm{v}_{\mathrm{x}}^2}{2kT}} d\mathrm{v}_{\mathrm{x}}}{\int_{-\infty}^{\infty} e^{-\frac{m\mathrm{v}_{\mathrm{x}}^2}{2kT}} d\mathrm{v}_{\mathrm{x}}}$$

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{\pi^{1/2}}{2\alpha^{3/2}}$$

$$\alpha = m/2kT$$

$$= \frac{1}{2}kT$$

Supporting Material

$$f(E) = Ae^{-\frac{E}{kT}}$$

1-D oscillator

$$E = KE + PE = \frac{1}{2}m\mathrm{v}_x^2 + \frac{1}{2}\kappa x^2$$

κ **= force constant**

Average Energy

$$\langle E \rangle = \frac{\int_{-\infty}^{\infty} Ef(E)d\mathrm{v}_x dx}{\int_{-\infty}^{\infty} f(E)d\mathrm{v}_x dx} = \frac{\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} d\mathrm{v}_x \left(\frac{m\mathrm{v}_x^2}{2} + \frac{\kappa x^2}{2}\right) e^{-m\mathrm{v}_x^2/2kT} e^{-\kappa x^2/2kT}}{\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} d\mathrm{v}_x e^{-m\mathrm{v}_x^2/2kT} e^{-\kappa x^2/2kT}}$$

$$= \frac{\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} d\mathrm{v}_x \left(\frac{m\mathrm{v}_x^2}{2}\right) e^{-m\mathrm{v}_x^2/2kT} e^{-\kappa x^2/2kT} + \left(\frac{\kappa x^2}{2}\right) e^{-m\mathrm{v}_x^2/2kT} e^{-\kappa x^2/2kT}}{\int_{-\infty}^{\infty} e^{-\kappa x^2/2kT} dx \int_{-\infty}^{\infty} e^{-m\mathrm{v}_x^2/2kT} d\mathrm{v}_x}$$

$$\langle E\rangle = \frac{\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} d\mathrm{v}_{\mathrm{x}} \left(m\mathrm{v}_{\mathrm{x}}^2/2\right) e^{-m\mathrm{v}_{\mathrm{x}}^2/2kT} e^{-\kappa x^2/2kT} + \left(\kappa x^2/2\right) e^{-m\mathrm{v}_{\mathrm{x}}^2/2kT} e^{-\kappa x^2/2kT}}{\int_{-\infty}^{\infty} e^{-\kappa x^2/2kT} dx \int_{-\infty}^{\infty} e^{-m\mathrm{v}_{\mathrm{x}}^2/2kT} d\mathrm{v}_{\mathrm{x}}}$$

$$\langle E\rangle = \frac{\int_{-\infty}^{\infty} \left(m\mathrm{v}_{\mathrm{x}}^2/2\right) e^{-m\mathrm{v}_{\mathrm{x}}^2/2kT} d\mathrm{v}_{\mathrm{x}} \int_{-\infty}^{\infty} e^{-\kappa x^2/2kT} dx}{\int_{-\infty}^{\infty} e^{-\kappa x^2/2kT} dx \int_{-\infty}^{\infty} e^{-m\mathrm{v}_{\mathrm{x}}^2/2kT} d\mathrm{v}_{\mathrm{x}}} + \frac{\int_{-\infty}^{\infty} (\kappa x^2/2) e^{-\kappa x^2/2kT} dx \int_{-\infty}^{\infty} e^{-m\mathrm{v}_{\mathrm{x}}^2/2kT} d\mathrm{v}_{\mathrm{x}}}{\int_{-\infty}^{\infty} e^{-\kappa x^2/2kT} dx \int_{-\infty}^{\infty} e^{-m\mathrm{v}_{\mathrm{x}}^2/2kT} d\mathrm{v}_{\mathrm{x}}}$$

$$\langle E\rangle = \frac{\int_{-\infty}^{\infty} \left(m\mathrm{v}_{\mathrm{x}}^2/2\right) e^{-m\mathrm{v}_{\mathrm{x}}^2/2kT} d\mathrm{v}_{\mathrm{x}}}{\int_{-\infty}^{\infty} e^{-m\mathrm{v}_{\mathrm{x}}^2/2kT} d\mathrm{v}_{\mathrm{x}}} + \frac{\int_{-\infty}^{\infty} (\kappa x^2/2) e^{-\kappa x^2/2kT} dx}{\int_{-\infty}^{\infty} e^{-\kappa x^2/2kT} dx} = \frac{1}{2}kT + \frac{1}{2}kT$$

$$= kT$$

Thinking of Physicists towards the end of 19^{th} century

"The more important fundamental laws and the facts of physical science have all been discovered and they are so firmly established that the possibility of their ever being supplanted in consequence of the new discoveries is exceedingly remote…. Our future discoveries must be looked for in sixth place of decimal"

Michelson (1899)

But there were problems looking for satisfactory answers………

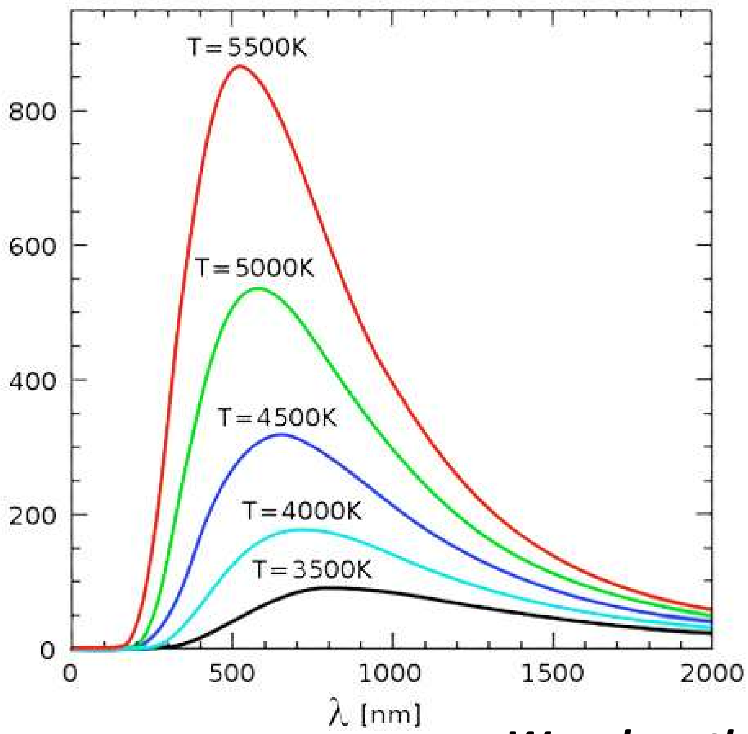
- **Black body radiation**
- **Specific heats of gases and solids**
- **Line spectra of atomic gases**
- **Photoelectric effect**
- **Cathode rays and X Rays**
- **Compton effect**

Blackbody Radiation

Any heated object radiates energy

- *The hotter the body, the higher the frequency of radiation*
- *The frequency (ν) of radiation is independent of the object being heated. It depends only on the temperature (T)*

Power emitted per unit area per unit frequency interval



Wavelength (nm)

Kirchhoff's Theorem (1859)

$$\boxed{e(\nu) = J(\nu, T)A(\nu)}$$

e(ν) : Emissivity; *Power emitted per unit area per unit frequency by a heated object*

A(ν) : *Fraction of incident power absorbed per unit area per unit frequency*

J(ν,T) : A universal function, same for all back bodies

Blackbody is a body for which *A(ν)*=1,

It absorbs all the power incident on it, $e(\nu) = J(\nu, T)$

Stefan's Law (1879)

Total power (e_{total}) per unit area emitted at all frequencies by a blackbody

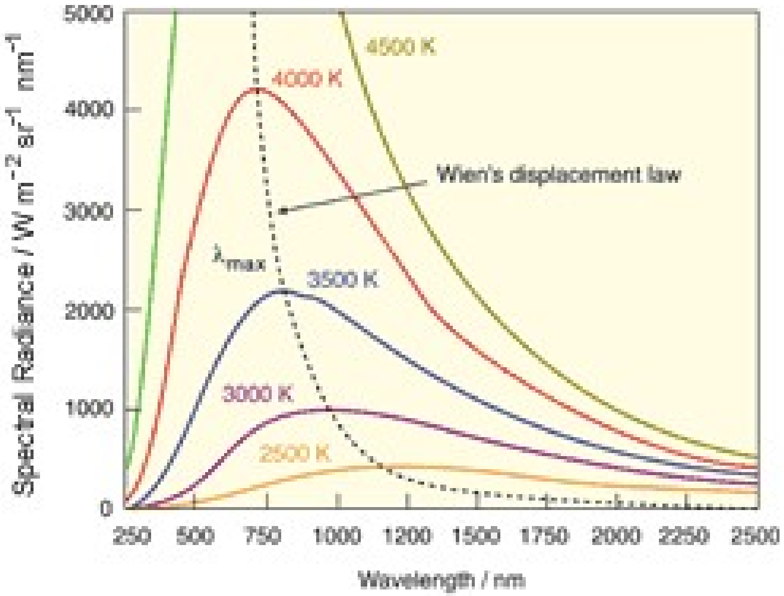
$$e_{total} = \int_0^\infty e(\nu)\,d\nu = \sigma T^4$$

σ = Stefan-Boltzmann constant
= $5.67\times10^{-8}\ \mathrm{W\cdot m^{-2}\cdot K^{-4}}$

Wien's displacement Law (1893)

The wavelength of maximum power emission shifts towards shorter wavelength when T is increased.

$$\lambda_{max} T = 2.898\times10^{-3}\ \mathrm{m\cdot K}$$



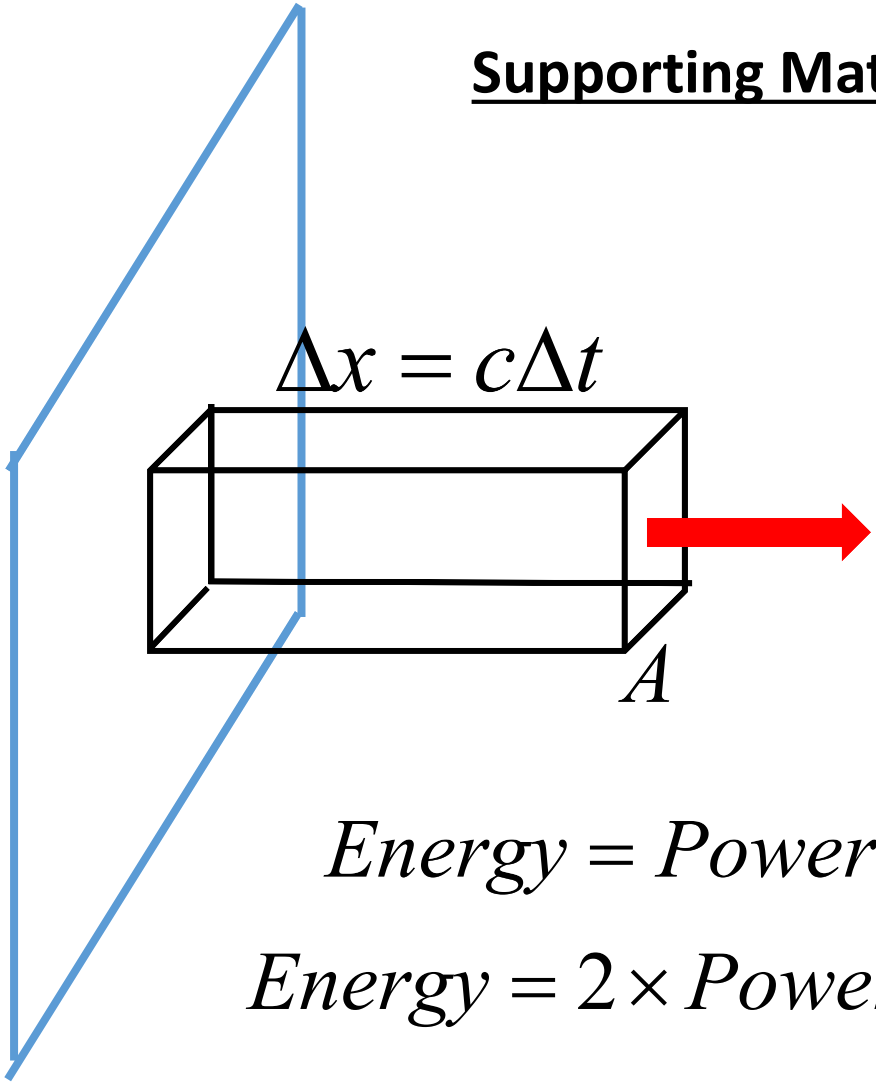
Energy density of a blackbody

$J(\nu, T)$ — ***Power emitted*** *by a blackbody per unit area per unit frequency*

$u(\nu, T)$ — *Energy density of a blackbody, i.e.,* ***energy per unit volume per unit frequency***

$$J(\nu, T) = \frac{c}{4} u(\nu, T)$$

Supporting Material: *How to show* $J(\nu,T)=\frac{c}{4}u(\nu,T)$



$$\Delta t = \frac{\Delta x}{c}$$

$$\Delta V = A\Delta x$$

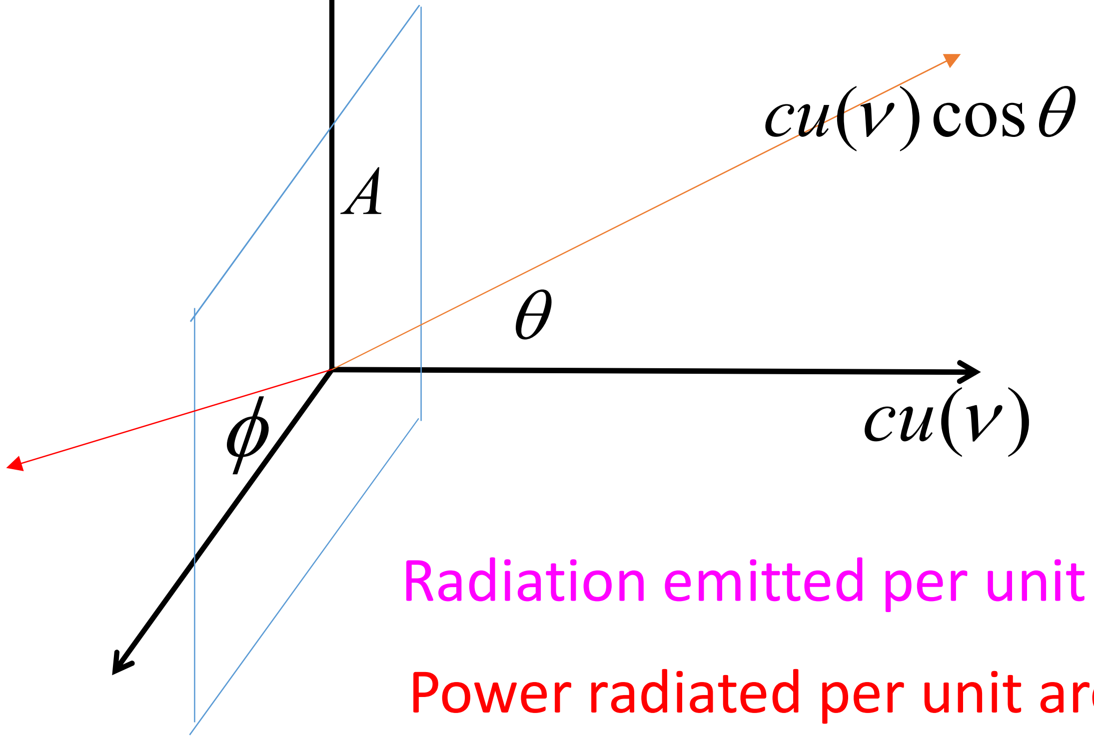
$$Energy = Power\ \ per\, unit\, area \times \Delta t \times A\ \ \times 2$$

$$Energy = 2\times Power\ \ per\, unit\, area \times (\Delta x / c)\times A$$

$$u = \frac{2}{c}J$$

Additional factor 2?

Supporting Material



Power emitted by surface A will spread out in the entire hemisphere defined by $0 \le \theta \le \pi/2$ and $0 \le \phi \le 2\pi$

Radiation emitted per unit area = $u(\nu,T)\,cdt$

Power radiated per unit area normal to the surface = $u(\nu,T)\,c\cos\theta$

Power radiated per unit area in solid angle dΩ = $cu(\nu,T)d\nu\cos\theta\dfrac{d\Omega}{4\pi}$

$$d\Omega = \sin\theta d\theta d\phi$$

$$J(\nu) = \frac{cu(\nu,T)}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} \sin\theta\cos\theta d\theta$$

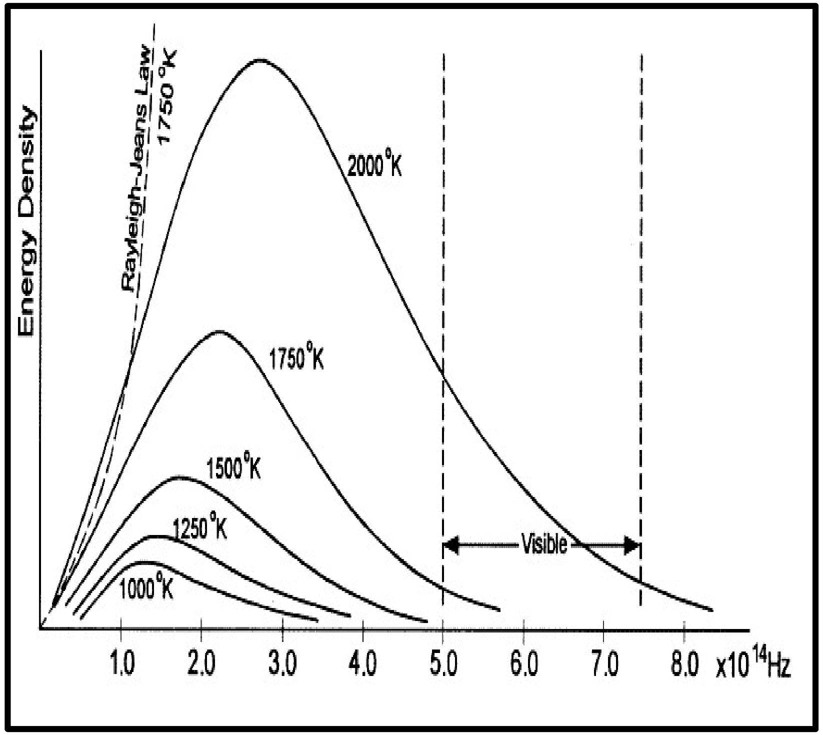
$$\boxed{J(\nu,T)d\nu = \frac{c}{4}u(\nu,T)d\nu}$$

Energy density of a black body : *u(ν,T)*

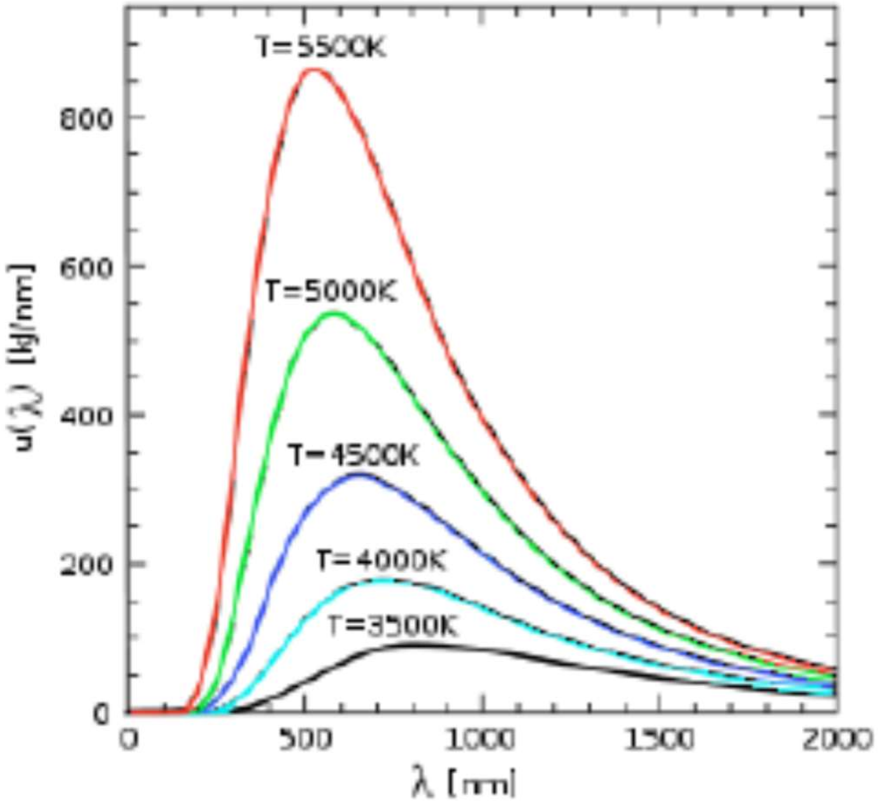
(Energy per unit volume per unit frequency)

Black body radiation curve

u(ν,T) vs ν



u(λ,T) vs λ



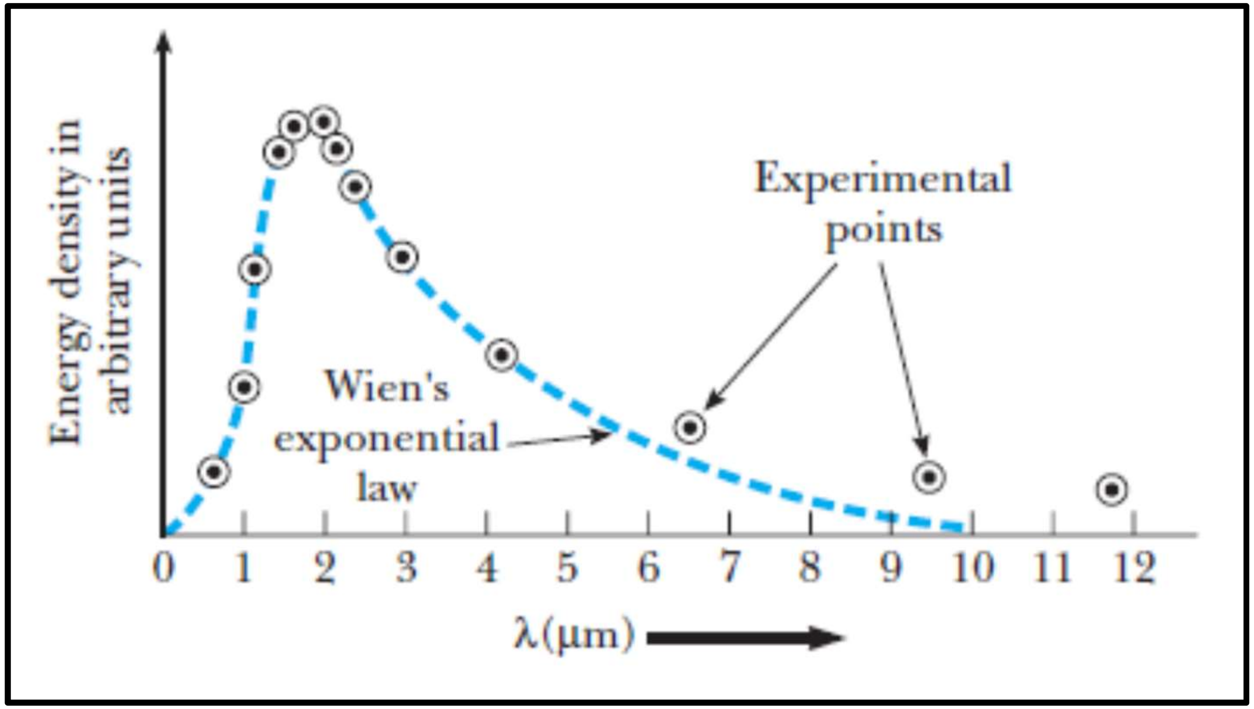
How to explain this behaviour?

Wien's Exponential Law

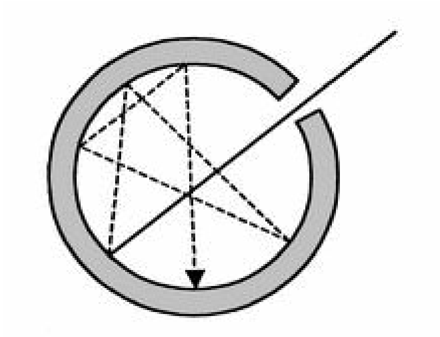
A guess work!

$$u(\nu, T) = A\nu^3 e^{-\beta\nu/T}$$

A and β are constants

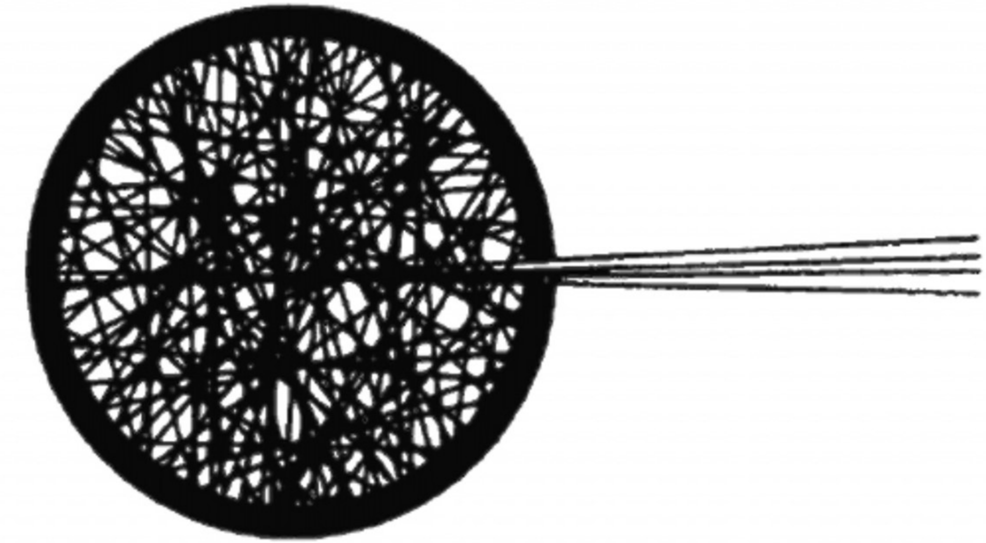


Does not agree for **longer wavelengths** (λ> 6μm (6000 nm)) !



Blackbody Cavity

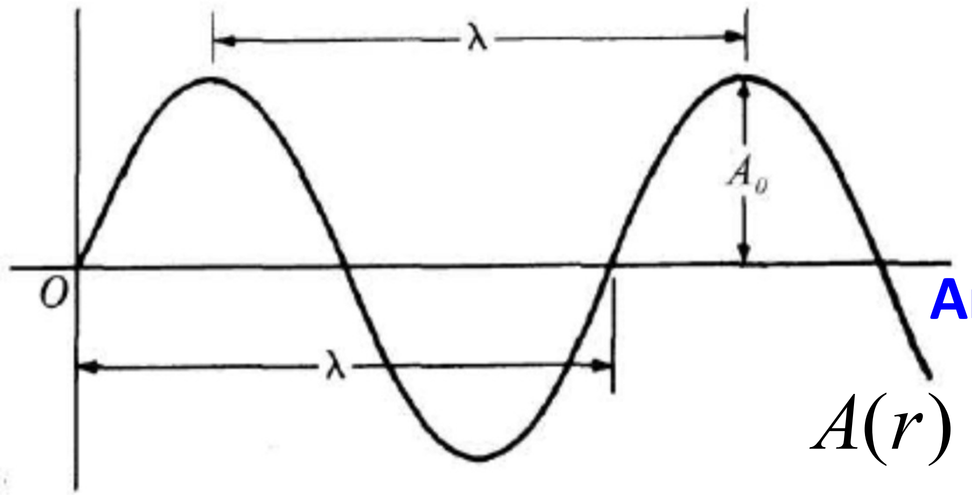
Light entering the small opening strikes the walls and gets reflected in the cavity.



At each reflection, a portion of the light is absorbed by the cavity walls. After many reflections, all of the incident energy is absorbed.

*Consider **properties of waves in a box** and work out an expression for the radiation spectrum at temperature T.*

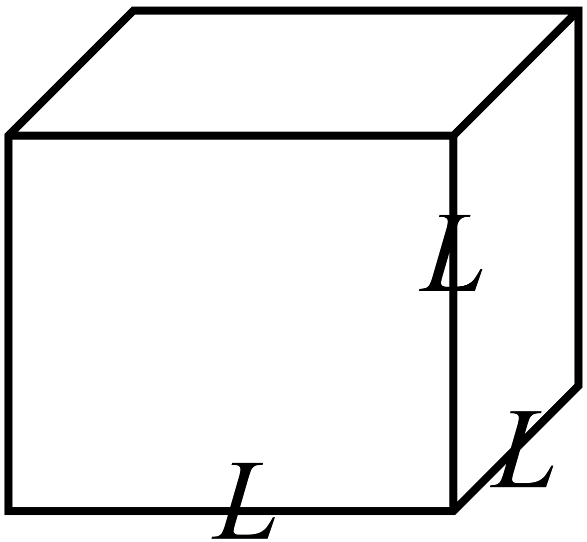
Waves in a box



Amplitude of wave in r-direction

$$A(r) = A_0 \sin(2\pi / \lambda) r = A_0 \sin kr$$

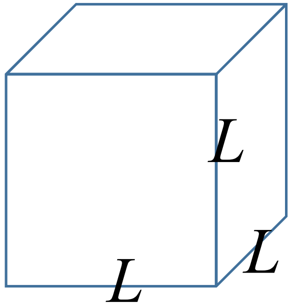
λ = wavelength, ***k*** = wave vector



Radiation in empty **volume = L^3** in **thermal equilibrium** with the container at **temperature T**

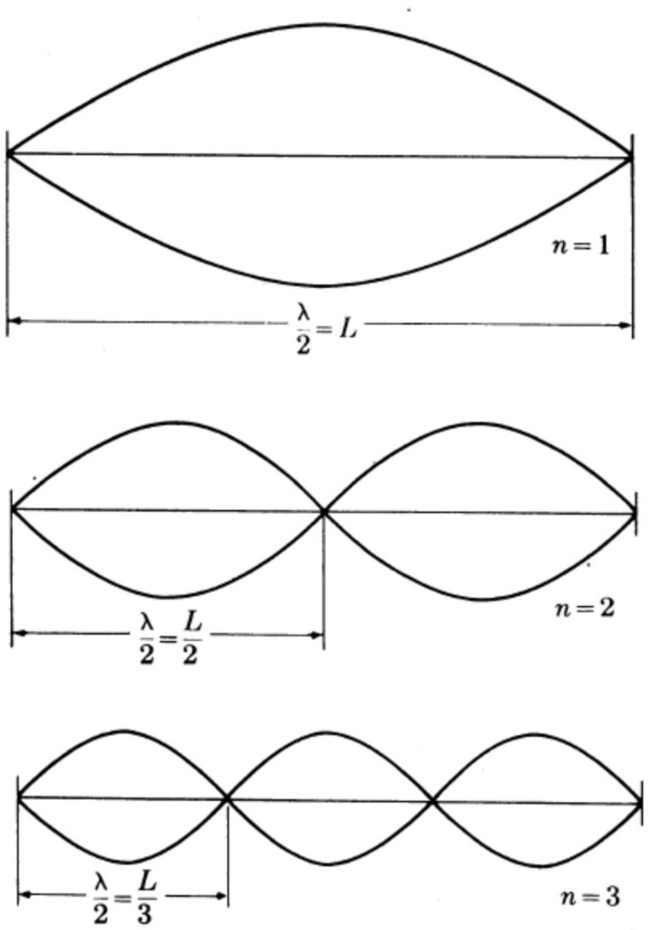
Can be viewed as the superposition of standing waves.

Waves in a box



$$A(r) = A_0 \sin(2\pi/\lambda)r = A_0 \sin kr$$

Waves in x-direction



Waves which can fitted in the box must satisfy

$$n_x \lambda_x / 2 = L$$

n_x are positive integers.

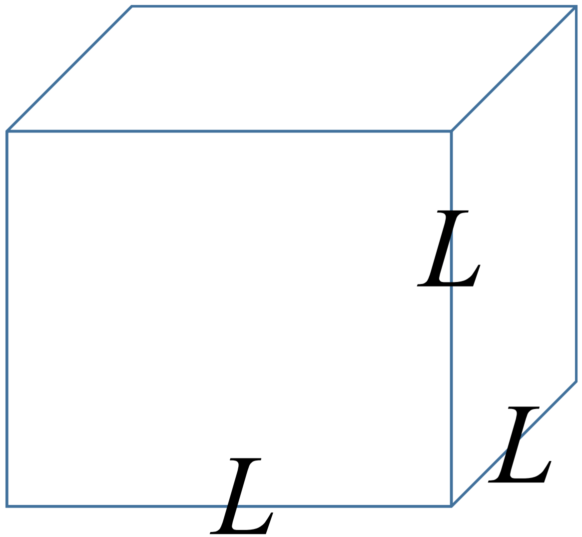
$$A(x) = A_0 \sin k_x x \qquad k_x = \pi n_x / L$$

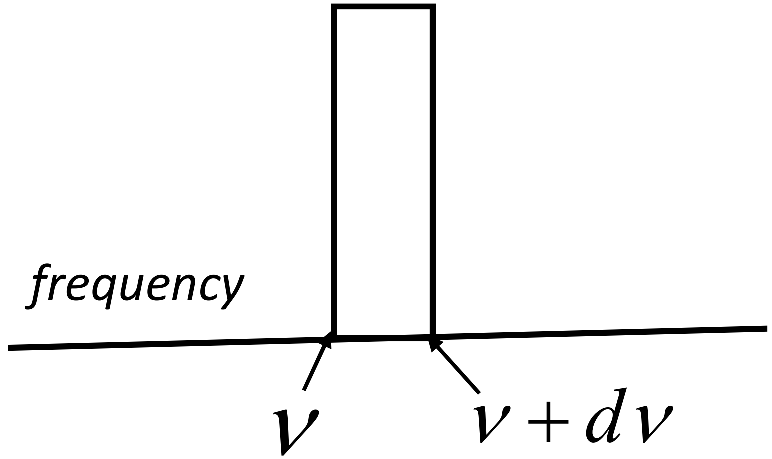
For y- and z-directions:

$$A(y) = A_0 \sin k_y y \qquad k_y = \pi n_y / L$$

$$A(z) = A_0 \sin k_z z \qquad k_z = \pi n_z / L$$

No. of standing waves in a box?





No. of modes per unit volume in frequency interval ν and $\nu + d\nu$

$$= \frac{8\pi\nu^2}{c^3} d\nu$$

Supporting Material

Modes of oscillation in 3-D

$$A(x,y,z) = A_0 \sin(k_x x)\sin(k_y y)\sin(k_z z)$$

$$k_x = \pi n_x / L \qquad k_y = \pi n_y / L \qquad k_z = \pi n_z / L$$

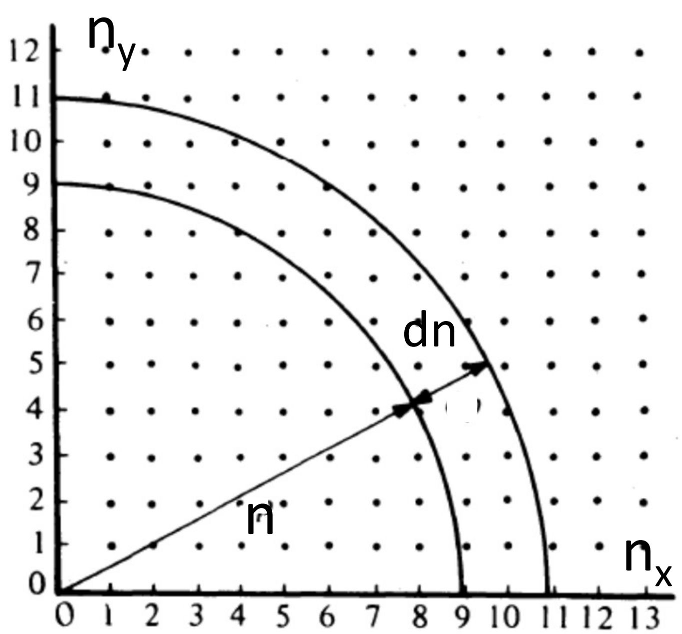
Define,

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2) = \frac{\pi^2}{L^2} n^2$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{c} = \frac{\omega}{c} = \frac{\pi n}{L}$$

Counting Number of modes in frequency interval ν and $\nu + d\nu$

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2) = \frac{\pi^2}{L^2} n^2$$



Volume of a spherical shell of radius *n* and thickness *dn* $= 4\pi n^2 dn$

No. of modes = $N(n)dn = \frac{1}{8} 4\pi n^2 dn$

(factor 1/8 since n_x, n_y, n_z all need be +ve integer)

$k = \pi n / L \Rightarrow n = Lk/\pi \qquad dn = L dk/\pi$

$$k = 2\pi\nu / c$$

$$dk = 2\pi d\nu / c$$

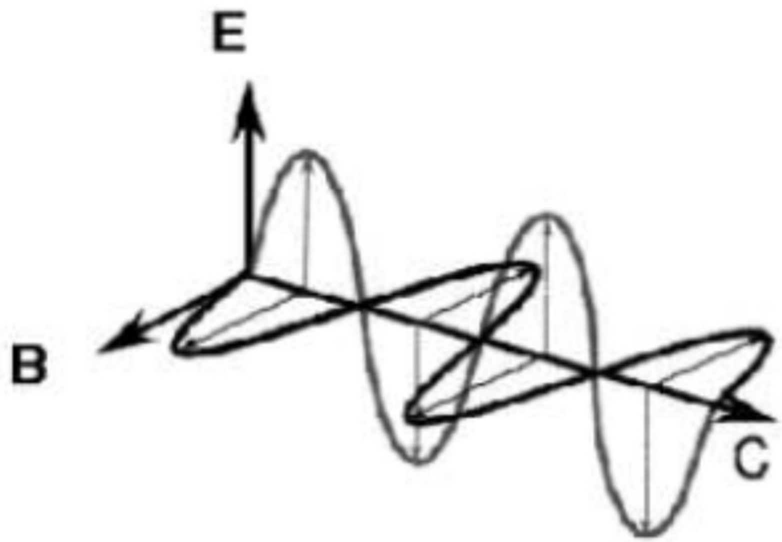
$$V = L^3$$

$$N(n)dn = \frac{1}{2}\pi\left(\frac{Lk}{\pi}\right)^2 \frac{Ldk}{\pi} = \frac{1}{2\pi^2} L^3 k^2 dk$$

$$= \frac{1}{2\pi^2} V \left(\frac{2\pi\nu}{c}\right)^2 \left(\frac{2\pi}{c}\right) d\nu$$

$$\boxed{\textbf{No. of modes per unit volume in } \nu \textbf{ and } \nu + d\nu = \frac{4\pi\nu^2}{c^3} d\nu}$$

Now account for the Polarization of Electromagnetic Wave



Electric (E) and Magnetic (B) fields of an electromagnetic wave are $\perp$ to each other and to the direction of propagation (C).

There is an independent mode of propagation in which E and B are rotated through 90^o w.r.t. C.

Any polarization of the wave can be expressed as the sum of these ***two independent modes of propagation****. Therefore multiplying previous expression by 2,*

No. of modes per unit volume in frequency interval ν and $\nu + d\nu$ $= \dfrac{8\pi\nu^2}{c^3} d\nu$

Energy density of a blackbody = $u(\nu, T)$

= **No. of modes per unit volume per unit frequency**

X **Average energy per mode**

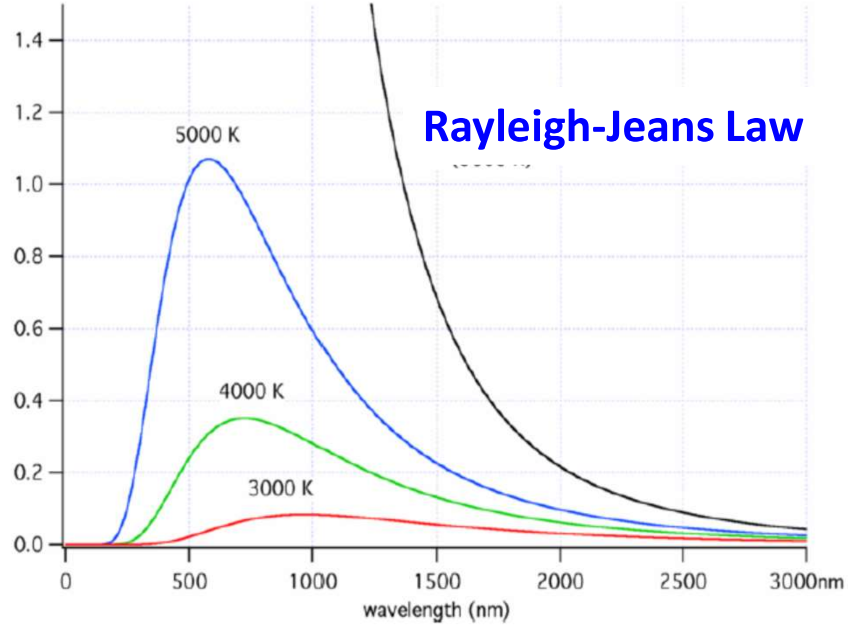
Invoke equipartition theorem:

$$\langle E \rangle = \frac{\int_0^\infty E e^{-E/kT}\, dE}{\int_0^\infty e^{-E/kT}\, dE} = kT$$

Average energy of a harmonic oscillator in thermal equilibrium = *kT*

$$\boxed{u(\nu, T) = \frac{8\pi\nu^2}{c^3} kT}$$

Rayleigh-Jeans Law



Valid for hν << kT

For high frequencies *u(ν,T)* diverges: **Ultraviolet Catastrophe**