THERMODYNAMICS AND STATISTICAL MECHANICS

CHAPTER 7 –THERMAL RADIATION AND PLANCK DISTRIBUTION

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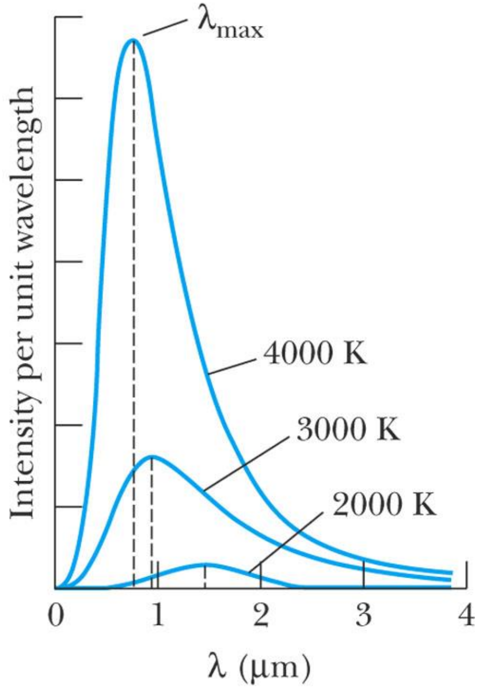
Outline

We will consider two problems: first the blackbody radiation problem, and then the problem of lattice vibrations in a solid. The two are similar in many regards.

Blackbody Radiation

Maxwell Theory light was attempted to apply to long-standing puzzle of blackbody radiation. The blackbody radiation that led to the concept of quantum theory.

At room temperature, thermal radiation is mostly in the infrared (IR). When we heat an object to higher temperature, they emit visible light.



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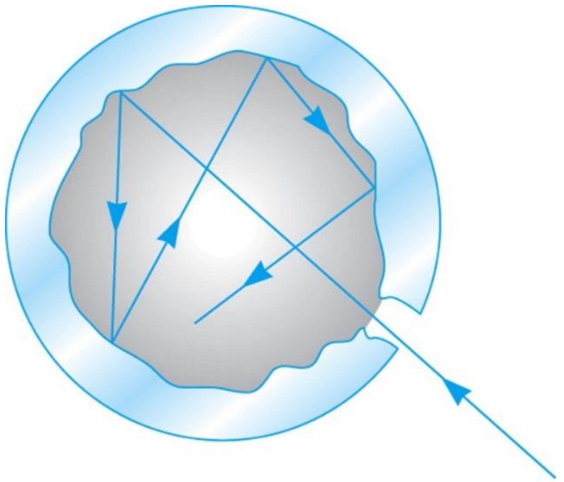

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Opening of a cavity inside a body is a good approximation of a block body.

Blackbody Radiation

- In 1859, Gustav Kirchhoff proved theorem based on thermodynamic that emitted power

$$e_f = J(f,T)A_f$$

Where e_f is the power emitted per unit area per unit frequency, A_f is the absorption power, and $J(f,T)$ is universal function depends only on f and T. Here, f is frequency and T is temperature of the object.

- For black body, $\mathrm{A_f} = 1$

$$e_f = J(f,T)$$

Where black body radiation depends only on f and T, but not on physical or chemical property.

Classical Theory of Thermal Radiation.

Rayleigh-Jeans Law: The classical theory of blackbody radiation formulated by Load Rayleigh, John William Strutt (1842-1919, English physicist), and James Jean (1842-1946, English astronomer and physicist), derived with idea that blackbody radiation energy per unit volume with frequency between f and $f + df$:

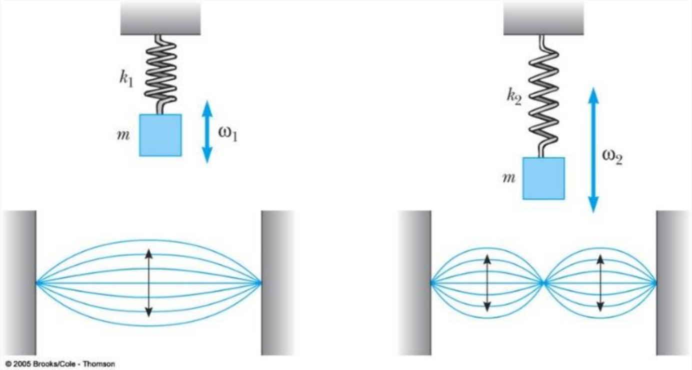
$$u(f,T) = \bar{E}\, N(f)\, df$$

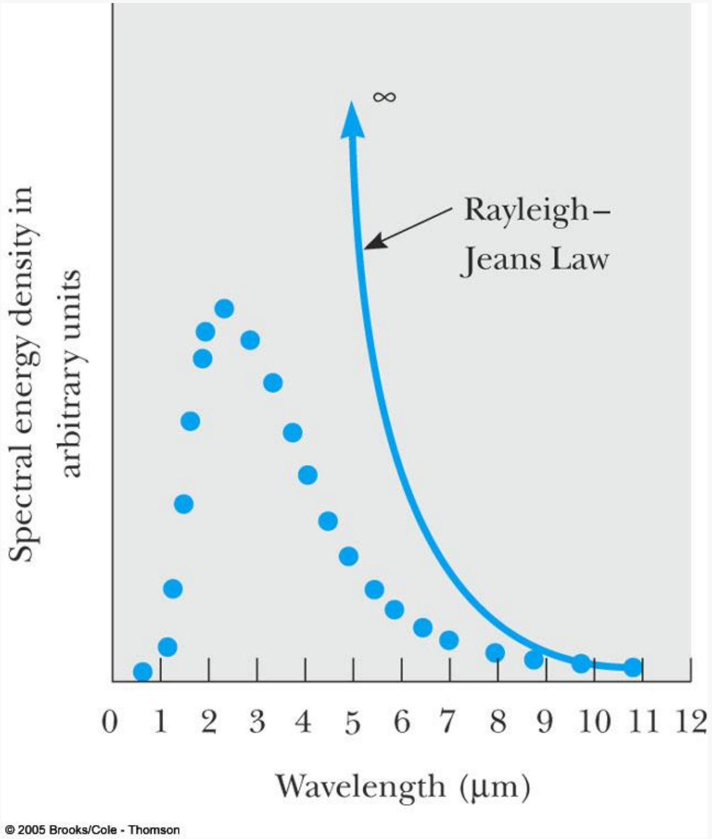
- ❖ Spectral energy density:

$$u(f,T)df = \frac{8\pi f^2}{c^3} k_B\, T\, df$$

- ❖ In terms of wavelength :

$$u(\lambda,T)d\lambda = \frac{8\pi}{\lambda^4} k_B\, T\, d\lambda$$



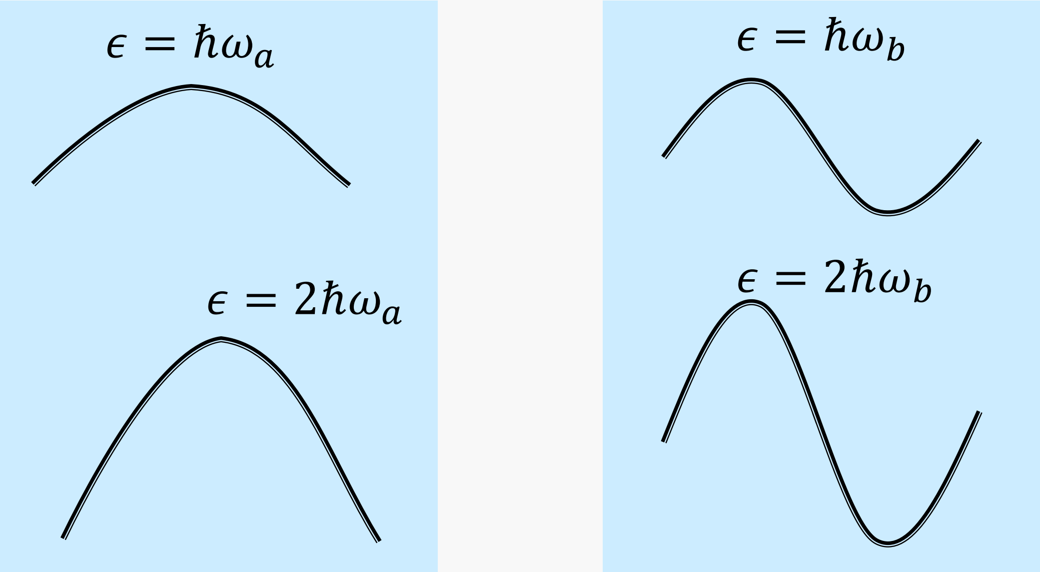


Plank and The Quantum Hypothesis

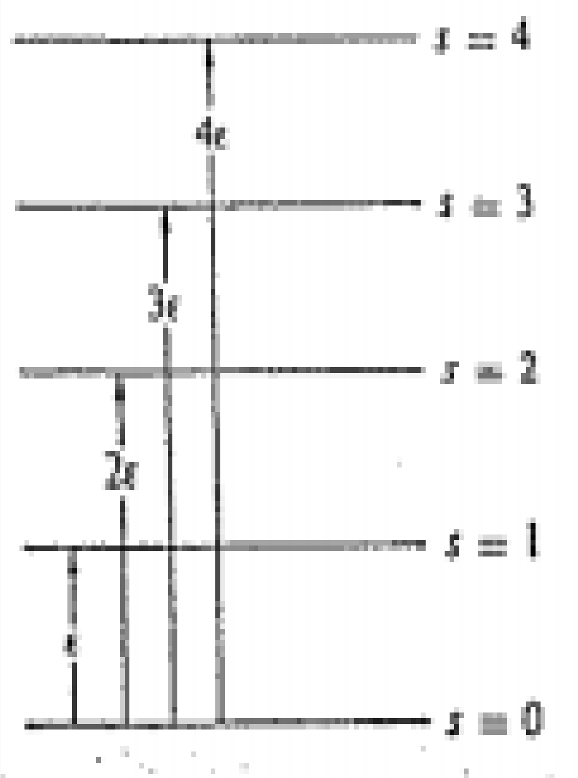
For blackbody radiation problem, Planck made the very radical assumption that the energy in a given mode of frequency ω could only change in integer multiples of $\hbar\omega$.

$$\varepsilon_s = s\,\hbar\omega$$

Where s is a positive integer or 0 and we are ignoring the zero-point energy, $(1/2)\hbar\omega$.



1-D & 2-D of two electromagnetic modes (a & b). The amplitude of EM field represents for 1 & 2 photon occupancy of each mode.



Plank and The Quantum Hypothesis

we can readily find the partition function for one mode inside the cavity. For a single mode $\varepsilon_s = s\,\hbar\omega$ and:

$$\mathrm{Z}(\tau) = \sum_{\substack{all\ states\\ s}} exp\left(-\frac{\mathcal{E}_s}{\tau}\right) = \sum_{s=0}^{\infty} exp\left(-\frac{s\hbar\omega}{\tau}\right)$$

$$\mathrm{Z}(\tau) = \sum_{s=0}^{\infty}\left(exp\left(-\frac{\hbar\omega}{\tau}\right)\right)^{s} = \sum_{s=0}^{\infty} x^{s} = \frac{1}{1-x} = \frac{1}{1-exp\left(-\frac{\hbar\omega}{\tau}\right)}$$

$$\mathrm{Z}(\tau) = \frac{1}{1-exp\left(-\frac{\hbar\omega}{\tau}\right)}$$

Plank and The Quantum Hypothesis

The probability for photons with mode ω

$$P_{\varepsilon_s} = \frac{exp\left(-\frac{\mathcal{E}_s}{\tau}\right)}{Z(\tau)} = \frac{exp\left(-\frac{s\hbar\omega}{\tau}\right)}{\left(\frac{1}{1 - exp\left(-\frac{\hbar\omega}{\tau}\right)}\right)} = exp\left(-\frac{s\hbar\omega}{\tau}\right)\left(1 - exp\left(-\frac{\hbar\omega}{\tau}\right)\right)$$

Average value of s, $\langle s \rangle$ can be calculated as follows:

$$\langle s \rangle = \sum_{\substack{all\,states\\ s}} P_s \cdot s = Z^{-1} \sum_{\substack{all\,states\\ s}} s \cdot exp\left(-\frac{s\hbar\omega}{\tau}\right)$$

$$= \left(1 - exp\left(-\frac{\hbar\omega}{\tau}\right)\right) \sum_{\substack{all\,states\\ s}} s \cdot exp\left(-\frac{s\hbar\omega}{\tau}\right)$$

Plank and The Quantum Hypothesis

Let's look at the expression:

$$\sum_{\substack{all\ states\\ s}} s \cdot exp\left(-\frac{s\hbar\omega}{\tau}\right) = \sum_{\substack{all\ states\\ s}} s \cdot exp(-sy) \quad \left(\text{with } y = \left(\frac{\hbar\omega}{\tau}\right)\right)$$

$$= -\frac{d}{dy} \sum_{\substack{all\ states\\ s}} exp(-sy) = -\frac{d}{dy}\left(\frac{1}{1 - \exp(-y)}\right)$$

$$\sum_{\substack{all\ states\\ s}} s \cdot exp\left(-\frac{s\hbar\omega}{\tau}\right) = = \frac{\exp(-y)}{(1 - \exp(-y))^2}$$

Plank and The Quantum Hypothesis

The thermal average energy in the mode is

$$\langle s\rangle = \left(1 - exp\left(-\frac{\hbar\omega}{\tau}\right)\right)\frac{\exp\left(-\frac{\hbar\omega}{\tau}\right)}{\left(1-\exp\left(-\frac{\hbar\omega}{\tau}\right)\right)^2} = \frac{1}{\left(\exp\left(\frac{\hbar\omega}{\tau}\right)-1\right)}$$

From the average value $\langle s\rangle$ it is straightforward to get the average energy in the mode:

$$\langle\varepsilon\rangle = \langle s\rangle\hbar\omega = \frac{\hbar\omega}{(e^{\hbar\omega/\tau}-1)}$$

Plank and The Quantum Hypothesis

So far, we have done all of this for a single value of the frequency (or for single mode). Let's look the values in the cavity (length L). The electrical field components of the form (below, the j component):

$$E_j = E_{jo} Sin(\omega t) Cos\left(\frac{n_j \pi j}{L}\right) Sin\left(\frac{n_i \pi i}{L}\right) Sin\left(\frac{n_k \pi k}{L}\right)$$

Where i, j, k corresponds (generically) to x, y, z. For example,

$$E_x = E_{xo} Sin(\omega t) Cos\left(\frac{n_x \pi x}{L}\right) Sin\left(\frac{n_y \pi y}{L}\right) Sin\left(\frac{n_z \pi z}{L}\right)$$
$$E_y = E_{yo} Sin(\omega t) Sin\left(\frac{n_x \pi x}{L}\right) Cos\left(\frac{n_y \pi y}{L}\right) Sin\left(\frac{n_z \pi z}{L}\right)$$
$$E_z = E_{zo} Sin(\omega t) Cos\left(\frac{n_x \pi x}{L}\right) Sin\left(\frac{n_y \pi y}{L}\right) Cos\left(\frac{n_z \pi z}{L}\right)$$

Where $E_x, E_y, \& \ E_z$ are three electric field components and corresponding amplitudes are $E_{x0}, E_{y0}, \& \ E_{z0}$

Plank and The Quantum Hypothesis

These three components are not independent, because field must be divergence-free

$$\text{div E} = \nabla E = \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = 0$$

which needs to be

$$E_{x0} n_x + E_{y0} n_y + E_{z0} n_z = E_0 \,.\, \boldsymbol{n} = 0$$

The electric field vectors must be perpendicular to the vector $\boldsymbol{n}$, components are $n_x, n_y,$ & n_z.

If the wave is propagating along the Z direction, the E field at any point will be in the X-Y plane and there will be no component along Z.

The EM field in the cavity is a transversely polarized; the direction of the E field is called the "polarization" direction of the field, E_0

Plank and The Quantum Hypothesis

The allowed frequencies are determined from the wave equation for the electromagnetic waves.

$$\nabla^2\psi = \frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2}$$

We get for EM waves

$$c^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) E_z = \frac{\partial^2 E_z}{\partial t^2}$$

Eventually we get that:

$$c^2\left[\left(\frac{n_x\pi}{L}\right)^2 + \left(\frac{n_y\pi}{L}\right)^2 + \left(\frac{n_z\pi}{L}\right)^2\right] = {\omega_n}^2 \;\Rightarrow\; \omega_n = \frac{c\pi}{L}\left({n_x}^2 + {n_y}^2 + {n_z}^2\right)^{1/2} = \frac{nc\pi}{L}$$

n in principle runs over positive integers

Plank and The Quantum Hypothesis

The total energy inside the blackbody at temperature τ:

$$U = \sum_{all\ states} \langle \varepsilon_n \rangle = \sum_{all\ states} \langle s_n \rangle \, \hbar\omega_n = 2 \cdot \sum_{n=0}^{\infty} \frac{\hbar\omega_n}{(e^{\hbar\omega_n/\tau} - 1)}$$

The factor of 2 in front of the sum takes care of the fact that since there are two perpendicular polarization directions for every frequency, there are two different states corresponding to each energy.

Classically valid equipartition theorem, which states that in equilibrium the average value of the energy of a system is:

$$\frac{U}{N} = \left(\frac{1}{2}\right) n k_{_B} T$$

where n is the number of quadratic terms that appear in the Hamiltonian of a system

Plank and The Quantum Hypothesis

We return to calculate U for the blackbody radiation problem:

$$U = 2 \cdot \sum_{n=0}^{\infty} \frac{\hbar\omega_n}{(e^{\hbar\omega_n/\tau} - 1)}$$

we recall that $\omega_n = \frac{nc\pi}{L}$

$$U = 2 \cdot \sum_{n=0}^{\infty} \frac{\left(\frac{\hbar nc\pi}{L}\right)}{\left(e^{\frac{\hbar nc\pi}{L\tau}} - 1\right)}$$

Rectangular coordinates in n-space (i.e., over all allowed of n_x, n_y and n_z). Instead of doing this we will integrate in terms of spherical coordinates in n-space. We have the following corresponding variables: $n \Leftrightarrow r;\ \theta \Leftrightarrow \theta;\ and\ \phi \Leftrightarrow \phi$. This represents (1/8) of all space.

Plank and The Quantum Hypothesis

Differential element of volume in rectangular and in spherical coordinates in n-space:

$dV = dn_x\, dn_y\, dn_z = n^2 dn\, Sin\theta\, d\theta\, d\phi$

$$U = 2 \cdot \sum_{n=0}^{\infty} \frac{\left(\frac{\hbar n c \pi}{L}\right)}{\left(e^{\frac{\hbar n c \pi}{L\tau}} - 1\right)} \to \frac{1}{8} \cdot 2 \int_0^{2\pi} d\phi \int_0^{\pi} Sin\theta d\theta \int_0^{\infty} \frac{\left(\frac{\hbar n c \pi}{L}\right)}{\left(e^{\frac{\hbar n c \pi}{L\tau}} - 1\right)} n^2 dn$$

The two integrals over the angles yield a factor 4π:

$$U = \frac{\hbar c \pi^2}{L} \int_0^{\infty} \frac{n^3 dn}{\left(e^{\frac{\hbar n c \pi}{L\tau}} - 1\right)}$$

In this last integral we change integration variables to: $x = \frac{\hbar n c \pi}{L\tau}$, with this the expression for U becomes:

Plank and The Quantum Hypothesis

$$U = \frac{\hbar c \pi^2}{L}\left(\frac{L\tau}{\hbar c\pi}\right)^4 \int_0^\infty \frac{x^3 dx}{(e^x - 1)} = \frac{\hbar c \pi^2}{L}\left(\frac{L\tau}{\hbar c\pi}\right)^4 \frac{\pi^4}{15} = \frac{\pi^2 L^3}{15(\hbar c)^3}\tau^4$$

Where the integral is $\pi^4/15$.

Since $V = L^3$, we can write an expression for the energy density:

$$\frac{U}{V} = \frac{\pi^2}{15\,(\hbar c)^3}\tau^4$$

The dependence of the energy density on the fourth power of the temperature is known as the Stefan-Boltzmann law of radiation.

In 1879, Jose Stefan, found experimentally

$$e_{tot} = \int_0^\infty e_f df = \sigma\, T^4$$

Where e_{tot} power per unit area from surface of block body at all frequency, and σ is the Stefan-Boltzmann constant, $5.67 \times 10^{-8}\ W.m^{-2}\ K^{-4}$

Plank’s Law of Radiation

The expression of the spectral energy density, that is, the energy per unit volume, per unit frequency interval, in the blackbody. This is what is called Planck’s law of radiation:

$$U = \pi \int_0^\infty \frac{\left(\frac{\hbar n c \pi}{L}\right)}{\left(e^{\frac{\hbar n c \pi}{L\tau}} - 1\right)} n^2 dn = \frac{\hbar c \pi^2}{L} \int_0^\infty \frac{n^3 dn}{\left(e^{\frac{\hbar n c \pi}{L\tau}} - 1\right)}$$

Since $\omega_n = \frac{nc\pi}{L}$ we get

$$\frac{U}{V} = \frac{\hbar}{c^3\pi^2} \int_0^\infty \frac{\omega^3 d\omega}{\left(e^{\frac{\hbar\omega}{\tau}} - 1\right)} = \int_0^\infty u_\omega d\omega \rightarrow u_\omega = \frac{\hbar}{c^3\pi^2} \frac{\omega^3}{\left(e^{\frac{\hbar\omega}{\tau}} - 1\right)}$$

The quantity u_ω is the spectral energy density, the expression first obtained by Planck.

Plank’s Law of Radiation

u_ω are positive or 0, and clearly u_ω goes to 0 at both high and low frequencies. Hence u_ω has a maximum for some ω. We determine the location of that maximum, next.

The maximum in the spectral energy density is given by:

$$\frac{du_\omega}{d\omega} = 0 = \frac{d}{d\omega}\left(\frac{\hbar}{c^3\pi^2}\frac{\omega^3}{\left(e^{\frac{\hbar\omega}{\tau}} - 1\right)}\right) = \frac{d}{dx}\left(\frac{x^3}{(e^x - 1)}\right) = 0$$

Carrying out the derivative the equation for the maximum becomes:

$$0 = \frac{3x^2(e^x-1)-x^3e^x}{(e^x-1)^2} \rightarrow 3(e^x - 1) = xe^x \rightarrow 3(1 - e^{-x}) = x$$

where $x = \frac{\hbar\omega}{\tau}$

The expression $3(1 - e^{-x}) = x$ is one that does not allow close form analytical solutions. Such expressions are called transcendental equations.

Plank’s Law of Radiation

Intersection point, x_{max}, is approximately 2.82. So:

$$2.82 \approx x_{max} = \frac{\hbar\omega_{max}}{\tau}$$

Or

$$2.82\tau \approx \hbar\omega_{max}$$

electromagnetic waves, we know that:

$$c = \lambda\nu = \lambda\left(\frac{\omega}{2\pi}\right) \rightarrow \omega = c$$

a given temperature.

$$\lambda_{max}\tau = constant$$

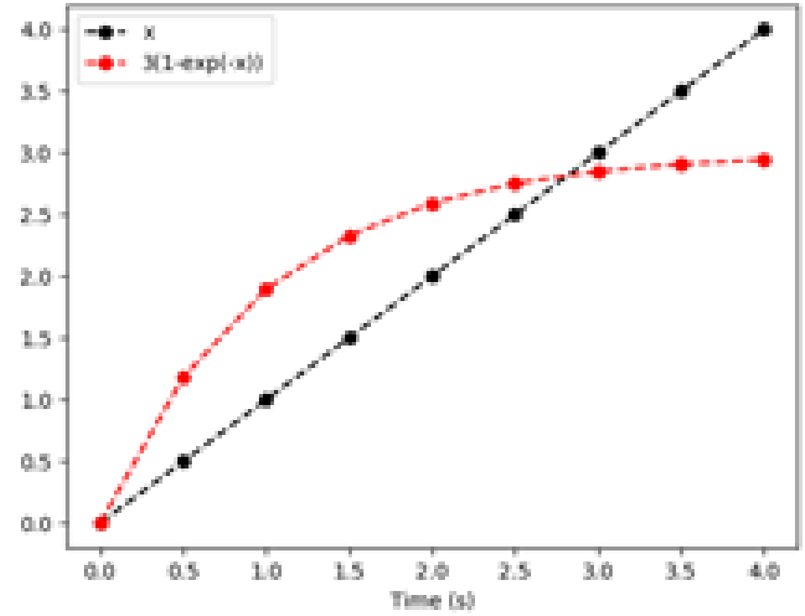


Fig-04: Graphical Solution of $3(1-e^{-x}) = x$

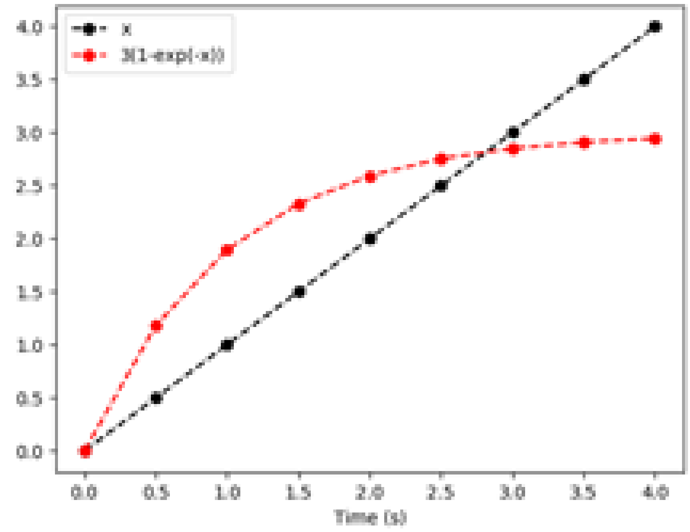
Plank’s Law of Radiation

The wavelength max at which the emitted intensity reaches its maximum value. max shift toward shorter wavelength as the blackbody get hotter,

$$\lambda_{max} \propto \frac{1}{T}$$

$$\lambda_{max}\, T = 2.898 \times 10^{-3}\ m.K$$

Where λ_{max} is the wavelength at maximum intensity, and T is absolute temperature.



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For electromagnetic waves, we know that:

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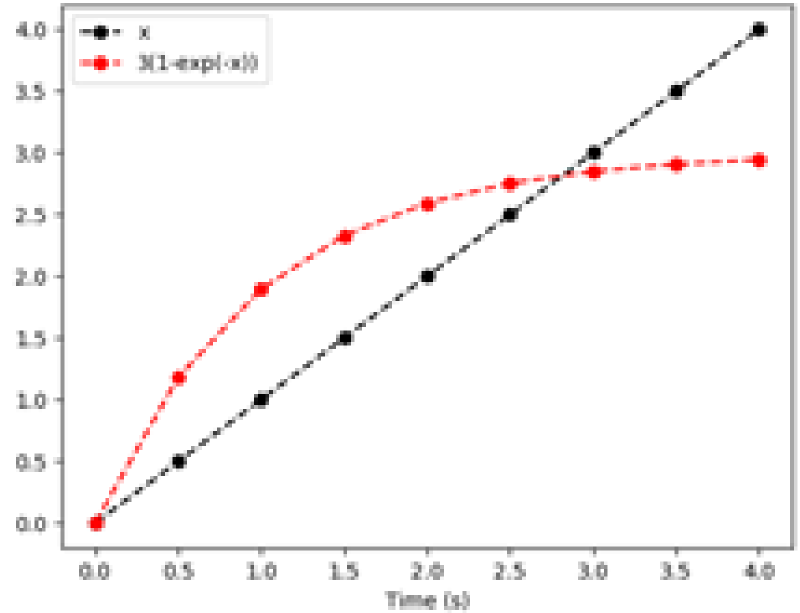
$$\lambda_{max}\tau = constant$$



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It is Wien’s displacement law.

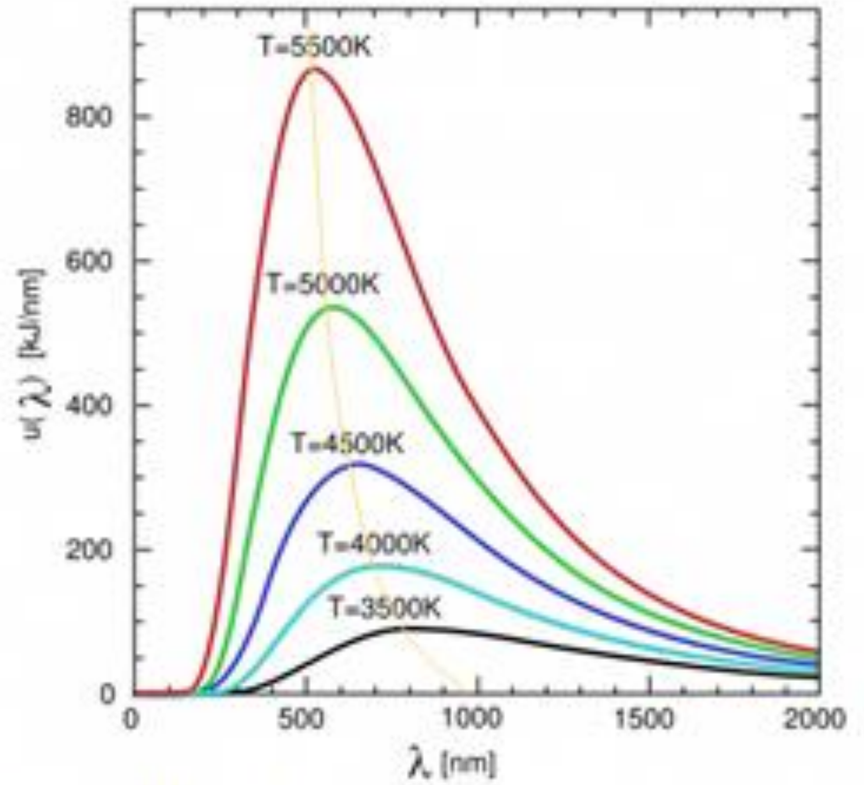

Fig-05: Blackbody radiation

Entropy of Blackbody Radiation

Let's consider a gas of photons in a volume V at a temperature. From the TdS equation that we had arrived at before: $\tau d\sigma = dU + pdV$. In this case the volume is fixed, so $dV = 0$:

$$d\sigma = \frac{dU}{\tau} = \frac{d\left(\frac{V\pi^2}{15\,(\hbar c)^3}\cdot\tau^4\right)}{\tau} = \frac{V\pi^2 d(\tau^4)}{\tau 15\,(\hbar c)^3} = \frac{V\pi^2(4\tau^2)d\tau}{15\,(\hbar c)^3}$$

Integrating this last expression to obtain σ we get:

$$\sigma = \frac{4V\pi^2\int\tau^2\,d\tau}{15\,(\hbar c)^3} = \frac{4V\pi^2\tau^3}{3\cdot 15\,(\hbar c)^3} = \frac{4\pi^2 V\tau^3}{45\,(\hbar c)^3}$$

We consider next what condition is satisfied by an expansion or a contraction that takes place reversibly and iso-entropically, i.e., adiabatically, for a gas of photons: σ is constant for a process if $V\tau^3$ is a constant.

Plank’s Law of Radiation

Energy per unit volume

$$\frac{U}{V} = \frac{\hbar}{c^3\pi^2}\int_0^\infty \frac{\omega^3 d\omega}{\left(e^{\frac{\hbar\omega}{\tau}} - 1\right)} = \int_0^\infty u_\omega d\omega \rightarrow u_\omega = \frac{\hbar}{c^3\pi^2}\frac{\omega^3}{\left(e^{\frac{\hbar\omega}{\tau}} - 1\right)}$$

The quantity u_ω is the spectral energy density,

The maximum in the spectral energy density is given by:

$$\frac{du_\omega}{d\omega} = 0$$

$$\lambda_{max}\, T = 2.898 \times 10^{-3}\, m.K$$

Where λ_{max} is the wavelength at maximum intensity, and T is absolute temperature.

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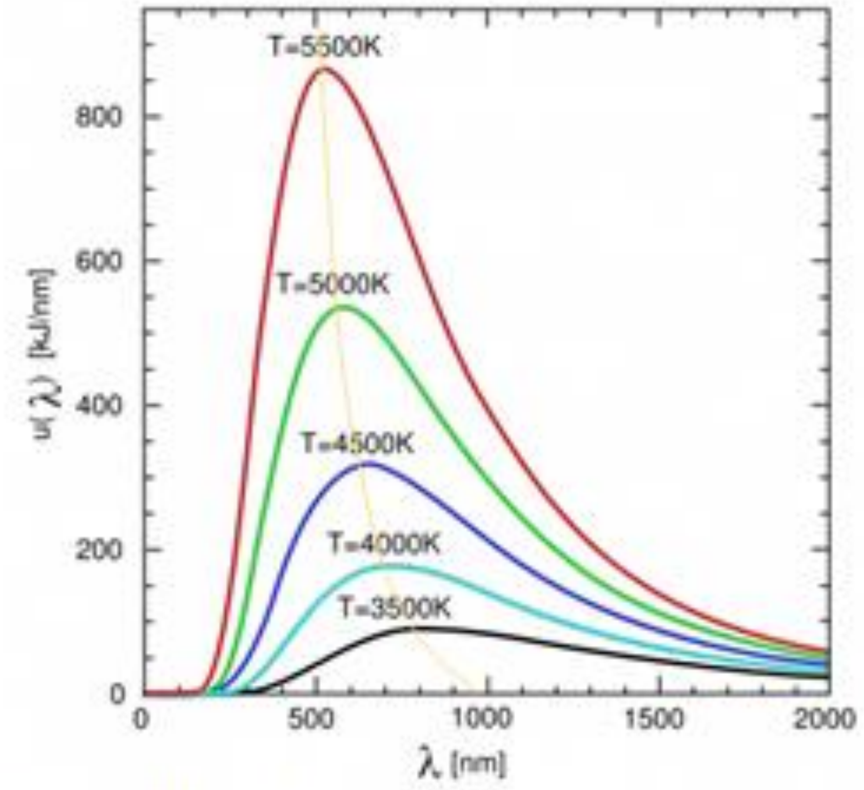

Fig-05: Blackbody radiation

Entropy of Blackbody Radiation

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Volume is fixed, so $dV = 0$:

$$d\sigma = \frac{dU}{\tau} = \frac{d\left(\frac{V\pi^2}{15\,(\hbar c)^3}\cdot\tau^4\right)}{\tau} = \frac{V\pi^2(4\tau^2)d\tau}{15\,(\hbar c)^3}$$

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For a gas of photons, σ is constant for a process if $V\tau^3$ is a constant.

As you may recall, for a classical ideal gas an adiabatic expansion is given by a constant value of $V\tau^{3/2}$.

Lattice Vibrations (Phonons)

Next, we consider a related problem: lattice vibrations on a crystalline non-conducting solid.

The lattice vibrations in a solid are directly connected to the heat capacity of the solid. In a solid, the lattice vibrations increase as the temperature increases. When energy is added to a non-conducting solid through heating, it goes into lattice vibrations.

Experimental results for crystalline solids at room temperature: when the heat capacity of solids, either non-conducting or metallic:

$$C_V = 3Nk_B \quad (where\ N\ the\ \#\ of\ atoms)$$

Where $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

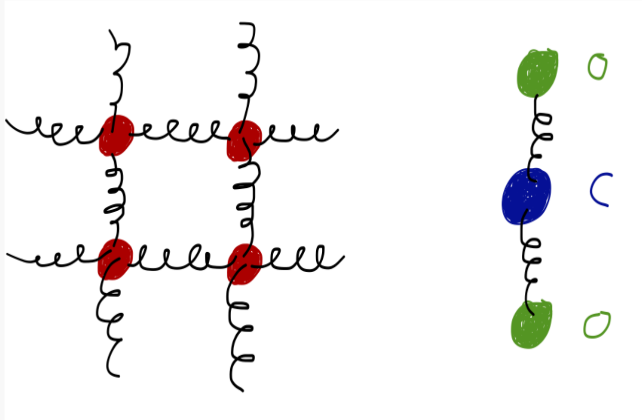
This result is called the "Dulong-Petit law". This "law" is not valid at lower temperatures.

Classical Picture (Phonons)

- For mass attached on spring, Hamiltonian is from kinetic energy from (e.g. $P_x^2/2M$) and contribution from potential energy of the spring from each coordinate we get: $-\frac{1}{2}kx^2$.
- There will be a total of 6N quadratic terms in the Hamiltonian for an N atom solid.

Classical picture: the heat capacity of our solid is

$$C_V = (6)\left(\frac{1}{2}\right)k_B N = 3Nk_B$$



Classical Picture (Phonons)

Classically, the picture would be as follows: the mass-spring for the lattice vibrations, yielding $3Nk_B$ heat capacity contribution should be present also for the metallic solid.

But for a metal, additional contribution a "gas" of free electrons. This contribution, just like that for any classical ideal gas, is $\left(\frac{3}{2}\right)Nk_B$.

So the total heat capacity for the metallic solid would be

$$\left[\left(\frac{3}{2}\right)+3\right]Nk_B = \left(\frac{9}{2}\right)Nk_B \quad (\,not\ 3Nk_{_B})$$

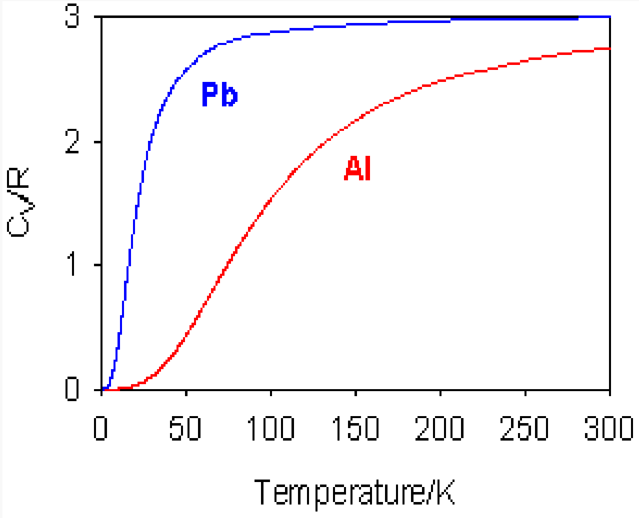
Where is the missing $\left(\frac{3}{2}\right)Nk_B$ from the electron gas? We will deal with in later.

Classical Picture (Phonons)

The second problem regarding the classical prediction, assuming we do not worry about electrons and concentrate only on non-conducting solids, is the following: the heat capacity prediction for the "nice" mass-spring classical model is $3Nk_B$, and it is a prediction that is independent of temperature.

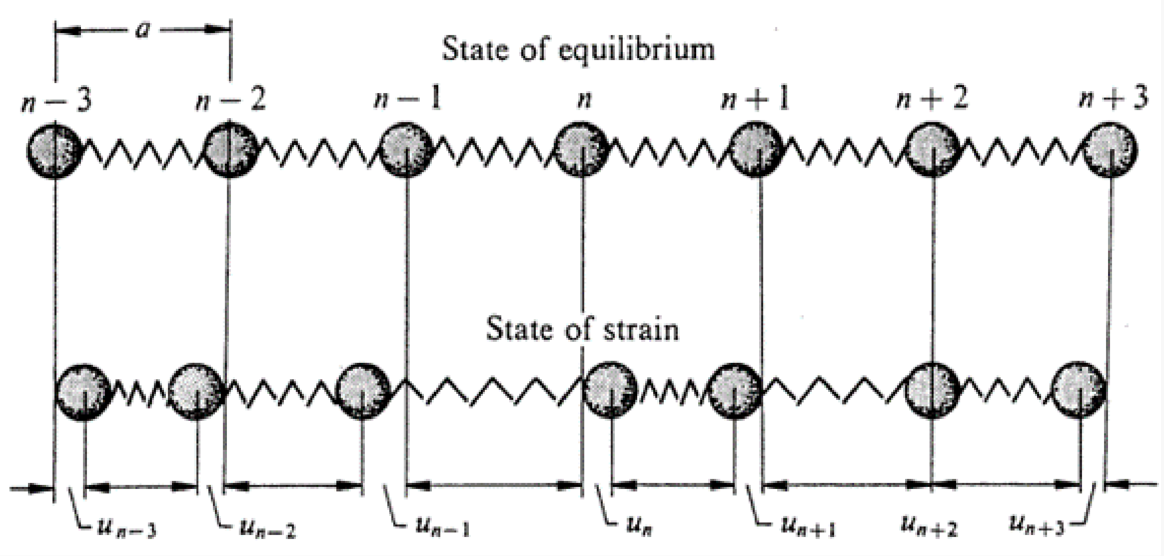
In fact, because the whole system is stiffer as temperatures become lower, the $3Nk_B$ prediction should become more and more accurate as the temperature of the non-conducting solid is lowered.

Exactly the opposite happens: In experiments, as T goes to 0, so does the heat capacity of the solid. So, not only is the heat capacity of the solid not independent from temperature, it goes to 0 as the temperature goes to 0.



Classical Picture (Phonons)

In classical model, Einstein model of a solid crystal, each atom can be treated as an independent 3-D harmonic oscillator. The problem with **Einstein model** is that the atoms don’t vibrate independently of each other. It is a complicated process which depend on the frequency. Instead of look into this, we learn the Quantum View. Now, we already know that the results we get from this classical picture of the non-conducting solid will fail at low temperature.



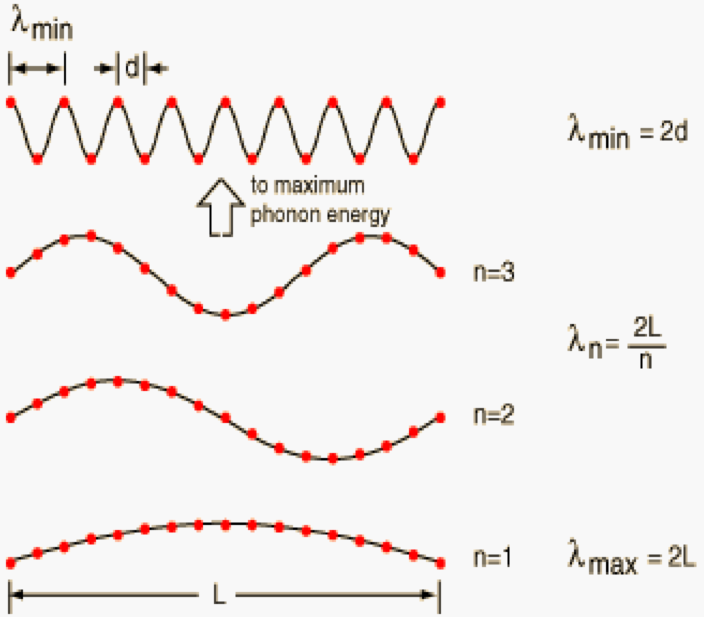
Waves in Crystals vs. Electromagnetic Waves: Quantum View!

Electromagnetic (EM) waves: In principle, can have arbitrarily short wavelengths (limited only by the theory/energy scale)

Lattice vibrations (phonons) in crystals:

- Atoms are arranged with spacing a → discrete structure
- Wavelengths shorter than 2a are not physically meaningful
- This sets a minimum wavelength:

$$\lambda \text{min} \approx 2a$$



Wavevector Limit (Brillouin Zone)

- The allowed wavevectors are bounded:

$$|\,k\,| \leq \frac{\pi}{a}$$

- This arises from the Brillouin zone and lattice periodicity

Waves in Crystals vs. Electromagnetic Waves: Quantum View!

Maximum Wavelength

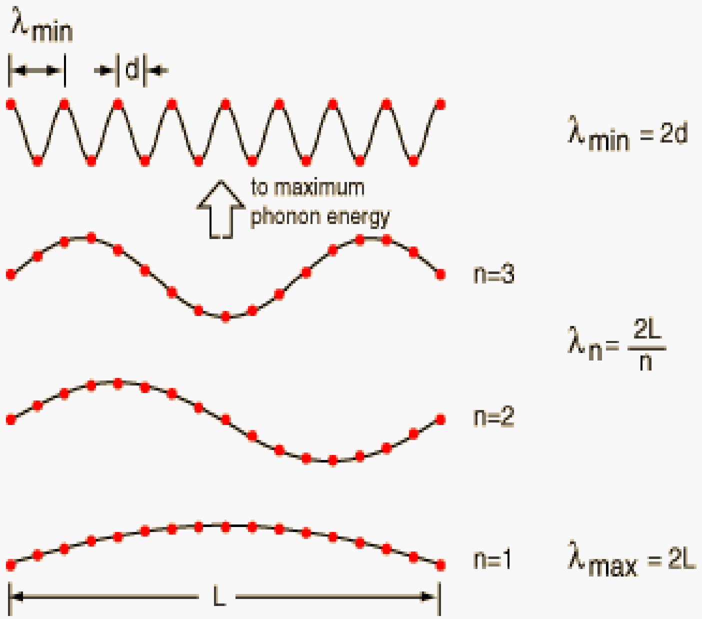
- The longest wavelength is limited by the crystal size L:

$$\lambda_{max} \approx 2L$$

- Corresponds to the lowest-frequency (long-wavelength) mode

Key Insight

- Unlike EM waves, lattice vibrations are discrete and bounded due to atomic spacing
- This leads to a finite number of vibrational modes (phonons)



Connection to Blackbody Radiation: Quantum View!

Another difference between EM waves and lattice vibrations in a solids: EM waves are transverse waves (perpendicular to the direction of propagation of the wave) lattice vibrations are both longitudinal (along the direction of propagation of the wave) and transverse.

Energy of lattice vibrations is quantized, similar to photons in a blackbody radiation field. Each vibrational mode has energy:

$$E = \hbar\omega$$

Many results from photon statistics can be applied to phonons.

Average Number of Phonons (Bose–Einstein Statistics)

$$\langle n \rangle = \langle s(\omega) \rangle = \frac{1}{(e^{\hbar\omega/\tau} - 1)}$$

Phonons obey Bose–Einstein statistics, just like photons

Debye Model of a Crystalline Solid

To explain the correct thermal behavior of solids, **Peter Debye** introduced a simplified model based on the following assumptions:

Only acoustic phonon modes considered: (i) Valid for thermal properties at low temperatures and (ii) Optical modes (present in multi-atom lattices) are neglected

Linear dispersion relation. Assumes long-wavelength behavior for all modes:

$$\omega(k) = ck$$

where c is speed of sound in the solid and $k = 2\pi/\lambda$

Debye assumed that The crystal is treated as a continuous elastic medium and atomic details and lattice structure are ignored,

Mode counting constraint

- Total number of vibrational modes is 3N for a solid with N atoms
- Introduces a cutoff frequency (Debye frequency) to preserve this limit

Phonons wave with Planck

Expression for the energy of a solid (we will use $\omega_n = v\,k_n = ck_n$, with c the speed of sound in the solid, and $k_n = (\pi n/L)$:

$$U = \sum_{all\,states} \langle s(\omega)\rangle\,\hbar\omega = \sum_{all\,states} \frac{\hbar\omega}{(e^{\hbar\omega/\tau} - 1)}$$

$$U = \frac{1}{8}\cdot 3\int_0^{2\pi} d\phi \int_0^{\pi} Sin\theta d\theta \int_0^{n_{max}} \frac{\left(\frac{\hbar nc\pi}{L}\right)}{\left(e^{\frac{\hbar nc\pi}{L\tau}} - 1\right)} n^2 dn$$

Debye Cutoff Condition: the cutoff n_D is determined by requiring the correct number of modes .

n_{max} by imposing the condition that the total number of modes has to be $3N$ for the N atom solid:

$$3\cdot\frac{1}{8}\cdot 4\pi \int_0^{n_{max}} n^2\,dn = 3N \rightarrow\ n_{max}^3 = \frac{6N}{\pi} \rightarrow\ n_{max} = \left(\frac{6N}{\pi}\right)^{1/3}$$

Usually, n_D (after Debye) is used instead of n_{max}

Phonons wave with Planck

We find

$$U = \frac{3}{2}\frac{\hbar c\pi^2}{L}\int_0^{n_D}\frac{n^3 dn}{\left(e^{\frac{\hbar n c\pi}{L\tau}}-1\right)}$$

change of variables:

$$\frac{n\hbar c\pi}{L\tau} = x \rightarrow dn = \frac{L\tau}{\hbar c\pi}dx$$

And $x_D = n_D\frac{\hbar c\pi}{L\tau}$

$$x_D = n_D\frac{\hbar c\pi}{L\tau} = \left(\frac{6N}{\pi}\right)^{1/3}\frac{\hbar c\pi}{Lk_B T} = \frac{\theta_D}{T} \quad \rightarrow \quad \theta_D = \left(\frac{6N}{\pi}\right)^{1/3}\frac{\hbar c\pi}{Lk_B}$$

The quantity θ_D is called the Debye temperature of the solid.

Phonons wave with Planck

We know

$$\int_{0}^{\infty} \frac{x^3 dx}{(e^x - 1)} = \frac{\pi^4}{15}$$

Unfortunately, the integral that we have is not available in closed form. So, we need to proceed with the limiting temperatures in which we are interested.

$$U = \frac{3}{2} \cdot \frac{V}{(\hbar c)^3} \cdot \frac{\tau^{\ 4}}{\pi^2} \int_{0}^{x_D} \frac{x^3 dx}{(e^x - 1)}$$

where $x_D = \frac{\theta_D}{T}$

Phonons wave with Planck

a. **In the high temperature limit**, $x_D \left(= n_D \frac{\hbar c\pi}{L\tau}\right) << \ 1$

We can use the approximation:

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \rightarrow \frac{1}{e^x - 1} = \frac{1}{x\left(1 + \frac{x}{2!} + \frac{x^2}{3!} + \cdots\right)}$$

Using the approximation: $\frac{1}{1+y} \approx 1 - y$ for small y, and calling $y = \frac{x}{2!} + \frac{x^2}{3!} + \cdots$ we get:

$$\frac{1}{e^x - 1} = \frac{1}{x}\left(1 - \frac{x}{2!} - \frac{x^2}{3!} - \cdots\right)$$

And with this:

$$\frac{x^3}{e^x - 1} = x^2\left(1 - \frac{x}{2!} - \frac{x^2}{3!} - \cdots\right) \approx x^2\left(1 - \frac{x}{2}\right)$$

$$U = \frac{3}{2} \cdot \frac{V}{(\hbar c)^3} \cdot \frac{\tau^4}{\pi^2} \int_0^{x_D} \frac{x^3 dx}{(e^x - 1)} \approx \frac{3}{2} \cdot \frac{V}{(\hbar c)^3} \cdot \frac{\tau^4}{\pi^2} \int_0^{x_D} x^2\left(1 - \frac{x}{2}\right)$$

Phonons wave with Planck

In the high temperature limit. This integral is easy to do. We will just keep the leading term (neglect the x/2):

$$U \approx \frac{3}{2} \cdot \frac{V}{(\hbar c)^3} \cdot \frac{\tau^{\,4}}{\pi^2} \int_0^{x_D} x^2 dx = \frac{3}{2} \cdot \frac{V}{(\hbar c)^3} \cdot \frac{\tau^{\,4}}{\pi^2} \left(\frac{{x_D}^3}{3}\right)$$

By replacing $x_D = \frac{\theta_D}{T} = \left(\frac{6N}{\pi}\right)^{\frac{1}{3}} \frac{\hbar c \pi}{L k_B T}$

$$U \approx \frac{1}{2} \cdot \frac{V}{(\hbar c)^3} \cdot \frac{(k_B T)^4}{\pi^2} \cdot \left(\left(\frac{6N}{\pi}\right)^{\frac{1}{3}} \frac{\hbar c \pi}{L k_B T}\right)^3$$

After cancelling things out this expression becomes just:

$$U \approx 3N k_B T \quad \rightarrow \; C_V \approx 3N k_B$$

Agreement with the Dulong-Petit law. So, the Debye approximation leads to the correct result in the high temperature limit.

Phonons wave with Planck

b. **Low temperature Limit:** low temperatures mean temperatures that are:

$$T \ll \theta_D \;\rightarrow\; x_D = \left(\frac{\theta_D}{T}\right) >> 1$$

for low temperatures. With all of this, we can replace x_D with ∞:

$$U = \frac{3}{2}\cdot\frac{V}{(\hbar c)^3}\cdot\frac{\tau^{\,4}}{\pi^2}\int_0^{x_D}\frac{x^3dx}{(e^x-1)} \rightarrow U = \frac{3}{2}\cdot\frac{V}{(\hbar c)^3}\cdot\frac{\tau^{\,4}}{\pi^2}\int_0^{\infty}\frac{x^3dx}{(e^x-1)} = \frac{3}{2}\cdot\frac{V}{(\hbar c)^3}\cdot\frac{\tau^{\,4}}{\pi^2}\cdot\frac{\pi^4}{15}$$

$$U = \frac{\pi^2}{10}\cdot\frac{{k_B}^4V}{(\hbar c)^3}T^4$$

which, of course looks very similar to the blackbody result. This expression for the energy leads to a heat capacity:

$$C_V = \frac{4\pi^2}{10}\cdot\frac{{k_B}^4V}{(\hbar c)^3}T^3 \;\rightarrow C_V\sim T^3$$

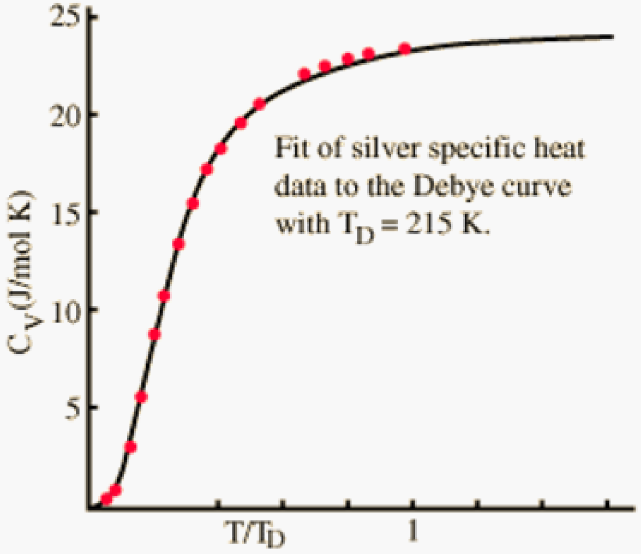
as the temperature approaches 0. This is the so-called, “Debye T^3 law”.

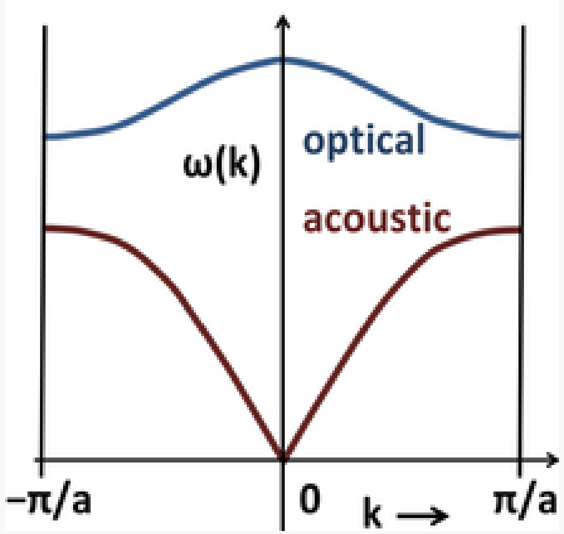
Phonons wave with Planck

The behavior observed in solids is such that, in fact, the contributions from lattice vibrations to the heat capacity does go like T^3 as the temperature goes to 0.

The Debye model does a very good job at capturing the behavior exhibited by solids.

So, the Debye model gives a nice, simple picture for the heat capacity of a solid, and provides us with a convenient interpolation formula for the heat capacity of solids, which has the basic physical behavior of the solid at high and low temperatures. It does not just determine that the overall behavior of the heat capacity but gives the correct temperature dependence of the behavior (i.e., it does not just tell you that the heat capacity goes to 0, but it tells you that it does so like T^3).





Quiz

(a) At what wavelength does a room-temperature ($T = 20^o\ C$) object emit the maximum thermal radiation?

(b) To what temperature must we heat it until its peak thermal radiation is in the red region of the spectrum @ 650nm?

(c) What is the ratio of thermal radiation between above two temperature?

Thank you very much for your attention