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Photons and Phonons

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1. Photons

1.1. Blackbody Radiation

All objects emit electromagnetic radiation, the peak wavelength is a function of temperature. In most cases the radiation is not in thermal equilibrium with matter. Consider an opaque enclosure whose walls are maintained at a constant temperature T. The radiation and walls will reach thermal equilibrium and the radiation will have definite properties.

To study the properties of this equilibrium radiation we can imagine cutting a small hole in the enclosure. If the hole is small enough, it will not disturb the radiation in the cavity. Radiation will be emitted through the hole and this radiation will have the same properties as the cavity radiation. This radiation will also have the same properties as the radiation emitted by a perfectly black body at the same temperature as the enclosure T. Why? A perfectly black body absorbs all radiation falling on it – the hole behaves in the same way – all incident radiation will enter the hole.

Thus, the terms cavity radiation and blackbody radiation are synonymous. We will analyze the situation by treating blackbody radiation as a gas of photons.

1.2. The Partition Function for Photons

Photons are particles of spin one and are bosons, we calculate their properties without making use of this fact. We will do this for now. We know that we can superimpose electric and magnetic fields, in other words they obey the principle of linear superposition. This means that photons do not interact, and we can treat them as an ideal gas.

The thermal equilibrium between the cavity radiation and the cavity walls is produced by the continuous emission and absorption of photons by the atoms of the cavity walls. This means that the number of photons in the cavity is not constant — instead, it fluctuates

about a mean value that depends on T.

$$Z = \sum_r e^{-\beta E_r}$$

where E_r is the energy of the rth state. We can write that

$$E_r = \sum_i n_i \epsilon_i$$

where the occupation numbers are $n_i = 0, 1, 2, \ldots$ for all i. So

$$Z = \sum_{n_1, n_2, \ldots} exp \left\{ -\beta \sum_i n_i \epsilon_i \right\}$$

There is no constraint on the total number of photons, this means that each of the occupation numbers assumes all possible values independently of the others, so rather than $Z(T, V, N)$ we have $Z(T, V)$

$$Z = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \ldots \sum exp \left\{ -\beta \sum_i n_i \epsilon_i \right\}$$

$$Z = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum e^{-\beta n_1 \epsilon_1} e^{-\beta n_2 \epsilon_2} e^{-\beta n_3 \epsilon_3} \cdots$$

$$Z = \left(\sum_{n_1} e^{-\beta n_1 \epsilon_1} \right) \left(\sum_{n_2} e^{-\beta n_2 \epsilon_2} \right) \cdots \left(\sum_{n_i} e^{-\beta n_i \epsilon_i} \right)$$

and so we write this as

$$Z = \prod_{j=1}^{\infty} \left(\sum_{n_j} e^{-\beta n_j \epsilon_j} \right).$$

Let's examine a single term of this equation. That is consider

$$\sum_{n_j=0}^{\infty} e^{-\beta n_j \epsilon_j}$$

n_j takes on the values $0, 1, 2, \ldots, \infty$, so we can expand it as

$$\sum_{n_j=0}^{\infty} e^{-\beta n_j \epsilon_j} = 1 + e^{-\beta \epsilon_j} + e^{-2\beta \epsilon_j} + e^{-3\beta \epsilon_j} + \ldots$$

Now, if we let $x = e^{-\beta\epsilon_j}$, and we see that we have the geometric series

$$1 + x + x^2 + x^3 + \ldots$$

Now

$$1 + x + x^2 + x^3 + \ldots = \frac{1}{1-x} \quad \text{if } x < 1.$$

$$x = e^{-\beta\epsilon_j} = \frac{1}{e^{\beta\epsilon_j}}$$

(Convince yourselves that this holds, you might use $\epsilon_j = \hbar\omega$.) So we can rewrite our photon partition function as

$$Z_{ph}(T, V) = \prod_{j=1}^{\infty} \frac{1}{1 - e^{-\beta\epsilon_j}}$$

In principle this gives us all the physics. To make any further progress, we need to calculate the mean occupation number, we know how to do this, but we haven't actually made the calculation.

1.3. Mean Occupation Number

$$\langle n_i \rangle = \frac{\sum_r n_i e^{-\beta E_r}}{Z} = \frac{\sum_{n_1, n_2, \ldots} n_i e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \ldots)}}{Z}.$$

Now consider

$$\sum n_i e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \ldots)}$$

we use it and

$$Z_{ph}(T, V) = \prod_{j=1}^{\infty} \frac{1}{1 - e^{-\beta \epsilon_j}}$$

to evaluate

$$\langle n_i \rangle.$$

To develop the result, it is useful to start from the first step of our calculation of the partition function for photons

$$Z \quad = \quad \sum_{n_1, n_2, \ldots} exp \left\{ -\beta \sum_i n_i \epsilon_i \right\}$$

$$= \sum_{n_1, n_2, \ldots} \mathrm{e}^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3 + \ldots)}.$$

Now

$$
\begin{aligned}
-\frac{1}{\beta} \left(\frac{\partial Z}{\partial \epsilon_i} \right)_{\beta, \epsilon_j} &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \sum_{n_1, n_2, \ldots} \mathrm{e}^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3 + \ldots)} \\
&= -\frac{1}{\beta} \sum_{n_1, n_2, \ldots} (-\beta n_i) \mathrm{e}^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3 + \ldots)} \\
&= \sum_{n_1, n_2, \ldots} n_i \mathrm{e}^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3 + \ldots)}.
\end{aligned}
$$

And so we can write

$$-\frac{1}{\beta Z} \left(\frac{\partial Z}{\partial \epsilon_i} \right)_{\beta, \epsilon_j} = \frac{1}{Z} \sum_{n_1, n_2, \ldots} n_i \mathrm{e}^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3 + \ldots)} \equiv n_i.$$

Where the equivalence is obvious from our starting point. Thus we have the result

$$\langle n_i \rangle = -\frac{1}{\beta Z}\left(\frac{\partial Z}{\partial \epsilon_i}\right)_{\beta,\epsilon_j} = -\frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \epsilon_i}\right)_{\beta,\epsilon_j}$$

At this point we can use the product form for our photon partition function

$$Z_{ph} = \prod_{j=1}^{\infty}\frac{1}{1-\mathrm{e}^{-\beta\epsilon_j}}$$

$$\begin{aligned} \ln Z_{ph} &= \ln\prod_{j=1}^{\infty}\frac{1}{1-\mathrm{e}^{-\beta\epsilon_j}} \\ &= \sum_{j=1}^{\infty}(\ln 1 - \ln(1-\mathrm{e}^{-\beta\epsilon_j})) \\ &= -\sum_{j=1}^{\infty}\ln(1-\mathrm{e}^{-\beta\epsilon_j}) \end{aligned}$$

$$\langle n_i \rangle = -\frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial \epsilon_i} \right)_{\beta, \epsilon_j}$$

so

$$\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \sum_{j=1}^{\infty} \ln(1 - e^{-\beta \epsilon_j})$$

we can rewrite this as

$$\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \ln(1 - e^{-\beta \epsilon_i})$$

as all the other terms would not contribute to the result. Thus,

$$\langle n_i \rangle = \frac{(1 - e^{-\beta \epsilon_i})^{-1}}{\beta} \frac{\partial}{\partial \epsilon_i} (1 - e^{-\beta \epsilon_i})$$

$$\langle n_i \rangle = \frac{e^{-\beta \epsilon_i}}{1 - e^{-\beta \epsilon_i}} = \frac{1}{e^{\beta \epsilon_i} - 1}$$

This is the Planck distribution function. It gives us average photon occupancies.

1.4. The Properties of Blackbody Radiation

The energy of a photon is $E = h\nu = \hbar\omega$. We know that the density of states fuunction in k-space is

$$
\begin{aligned}
f(k)dk &= \frac{Vk^2\mathrm{d}k}{2\pi^2} \\
&= \text{number of states between } k \text{ and } \mathrm{d}k.
\end{aligned}
$$

When we are dealing with photons, we need to multiply the density of states function by 2 because the electromagnetic field has two polarizations. First, we'll find the numbers of states between ω and $\omega + \mathrm{d}w$. Using $k = 2\pi/\lambda$, $\omega = 2\pi\nu$, and $c = \lambda\nu$, we have $k = \omega/c$ and

$$
f(\omega)\mathrm{d}\omega = \frac{V\omega^2}{2\pi^2 c^2}\frac{\mathrm{d}k}{\mathrm{d}\omega}\mathrm{d}\omega.
$$

Now $c = \omega/k$ and $v_g = \frac{\mathrm{d}\omega}{\mathrm{d}k}$ and we rewrite the density of states function as

$$
f(\omega)\mathrm{d}\omega = \frac{V\omega^2\mathrm{d}\omega}{2\pi^2 c^2 v_g}.
$$

For a non-dispersive medium (i.e. one in which $c \neq c(\omega)$, $v_g = c$, and

$$f(\omega)\mathrm{d}\omega = \frac{V\omega^2 \mathrm{d}\omega}{2\pi^2 c^3},$$

and finally multiplying by 2 as we are dealing with photons, we arrive at

$$f(\omega)\mathrm{d}\omega = \frac{V\omega^2 \mathrm{d}\omega}{\pi^2 c^3}.$$

Now, let the number of photons with frequency between ω and $\omega + \mathrm{d}\omega$ be $\mathrm{d}N_\omega$ where we can write

$$\mathrm{d}N_\omega = \langle n_i \rangle f(\omega)\mathrm{d}\omega$$

Let the energy in the frequency range between ω and $\omega + \mathrm{d}\omega$ be $\mathrm{d}E_\omega$, then

$$
\begin{aligned}
\mathrm{d}E_\omega &= \hbar\omega \mathrm{d}N_\omega \\
&= \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3 \mathrm{d}\omega}{\mathrm{e}^{\beta\hbar\omega} - 1}.
\end{aligned}
$$

The density of states $f(\omega)d\omega$ depends only on the size of the container. This means that the photon density and the energy density in the cavity are uniform. So we write

$$\frac{dE_\omega}{V} = \frac{\hbar\omega^3 d\omega}{\pi^2 c^3(e^{\beta\hbar\omega} - 1)} = u(\omega, T)d\omega,$$

where

$$
\begin{aligned}
u(\omega, T) &= \text{energy/unit volume/unit frequency range} \\
&= \text{spectral density} \\
&= \frac{\hbar\omega^3}{\pi^2 c^3(e^{\beta\hbar\omega} - 1)}.
\end{aligned}
$$

This is the Planck radiation law. A plot of $u(\omega, T)$ against (usually inverse) wavelength would show a different peak for each temperature.

So for every temperature there is a unique frequency that is the peak emission frequency. At 6000 K, the peak lies at the edge of the

visible spectrum. Starting from

$$u(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3(e^{\beta\hbar\omega} - 1)}$$

we can find the frequency of peak emission by calculating the derivative

$$\left(\frac{\partial u(\omega, T)}{d\omega}\right)_T = 0$$

so

$$\frac{\partial}{\partial\omega} \frac{\hbar\omega^3}{\pi^2 c^3}(e^{\beta\hbar\omega} - 1)^{-1} = 0$$

$$3\frac{\hbar\omega^2}{\pi^2 c^3}(e^{\beta\hbar\omega} - 1)^{-1} + \frac{\hbar\omega^3}{\pi^2 c^3}(-1)(e^{\beta\hbar\omega} - 1)^{-2}e^{\beta\hbar\omega}\beta\hbar = 0$$

$$3\omega^2 = \frac{\omega^3 e^{\beta\hbar\omega}\beta\hbar}{(e^{\beta\hbar\omega} - 1)}$$

$$3(e^{\beta\hbar\omega} - 1) = \beta\hbar\omega e^{\beta\hbar\omega}.$$

Now, let $x = \beta\hbar\omega$, and note that $\omega = \omega_{max}$, we *are* locating the maximum. Thus rewriting, we get

$$3(\mathrm{e}^x - 1) = x\mathrm{e}^x.$$

To find the value of x satisfying this equation, we can use numerical or graphical methods.

What value of x satisfies

$$\frac{3(\mathrm{e}^x - 1)}{\mathrm{e}^x} = x.$$

One way to approach this is to guess an answer and iterate, let's try it with an initial guess of $x = 3$. Then we find

$$
\begin{aligned}
\frac{3(\mathrm{e}^3 - 1)}{\mathrm{e}^3} &= 2.8506, \text{ this becomes our new guess} \\
&= 2.8266 \\
&= 2.8824 \\
&\vdots \\
&= 2.822.
\end{aligned}
$$

Thus, our result is $x = \beta\hbar\omega_{max} = 2.822$ or $\frac{\hbar\omega_{max}}{kT} = 2.822$. This is the Wien displacement law. You can use it to estimate surface temperature from peak emission wavelength. It is used to estimate the surface temperatures of stars.

1.5. Total Energy Density of Blackbody Radiation

$$U(T) = \frac{E}{V} = \int\limits_0^\infty u(\omega, T)\mathrm{d}\omega$$

$$U(T) = \int\limits_0^\infty \frac{\hbar\omega^3}{\pi^2 c^3 (\mathrm{e}^{\beta\hbar\omega} - 1)}\mathrm{d}\omega$$

Let $x = \beta\hbar\omega$, so $\mathrm{d}x = \beta\hbar\mathrm{d}\omega$, then

$$U(T) = \frac{\hbar}{\pi^2 c^3} \frac{1}{(\beta\hbar)^3} \frac{1}{\beta\hbar} \int\limits_0^\infty \frac{x^3 \mathrm{d}x}{\mathrm{e}^x - 1}$$

where

$$\int\limits_0^\infty \frac{x^3 \mathrm{d}x}{\mathrm{e}^x - 1} = \frac{\pi^4}{15}, \text{ a simple contour integral}$$

leading to

$$U(T) = \frac{\pi^2 k^4 T^4}{15 c^3 \hbar^3} = \frac{E}{V} = aT^4.$$

This is the Stefan-Boltzmann law, where $\sigma = \frac{c}{4}a$ is the Stefan-Boltzmann constant.

1.6. Photon Entropy

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

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$$

Let E, V be constant so that $\mathrm{d}E = T\mathrm{d}S$, then

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

$$\left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{4}{15}\frac{\pi^2 k^4 V T^3}{c^3 \hbar^3}$$

so, provided N, V are constants, we can write

$$dE = \frac{4}{15}\frac{\pi^2 k^4 V T^3}{c^3 \hbar^3}dT$$

$$dS = \frac{dE}{T} = \frac{4}{15}\frac{\pi^2 k^4 V T^2}{c^3 \hbar^3}dT$$

$$S = \frac{4}{15}\frac{\pi^2 k^4 V}{c^3 \hbar^3}\int T^2 dT$$

$$S = \frac{4}{45}\pi^2 k^4 V \left(\frac{T}{c\hbar}\right)^3 + \text{constant}.$$

Now, as we have previously noted, by the strong form of the third law of thermodynamics, $\lim_{T \to 0} S = 0$ resulting in

$$S = \frac{4}{45}\pi^2 k^4 V \left(\frac{T}{c\hbar}\right)^3.$$

From this, we can conclude that a process carried out at constant entropy (called an *isentropic* process is one for which $VT^3 = $ constant.

1.7. Radiation Pressure

For an ideal gas of N particles, each of mass m, we can write

$$pV = \frac{1}{3}Nm\langle v^2 \rangle$$

where

$$\langle v^2 \rangle^{\frac{1}{2}} = \text{r.m.s. velocity of the particles}$$

Now, if we let $Nm = M$ be the mass of the gas, then

$$pV = \frac{1}{3}\frac{M}{V}\langle c^2 \rangle.$$

Now for a photon gas where all the particles have the same velocity c,

$$p = \frac{1}{3}\frac{M}{V}c^2 = \frac{1}{3}\frac{E}{V} = \frac{1}{3}\frac{\langle E \rangle}{V} = \frac{1}{3}U(T)$$

for a photon gas.

2. Phonons

The energy of elastic waves is quantized – just as the energy of electromagnetic waves in a cavity is quantized. When we talk about phonons, we are talking about the allowed vibrational modes in solids. The energies of these *lattice vibrations* are quantized because only certain modes of vibration are allowed. Thus, we can treat elastic vibrations in solids as particles or waves. The energy in a vibrational mode can be treated as a quantum mechanical oscillator of the same frequency. We can develop our treatment based on the properties of quantum mechanical oscillators. Ultimately, we shall calculate heat capacities — before embarking on those calculations, let's look at the heat capacity of solids.

2.1. The heat capacity of solids

When we transfer an amount of heat $\triangle Q$ to raise the temperature of a material by $\triangle T$, we define the heat capacity of the material as

$$\lim_{\triangle T \to 0} \frac{\triangle Q}{\triangle T} = C$$

or

$$C = \frac{\text{d}Q}{\text{d}T}$$

Then using

$$\text{d}E = T\text{d}S - p\text{d}V \text{ where } T\text{d}S = \text{d}Q,$$

we have

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_v, \ \text{d}V = 0, \ so \ C_v = \left(\frac{\partial E}{\partial T}\right)_v.$$

We will now investigate the contributions of crystal lattice vibrations to the heat capacity of solids. By the heat capacity, we shall usually mean the heat capacity at constant volume. Let's review the properties of a representative solid.

- At room temperature, in most cases, the value of the heat capacity is $3Nk = 3R$ per mole $= 25$ J mol^{-1}deg^{-1}. This result, derived from data is called the Dulong and Petit law. While derived from data, it can be "justified."

  Consider a crystal consisting of N identical atoms. Each atom is bound to its equilibrium position by forces that we can model using springs. (We introduce the principle of equipartition as an axiom here, but should note that it can be deduced from statistical mechanics.) The equipartition theorem says that each velocity component (linear or angular) has an average energy of $kT/2$ per molecule associated with it. The number of velocity components needed to describe the motion is called the *number of degrees of freedom.* A monatomic gas has 3 degrees of freedom. So $E = \frac{3}{2}kT$ per molecule or $\frac{3}{2}R$ per mole.

  Now consider a solid, each atom vibrates about an equilibrium position. By the equipartition theorem, each atom should have an average kinetic energy of $\frac{kT}{2}$, for each of its three vibrational

degrees of freedom. In addition, each atom has potential energy associated with elastic deformation. For simple harmonic motion, the instantaneous oscillator energy is

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

and the average kinetic energy is equal to the average potential energy. In a crystal lattice, each atom is essentially a three-dimensional harmonic oscillator. Provided that the springs are Hooke's law springs, it can be shown that:

$$\langle KE \rangle = \langle PE \rangle = \frac{3}{2}kT$$

so

$$\langle E \rangle = 3kT$$

For N atoms

$$\langle E \rangle = 3NkT$$

and

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = 3Nk = 3R\text{mole}$$

this is the Dulong and Petit law.

- At lower temperatures the heat capacity drops markedly and approaches zero as T^3 in insulators and as T in conductors.

- In magnetic material, there is a large contribution to the heat capacity over the range of temperatures at which the magnetic moments become ordered. Why? A change in order $\Rightarrow$ a change in entropy. We know that we can write

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v$$

So a change in entropy contributes to a change in heat capacity. Below 0.1 K the ordering of nuclear magnetic moments can give rise to very large heat capacities.

2.2. The quantum mechanical harmonic oscillator

For such an oscillator we write

$$\varepsilon_s = \left(s + \frac{1}{2}\right)\hbar\omega \quad s = 0, 1, 2, \ldots$$

$\hbar\omega/2$ is called the zero point energy (zpe), we will often set it to zero since it doesn't affect the heat capacity. If a mode is excite to a quantum number s, we say that there are s phonons in the mode. If Hooke's law is applicable, the normal modes of vibration of lattice atoms are independent. The average energy of a lattice mode depends only on its frequency ω and the number of phonons in the mode s.

- **The partition function for a single oscillator**

$$Z = \sum_r e^{-\varepsilon_r/kT} = \sum_{s=0}^{\infty} e^{-(s+\frac{1}{2})\hbar\omega/kT}$$

let $\hbar\omega/kT = x$ then

$$Z = \sum e^{-(s+\frac{1}{2})x} = e^{-\frac{x}{2}} \sum e^{-sx}$$

The sum is of the form $\sum y^s$ where $y = e^{-\hbar\omega/kT}$, if $y < 1$ we have a geometric series, $\sum = \frac{1}{1-y}$. So

$$Z = \frac{e^{-x/2}}{1 - e^{-x}} = \frac{e^{-\hbar\omega/2kT}}{1 - e^{-\hbar\omega/kT}}$$

We can use this result to calculate a variety of properties.

- **Helmholtz Free energy of an oscillator**

$$F = -kT \ln Z = \frac{\hbar\omega}{2} + kT \ln(1 - e^{-\hbar\omega/kT})$$

- **Average oscillator energy**

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$Z = \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1 - \mathrm{e}^{-\beta\hbar\omega}}$$

$$\ln Z = -\frac{\beta\hbar\omega}{2} - \ln(1 - \mathrm{e}^{-\beta\hbar\omega})$$

so

$$
\begin{aligned}
\langle E \rangle &= -\frac{\partial \ln Z}{\partial \beta} \\
&= \frac{\hbar\omega}{2} + \frac{\partial}{\partial \beta}\ln(1 - \mathrm{e}^{-\beta\hbar\omega}) \\
&= \frac{\hbar\omega}{2} + \frac{1}{1 - \mathrm{e}^{-\beta\hbar\omega}}\hbar\omega\mathrm{e}^{-\beta\hbar\omega} \\
&= \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega} - 1}
\end{aligned}
$$

Now, comparing this with $E = (s + 1/2)\hbar\omega$, we see that we can write

$$E = \left(\langle s \rangle + \frac{1}{2} \right) \hbar\omega$$

where

$$\langle s \rangle = \frac{1}{e^{\hbar\omega/kT} - 1}.$$

We can interpret this as the average occupancy of a photon mode ω. As we have already seen (when we derived it directly for photons) this is the Planck distribution.

3. The Einstein Model (1907)

This was the first application of quantum theory to solid state physics. In this model, we treat the system as N oscillators connected by springs in one dimension. Einstein assumed that all the oscillators oscillate with a common frequency.

The average thermal energy of an oscillator of frequency ω is

$$E = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$$

for N oscillators in one dimension, the average thermal energy is

$$E = N\langle s \rangle \hbar\omega, \text{ ignoring the ZPE.}$$

Then using

$$E = \frac{N\hbar\omega}{e^{\hbar\omega/kT} - 1}$$

and

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v$$

We find

$$
\begin{aligned}
C_v &= N\hbar\omega \frac{\partial}{\partial T}[e^{\hbar\omega/kT} - 1]^{-1} \\
&= N\hbar\omega(-1)[e^{\hbar\omega/kT} - 1]^{-2}e^{\hbar\omega/kT}\left(-\frac{\hbar\omega}{kT^2}\right) \\
&= Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2}.
\end{aligned}
$$

This is for the one-dimensional Einstein solid. In three dimsnsions, we replace N ny $3N$, since each atom has three degrees of freedom

and we find

$$C_v = 3Nk \left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2}.$$

How good is this expression? Let $x = \hbar\omega/kT$, then

$$C_v = 3Nk \frac{x^2 e^x}{(e^x - 1)^2},$$

we can then examine the behavior of this expression at high and low temperature.

3.1. High Temperature Limit

At high temperatures,

$$x = \frac{\hbar\omega}{kT} \ll 1$$

so let's examine the term $\frac{x^2 e^x}{(e^x-1)^2}$ as $x \to 0$.
Let

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

so we have

$$\frac{x^2(1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots)}{(x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots)^2}.$$

This obviously goes to 1 as $x \to 0$. This yields the classical result of Dulong and Petit, $C_v = 3Nk$.

3.2. Low temperature limit

In the low temperature limit, $x \gg 1$, $e^x \gg 1$ so

$$C_v = 3Nk\frac{x^2 e^x}{(e^x - 1)^2} \simeq 3Nkx^2 e^x = 3Nk\left(\frac{\hbar\omega}{kT}\right)^2 e^{-\hbar\omega/kT}.$$

In this expression, $C_v \to 0$ as $T \to 0$ as required. (The exponential always wins.)

3.3. Summary

Thus, in the Einstein model, the high temperature behavior is good, the behavior at $T = 0$ is good, the low temperature behavior is not

very good. While we measure that $C_v \propto T^3$, but in this expression at low temperature $C_v \propto e^{-\hbar\omega/kT}$.

It is customary to introduce the Einstein temperature Θ_E, through

$$x = \frac{\hbar\omega}{kT} = \frac{\Theta_E}{T},$$

and we call $\omega = \omega_E$ the Einstein frequency. If $T \gg \Theta_E$, $C_v = 3Nk$. Einstein temperatures are properties of the material and are tabulated. If $T \ll \Theta_E$ we are in the low temperature regime. This model is so simple, it is surprising that it works at all.

4. The Debye Model, 1912

This model is similar to the Einstein model in that we consider a lattice consisting of N atoms, the system having $3N$ degrees of freedom corresponding to the $3N$ coordinates required to specify the positions of the atoms.

The atoms execute complex, coupled motions; the oscillations of

such a system can be described in terms of the $3N$ normal modes of vibration of the system. Each mode has its own characteristic frequency $\omega_1, \omega_2, \omega_3, \ldots, \omega_{3N}$. The lattice vibrations are then equivalent to $3N$ independent harmonic oscillators with frequencies $\omega_1, \omega_2, \omega_3, \ldots, \omega_{3N}$. If we knew the frequencies, we could immediately solve the problem. We have shown that the average energy of an oscillator is given by

$$\langle \varepsilon_i \rangle = \frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i}{e^{\hbar\omega_i/kT} - 1}.$$

The average energy of the $3N$ equivalent oscillators is then

$$E = \sum_{i=1}^{3N} \langle \varepsilon_i \rangle$$

The calculation was taken this far by Biot and von Karman, also in 1912. Since we don't know the frequencies, we use Debye's approach.

4.1. The Debye Approach

Treat the solid as a continuum. We can then consider standing waves in the sold. We will count the standing waves using the denisty of modes calculation. It could also be done with the density of states calculation.

4.2. The Density of Modes

As in the density of states, we consider a cube of side L, a three dimensional standing electromagnetic wave is specified by

$$E_x = E_{x0} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

where

$$n_x, n_y, n_z = 1, 2, 3, \dots$$

and similar expressions exist for the y and z components of the field. The solutions vanish at

$$x, y, z = 0, L.$$

If the n_i were zero there would be no wave. Consider light, for any given triplet n_i, there are two polarizations, and on substituting into the wave equation

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

where c is the velocity of light, we find

$$c^2 \pi^2 (n_x^2 + n_y^2 + n_z^2) = \omega^2 L^2.$$

This determines the frequency of the mode in terms of the triplet of integers $n_x, n_y,$ and n_z. Defining

$$n \equiv (n_x^2 + n_y^2 + n_z^2)^{1/2},$$

and the frequencies are given by

$$\omega_n = \frac{n \pi c}{L}.$$

For cavity radiation, we could use this to write the total energy of photons in a cavity as

$$E = \sum_n \langle \varepsilon_i \rangle = \sum_n \frac{\hbar \omega_n}{e^{\hbar \omega_n / kT} - 1}.$$

This sum is taken over all positive triplets n_x, n_y, n_z, as positive integers are sufficient to describe all the independent standing modes.

We can replace the sum over n_x, n_y, n_z by an integral over the volume element $dn_x dn_y dn_z$ in the mode index space. In other words, we can write

$$\sum_n (\ldots) = \frac{1}{8} \int_0^\infty 4\pi n^2 dn (\ldots).$$

If we were making the calculation for photons, we would multiply by two to deal with the two polarizations. We could complete the calculation to find the energy density of electromagnetic radiation. (The factor $1/8$ restricts us to the positive octant of mode index space, this is similar to our density of states calculation.) In this instance

we are interested in phonons.

For elastic waves, there are three possible polarizations, two transverse and one longitudinal. Thus for elastic modes, the sum of a quantity over all modes is given by:

$$\sum_n (\ldots) = \frac{3}{8} \int 4\pi n^2 dn (\ldots),$$

where the definition of n is identical to the one arising from photons.

4.3. Density of Modes and the Debye Model

In the Debye model, there are are $3N$ allowed modes. Thus, we want to find n_D such that the total number of modes is $3N$. We find this by evaluating:

$$\frac{3}{8} \int\limits_0^{n_D} 4\pi n^2 dn = 3N$$

So

$$\frac{3}{8} 4\pi \left(\frac{n^3}{3} \right)_0^{n_D} = 3N$$

and

$$n_D = \left(\frac{6N}{\pi} \right)^{1/3}.$$

The average energy of an oscillator is

$$\langle E \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}.$$

Now omitting the zero point energy (it doesn't affect C_v),

$$E = \sum_n \langle \varepsilon_n \rangle = \sum \frac{\hbar\omega_n}{e^{\hbar\omega_n/kT} - 1}$$

and

$$E = \frac{3}{8} \int\limits_0^{n_D} 4\pi n^2 dn \frac{\hbar\omega_n}{e^{\hbar\omega_n/kT} - 1}.$$

• **Evaluation of the Debye Integral**

Now $\omega_n = \frac{n\pi c}{L}$, and we rewrite the energy integral as

$$E = \frac{3}{8} \int\limits_0^{n_D} 4\pi n^2 dn\hbar\frac{n\pi c}{L}\frac{1}{e^{\hbar n\pi c/LkT} - 1}.$$

Transforming the integral to one over a dimensionless variable by

$$x = \frac{\pi\hbar cn}{LkT}, \ x_D = \frac{\pi\hbar cn_D}{LkT}$$

we have

$$n = \frac{LkTx}{\pi\hbar c}, \ dn = \frac{Lkt}{\pi\hbar c}\mathrm{d}x.$$

Therefore,

$$n^3 dn = \left(\frac{LkT}{\pi\hbar c}\right)^4 x^3 dx$$

and

$$
\begin{aligned}
E &= \frac{3}{2} \int\limits_0^{n_D} \frac{\pi^2 \hbar c}{L} (n^3 \mathrm{d}n) \frac{1}{\mathrm{e}^x - 1} \\
&= \frac{3}{2} \int\limits_0^{n_D} \frac{\pi^2 \hbar c}{L} \left(\frac{LkT}{\pi \hbar c}\right)^4 \frac{x^3 \mathrm{d}x}{\mathrm{e}^x - 1} \\
&= \frac{3}{2} \frac{\pi^2 \hbar c}{L} \left(\frac{LkT}{\pi \hbar c}\right)^4 \int\limits_0^{x_D} \frac{x^3 \mathrm{d}x}{\mathrm{e}^x - 1}.
\end{aligned}
$$

The upper limit of integration is

$$
x_D = \frac{\pi \hbar c n_D}{LkT} = \frac{\pi \hbar c n_D}{V^{1/3} kT},
$$

since

$$
L^3 = V \text{ and } n_D = \left(\frac{6N}{\pi}\right)^{1/3}.
$$

Then we can write

$$x_D = \frac{\hbar c}{kT} \left(\frac{6\pi^2 N}{V} \right)^{1/3} = \frac{\Theta_D}{T}$$

where

$$\Theta_D = \frac{\hbar c}{k} \left(\frac{6\pi^2 N}{V} \right)^{1/3} = \text{Debye Temperature}$$

The Debye temperature is fixed for a particular temperature - it basically depends on $(N/V)^{1/3}$.

4.4. The Debye Model at Low Temperture

Let's find C_v at low temperature. At low temperatures, $T \ll \Theta_D$ and so $x_D \gg 1$. We can write $x_D = \infty$ here, since beyond $x = 10$ the integrand is approximately zero.

From tables we find

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

Using this in

$$E = \frac{3}{2} \frac{\pi^2 \hbar c}{L} \left(\frac{LkT}{\pi \hbar c} \right)^4 \int\limits_0^{x_D} \frac{x^3 \mathrm{d}x}{\mathrm{e}^x - 1}$$

we find

$$E \simeq \frac{3}{2} \frac{L^3 k^4 T^4}{\pi^2 \hbar^3 c^3} \frac{\pi^4}{15}.$$

But

$$\Theta_D = \frac{\hbar c}{k} \left(\frac{6\pi^2 N}{V} \right)^{1/3}, \ \ \Theta_D^3 = \left(\frac{\hbar c}{k} \right)^3 \frac{6\pi^2 N}{V}$$

so

$$\begin{aligned}
E &= \frac{3}{2} \frac{\pi^4}{15} NkT^4 \frac{V}{6N\pi^2} \frac{6k^3}{\hbar^3 c^3} \\
&= \frac{3}{2} \frac{\pi^4}{15} NkT^4 \frac{6}{\Theta_d^3} \\
&= \frac{3}{5} \frac{NkT^4 \pi^4}{\Theta_D^3}.
\end{aligned}$$

Then

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v$$

yields

$$C_v = \frac{12}{5}\frac{NkT^3\pi^4}{\Theta_D^3} \simeq 234Nk\left(\frac{T}{\Theta_D}\right)^3.$$

In other words $C_v \to 0$ as $T \to 0$ and at low temperatures $C_v \propto T^3$. This is the Debye T^3 approximation. At high temperatures the model yields the Dulong and Petit result. This model is "exact" at low and high temperature and an interpolation formula in between.

At "sufficiently" low temperatures, the T^3 approximation is good. At such temperatures only long wavelength acoustic modes are excited. These are just the modes that can safely be treated as an elastic continuum with macroscopic elastic constants. The energy of short wavelength modes (for which this approximation fails) is too high for them to be significantly populated. For actual crystals, the temperatures for which the T^3 law holds is quite low, typically $\Theta_D/50$. As examples $\Theta_D = 645$ K for Si, in fact, let's look at this column of

the periodic table.

Element	Θ_D (K)
C	2230
Si	645
Ge	374
Sn	200
Pb	105

Note that the heavier atoms have the lowest Θ_D's, this is because the velocity of sound decreases as density increases.

In a later course, you will study optic and acoustic phonons. A common practice is to model acoustic phonons with the Einstein model being used to model the optical phonon part of the phonon spectrum. Further discussion is beyond the scope of our course at this point.[1]

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[1]If you really want to know more at this point refer to Kittel's *Introduction to Solid State Physics*