Blackbody Radiation, Planck's Quantum Hypothesis, and Specific Heats of Gases and Solids

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Recapitulate

- ***The frequency (ν) of radiation emitted by a body is independent of the object being heated. It depends only on the temperature (T)***

- **Kirchhoff's Theorem**

$$e(\nu) = J(\nu, T)A(\nu)$$

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

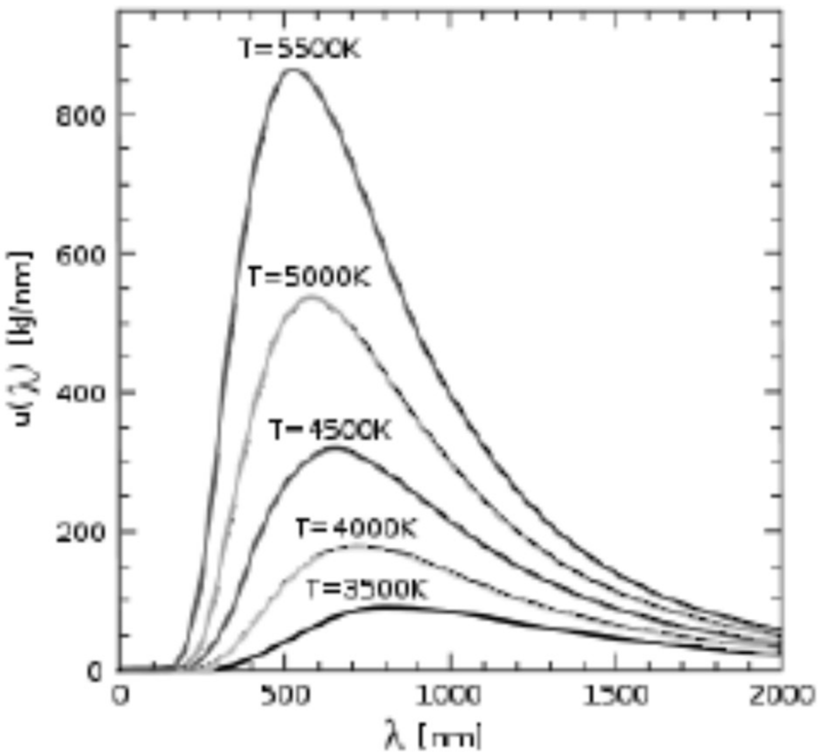
- **Blackbody is a body for which *A(ν)*=1,**

- **Stefan's Law**

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
= 5.67×10^{-8} W·m^{-2}·K^{-4}



- **Black body radiation curve**

  $u(\nu, T)$ vs ν

  (Energy per unit volume per unit frequency)

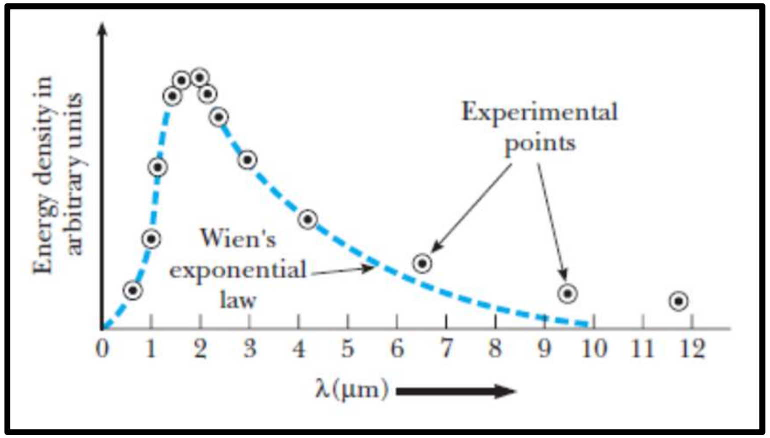
- **Wien's displacement Law**

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

- **Wien's Exponential Law**

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

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



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

$$u(\nu, T) = \text{No. of modes per unit volume per unit frequency}$$
$$\times \text{ Average energy per mode}$$

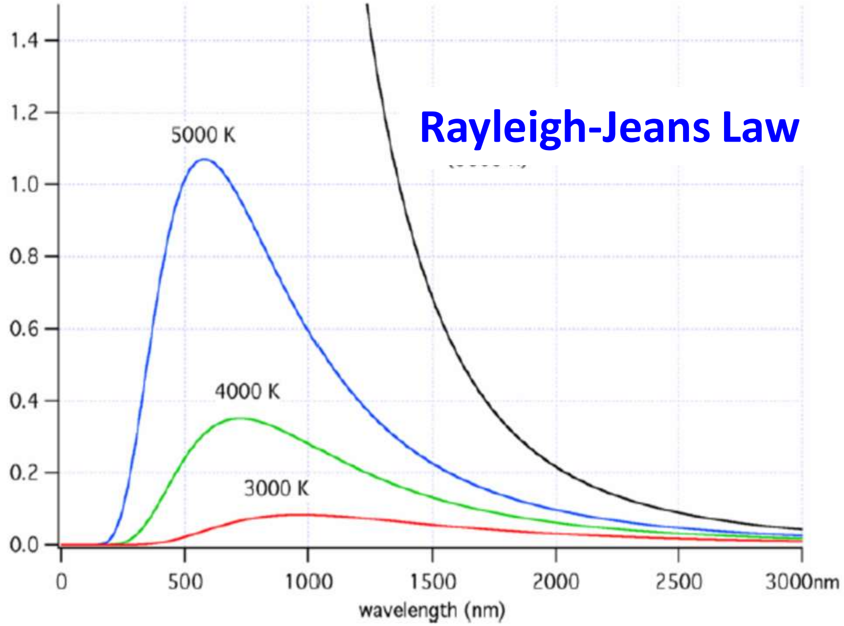
- **Rayleigh-Jeans Law (1900)**

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

For high frequencies $u(\nu, T)$ diverges:

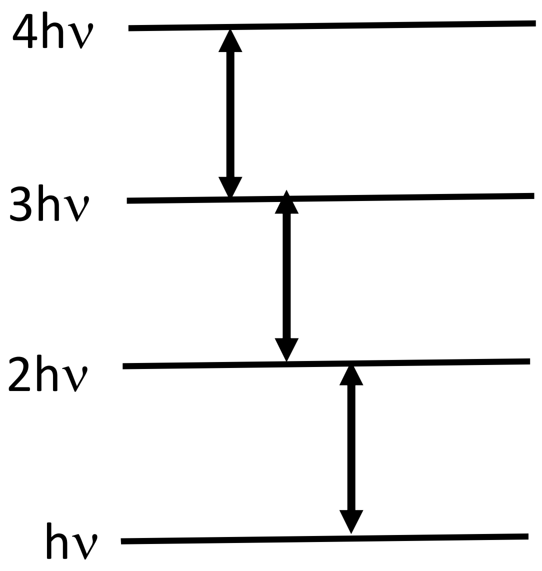
Ultraviolet Catastrophe

$$\int_0^\infty \frac{8\pi\nu^2 kT}{c^3} d\nu \to \infty$$



Planck's Quantum Hypothesis (1900)

- *Energy of the oscillators is quantized*
- ***Energy of a particular mode of frequency ν can not have arbitrary value, but only those values that are integral multiple of $h\nu$***



$$E = nh\nu$$ ν = ***frequency***

h **= Planck's constant = 6.626 x 10^{-34} J.s**

- *All modes are in thermal equilibrium*
- *The equilibrium is established by exchange of energy between modes and this can happen through interaction with walls of the cavity.*

Average energy of a mode of frequency ν

$$E = nh\nu$$

Quantum average

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} nh\nu \, e^{-(nh\nu/kT)}}{\sum_{n=0}^{\infty} e^{-(nh\nu/kT)}}$$

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

Classical average

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

$$= kT$$

Black Body Radiation Formula

Energy density per unit volume per unit frequency interval = No. of modes per unit volume per unit frequency × Average energy per mode

Quantum

$$\langle E \rangle = \frac{h\nu}{e^{h\nu/kT}-1}$$

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

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

Planck's blackbody radiation formula

Classical

$$\langle E \rangle = kT$$

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

Rayleigh-Jeans Law

Supporting material:

Finding quantum average

$$Let \quad x = e^{-(h\nu/kT)}$$

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} nh\nu \, e^{-(nh\nu/kT)}}{\sum_{n=0}^{\infty} e^{-(nh\nu/kT)}} = h\nu \frac{\sum_{n=0}^{\infty} nx^n}{\sum_{n=0}^{\infty} x^n} = h\nu \frac{x + 2x^2 + 3x^3 + \ldots\ldots}{1 + x + x^2 + \ldots\ldots}$$

$$= h\nu x \frac{(1 + 2x + 3x^2 + \ldots\ldots)}{(1 + x + x^2 + \ldots\ldots)}$$

$$= \frac{h\nu x}{1-x} = \frac{h\nu}{x^{-1} - 1}$$

$$= \frac{h\nu}{e^{(h\nu/kT)} - 1}$$

$$\boxed{\begin{aligned} \frac{1}{1-x} &= 1 + x + x^2 + x^3 + \ldots. \\ \frac{1}{(1-x)^2} &= 1 + 2x + 3x^2 + \ldots\ldots \end{aligned}}$$

Planck's Law

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

$$\boxed{e^{h\nu/kT} = 1 + \frac{h\nu}{kT} + \frac{1}{2!}\left(\frac{h\nu}{kT}\right)^2 + \dots}$$

For $h\nu << kT$ $\Rightarrow$ $e^{h\nu/kT} - 1 \approx h\nu / kT$

$$\langle E \rangle = \frac{h\nu}{e^{h\nu/kT}-1} \approx \frac{h\nu}{h\nu/kT} = kT$$ $\Rightarrow$ Classical average

$$u(\nu,T)d\nu = \frac{8\pi\nu^2}{c^3}kTd\nu$$ $\Rightarrow$ **Rayleigh-Jeans Law**

Planck's Law

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

For $h\nu >> kT$ $\Rightarrow$ $\frac{1}{e^{h\nu/kT}-1} \approx e^{-h\nu/kT}$

$$u(\nu,T)d\nu \approx \frac{8\pi h\nu^3}{c^3}e^{-(h\nu/kT)}d\nu$$

$$= A\nu^3 e^{-\beta\nu/T}$$

$\Rightarrow$ **Wien's Law**

Planck's Law

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

In wavelength (λ) units

$$u(\lambda,T)d\lambda = \frac{8\pi^2\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT}-1}\frac{c}{\lambda^2}d\lambda$$

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

One can now find λ_{max}

$\lambda_{max}T = 2.898\times10^{-3}$ m·K $\Rightarrow$ **Wien's displacement Law**

Supporting material: From Planck's Law to Wien's Displacement Law

$$u(\lambda,T)=\frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT}-1}d\lambda \qquad \beta = 8\pi hc \qquad \alpha = hc/k$$

$$=\frac{\beta}{\lambda^5}\frac{1}{(e^{\alpha/\lambda T}-1)}$$

$$\frac{du(\lambda,T)}{d\lambda}=\frac{\beta}{\lambda^6(e^{\alpha/\lambda T}-1)}\left[5-\left(5-\frac{\alpha}{\lambda T}\right)e^{\alpha/\lambda T}\right]=0$$

$\beta \neq 0 \quad \Longrightarrow \quad 5-(5-x)e^x = 0$ where $x=\alpha/\lambda T$

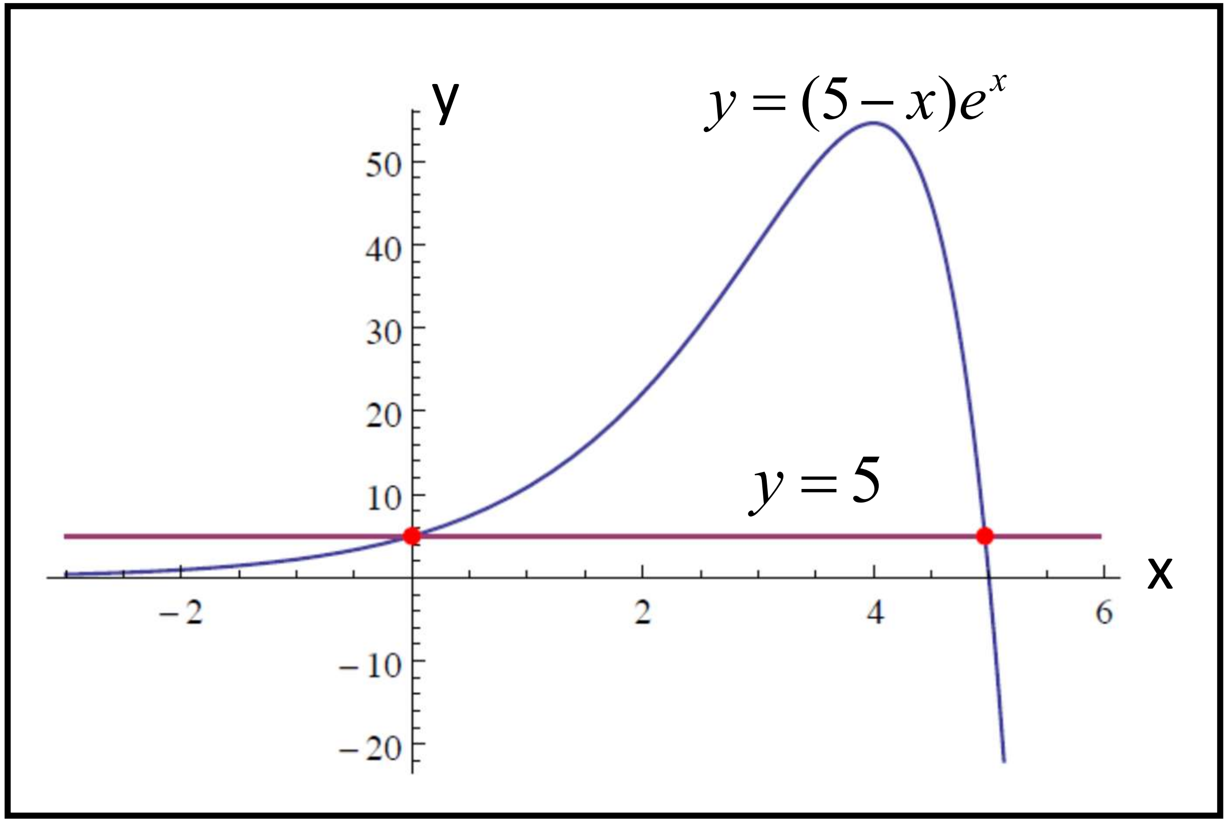
Solution of the transcendental equation gives λ_{max} where u(λ,T) becomes maximum

$$5-(5-x)e^{x}=0$$

Trivial solution is x=0

General solution can be found graphically using two equations

$$y=5 \qquad y=(5-x)e^{x}$$



$$x=4.96511$$

$$x=\frac{\alpha}{\lambda T}=\frac{hc}{\lambda kT}$$

$$\lambda_{max}T=\frac{hc}{k}\frac{1}{4.96511}$$

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

From Planck's Law to Stefan's law

Total power per unit area radiated at all frequencies

$$e_{Total} = \frac{c}{4}\int_0^\infty u(\nu)d\nu = \frac{c}{4}\frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3}{e^{h\nu/kT}-1}d\nu$$

$$= \frac{c}{4}\frac{8\pi h}{c^3}\left(\frac{kT}{h}\right)^3\int_0^\infty \frac{x^3}{e^x-1}dx$$

$$= \left(\frac{2\pi^5 k^4}{15c^2h^3}\right)T^4 = \sigma T^4$$

$$x = h\nu/kT$$

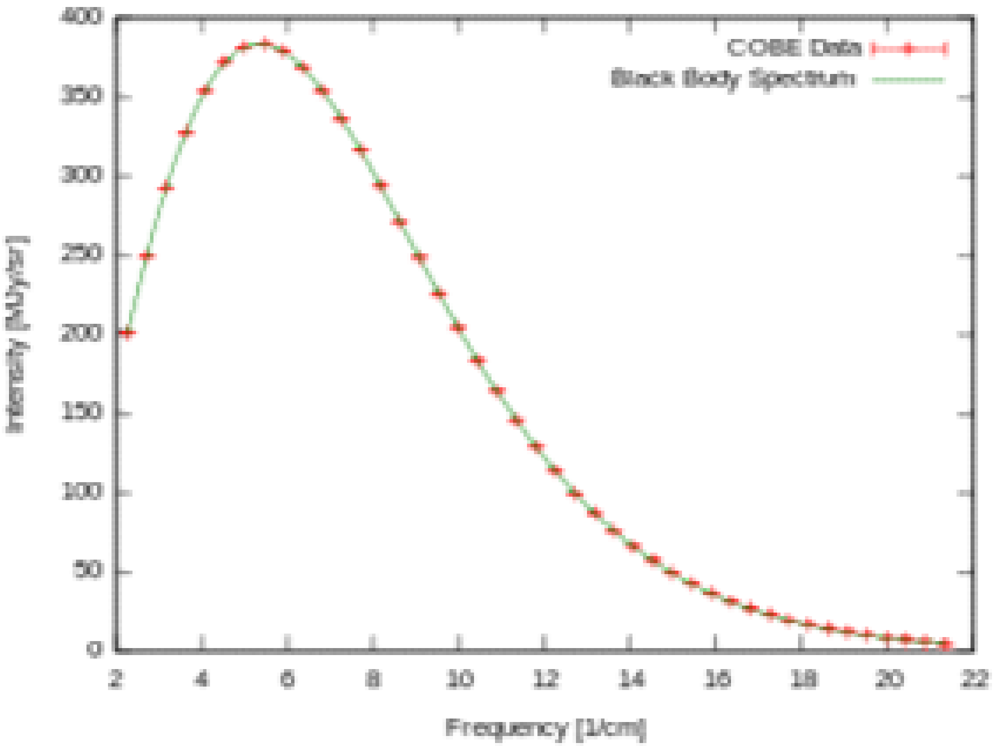
$$\int_0^\infty \frac{x^3}{e^x-1}dx = \frac{\pi^4}{15}$$

σ = Stefan-Boltzmann constant = 5.67×10^8 Wm^{-2} K^{-4}

Planck's Law for Blackbody Radiation

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

'Cosmic Microwave Background (CMB)' was discovered by Arno Penzias and Robert Wilson, Bell Labs in 1964. They received Nobel Prize in 1978.



Energy of CMB was measured in 1990 by Cosmic Background Explorer (COBE), NASA Spacecraft.

The spectrum fits blackbody spectrum at T=2.726 K

Specific heats of gases

Specific heat deals with the increase of temperature as heat is being consumed by the system.

$C_V =$ Molar specific heat at constant volume

$$= \left(\frac{\partial \varepsilon}{\partial T}\right)_V$$

Monoatomic gases

Degrees of freedom = 3 *(only translational)*

$$\varepsilon = N_A \times 3 \times \frac{1}{2} kT$$

$N_A =$ No. of atoms

$$C_V = \frac{3}{2} N_A k = \frac{3}{2} R$$

R **=gas constant = 8.31 J mole^{-1} K^{-1}**

Diatomic gases

Rigid molecule

Degrees of freedom = 5

3 Translational + 2 Rotational

$$\varepsilon = N_A \times 5 \times \frac{1}{2} kT$$

$$C_V = \frac{5}{2} N_A k = \frac{5}{2} R$$

Flexible molecule

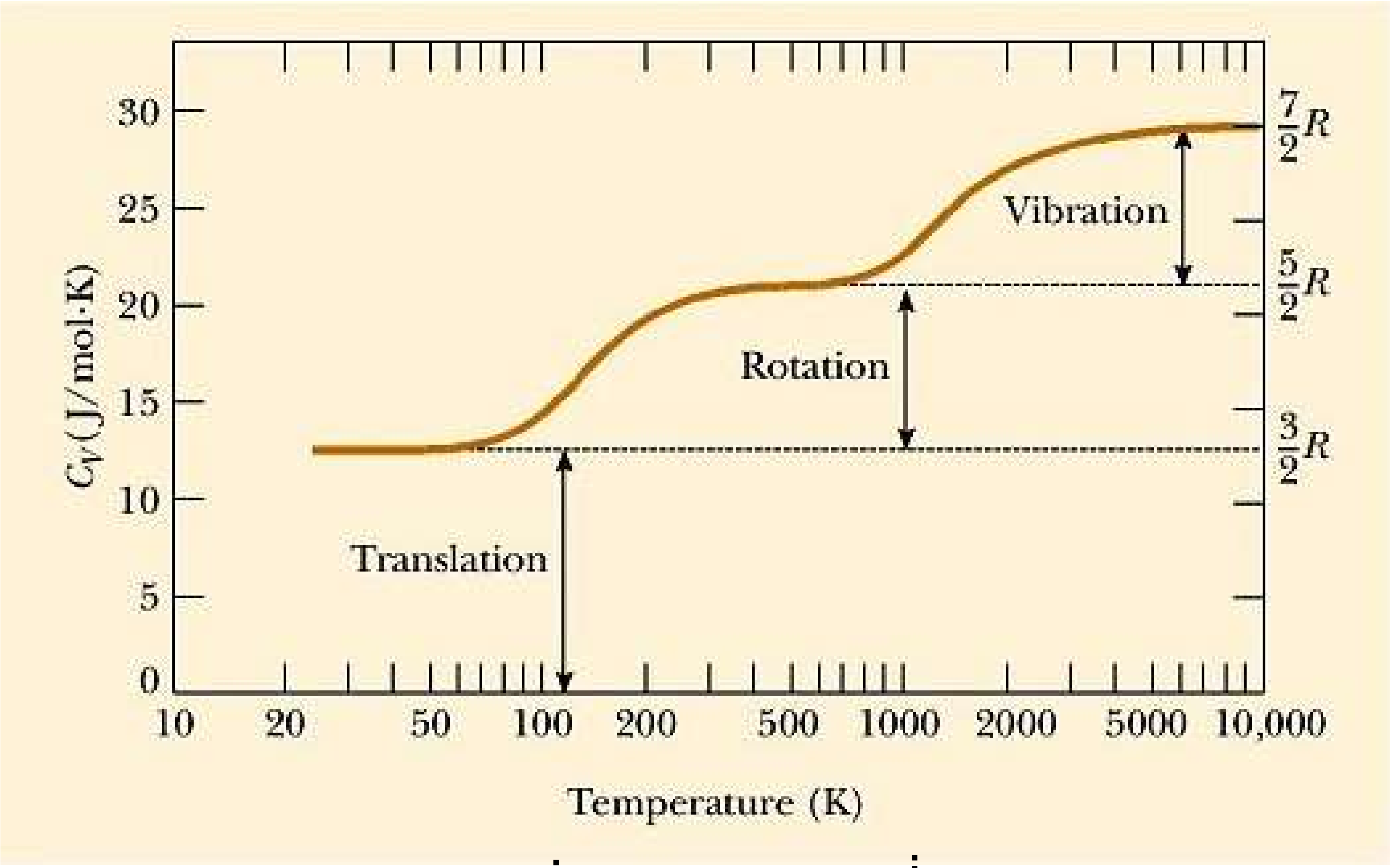
Degrees of freedom = 6

3 Translational + 2 Rotational + 1 Vibrational

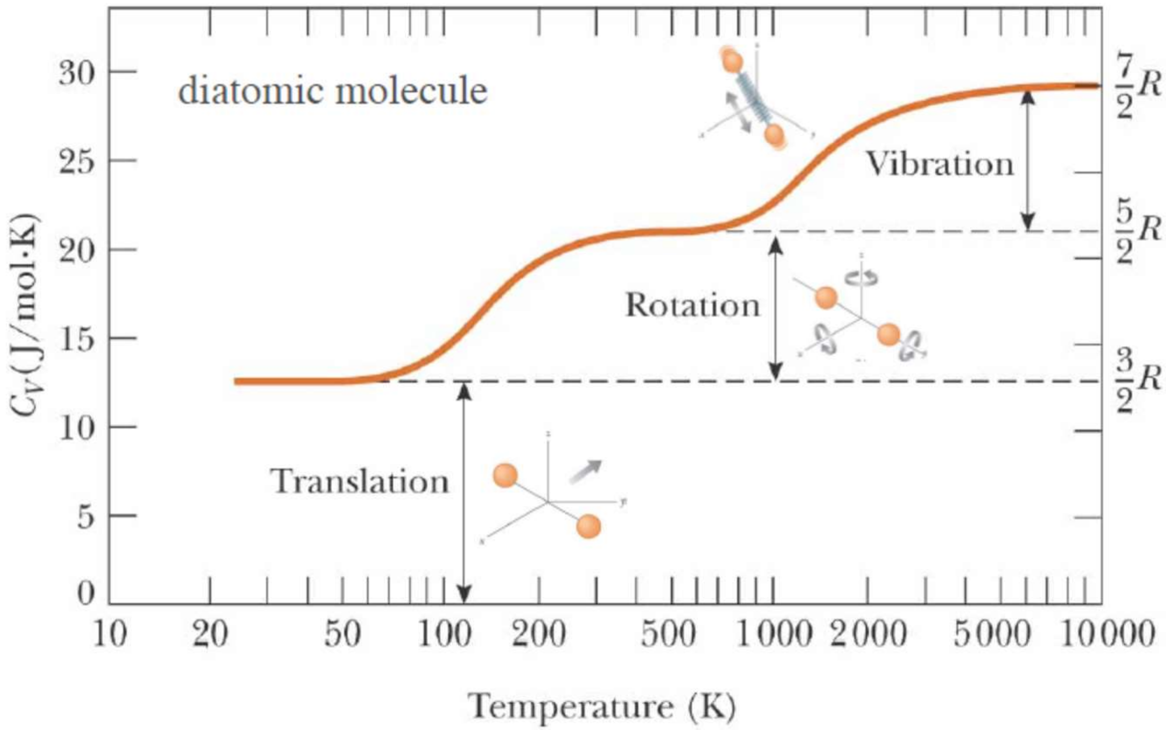
$$\varepsilon = N_A \left(5 \times \frac{1}{2} kT + kT \right)$$

$$C_V = \frac{7}{2} N_A k = \frac{7}{2} R$$

Molar specific heat of hydrogen at constant volume



Only translation | Translation + Rotation | Translation + Rotation + vibration



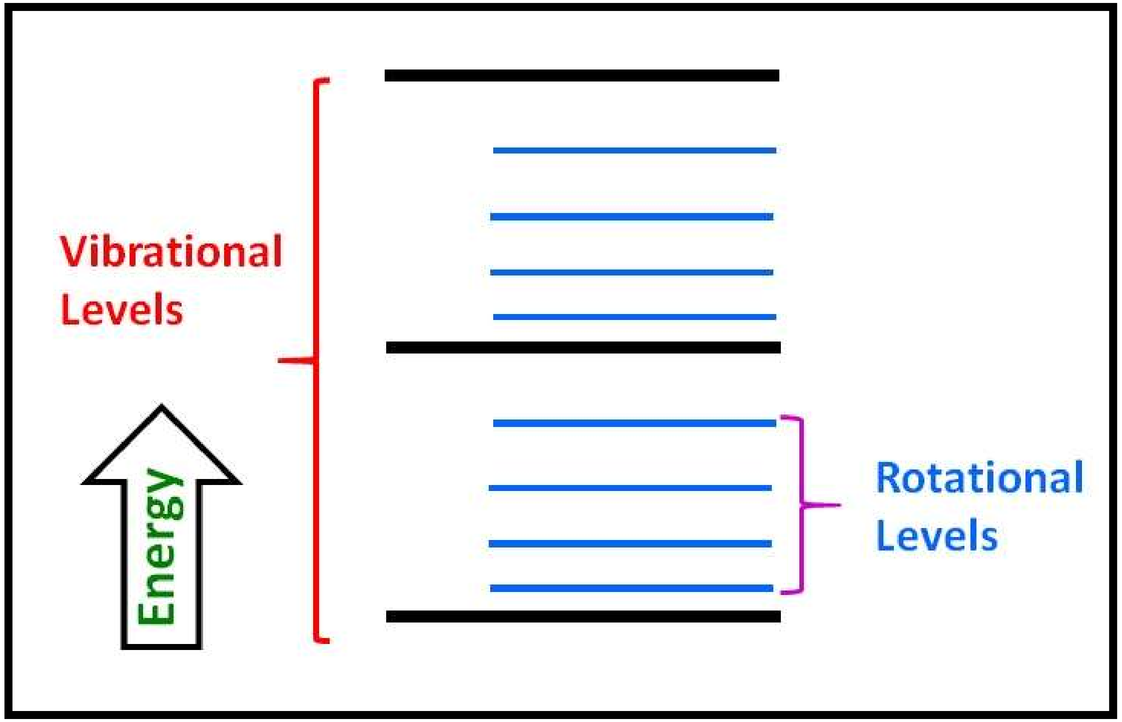
- **At low temperature a diatomic molecule acts like a mono atomic gas, $C_v = 3R/2$**

- AT high temperature, C_v increases to **5R/2 consistent with adding rotational energy and not vibrational energy**

- At still high temperature, **$C_v = 7R/2$ consistent with adding rotational energy as well as vibrational energy**

- **No explanation in 'Classical' theory. Does it smell 'Quantization' of rotational and vibrational motion?**

'Quantization' of rotational and vibrational motion



• At low temperatures, all molecules are in the ground state of rotation and vibration, only translational motion contributes: $C_v = 3R/2$

•At high temperature, molecule is excited to higher rotational energy levels and rotational motion contributes to C_v (=5R/2)

•At still higher temperature, molecule is excited to higher vibrational energy levels and both vibrational and rotational motion contribute to C_v (=7R/2)

Heat capacity of solids

Dulong and Petit Law : The specific heat of all solids is *3R*

Total degrees of freedom = $3N_A$

Total vibrational degrees of freedom = $3N_A$-6

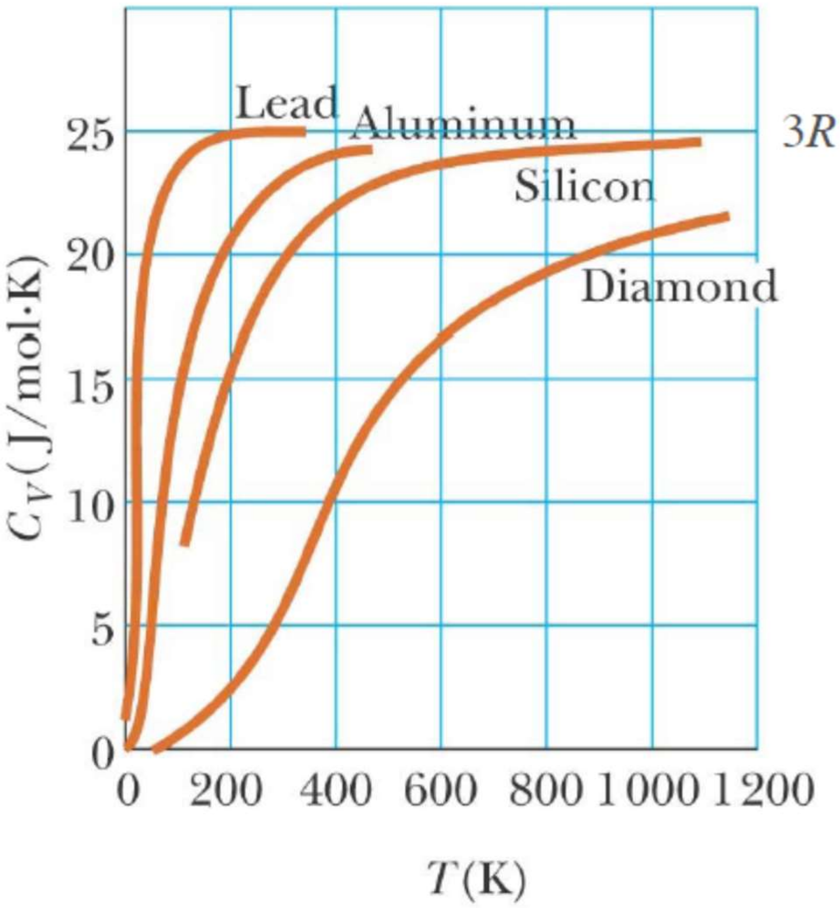
$$\varepsilon = (3N_A - 6) \times kT$$

Each vibrational degree of freedom contributes energy = kT

$$C_V = \frac{\partial \varepsilon}{\partial T} = 3N_A kT = 3R$$

= 24.93 J mole^{-1} K^{-1}

Experimental Observations on C_v of Solids



Dulong and Petit Law :
C_v=3R for all solids

- C_v shows marked temperature dependence
- At high temperatures, **$C_v \rightarrow$ 3R.**
- C_v decrease in a nonlinear manner with decreasing temperature; at low temperature, **$C_v = aT^3$**
- **$C_v \rightarrow$ 0** as **$T \rightarrow$ 0.**

Einstein Model for specific heat of solids (1907)

$$\varepsilon = (3N_A - 6) \times \langle E \rangle$$

$$= (3N_A - 6)\frac{h\nu}{e^{h\nu/kT} - 1}$$

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

Treat each oscillator as a quantized harmonic oscillator:

$$E = nh\nu$$

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} nh\nu \, e^{-(nh\nu/kT)}}{\sum_{n=0}^{\infty} e^{-(nh\nu/kT)}} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

$$C_V = 3R\frac{x^2 e^x}{(e^x - 1)^2} \qquad x = \frac{h\nu}{kT} = \frac{\theta_E}{T}$$

$$\theta_E = \frac{h\nu}{k}$$

Einstein Temperature

$$C_V = 3R\frac{x^2 e^x}{(e^x - 1)^2} \qquad x = \frac{h\nu}{kT} = \frac{\theta_E}{T}$$

High temperature limit:

$$T >> \theta_E \Rightarrow x << 1 \Rightarrow e^x - 1 \approx x$$

$$C_V \to 3R$$

Low temperature limit:

$$T << \theta_E \Rightarrow x >> 1 \Rightarrow e^x - 1 \approx e^x$$

$$T \to 0, \qquad C_V \to 0$$

Yet another success of Quantum Hypothesis