

Summary : Lecture 5

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1 Starting equations

Starting from the wave equation encountered before :

$$\frac{\partial^2 u}{\partial x^2} - v_s^2 \frac{\partial^2 u}{\partial t^2} = 0, \quad (1)$$

we plug in the Ansatz:

$$u = Ae^{i(kx - \omega t)}, \quad (2)$$

and obtain the **Dispersion Relation**:

$$\omega = v_s k, \quad v_s = \sqrt{\frac{E}{\rho}} \quad (3)$$

with this in mind we derive the rest:

2 Enumeration of Modes; Density of states of a continuous Medium

We now take our ansatz, without the time contribution as we are not interested (for now) how states vary with time.

So our solution reads:

$$u = Ae^{i(kx)}, \quad (4)$$

For demonstration purposes we will introduce boundary conditions. Have in mind however, it can be show that when the wavelength of the modes are small compared with the dimension of the sample, the density of states which we are about to derive does not depend on these conditions. Hence we choose them here so as to be suitable for the maths we are about to do:

Boundary conditions :

$$u(x = 0) = u(x = L), \quad (5)$$

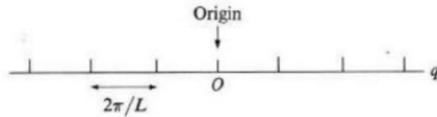
where L is the length of our sample i.e for a chain of atoms this would be the length of the chain. With these boundary conditions we have then:

$$e^0 = 1 = e^{ikL}, \quad (6)$$

which basically is a condition of the admissible values of k. From the complex plane we know that $e^{in2\pi} = 1 \quad \forall n$, hence:

$$k = n \frac{2\pi}{L} \quad (7)$$

Plotting this on the q axis we get a 1D mesh of equally separated points, the separation being $2\pi/L$:



For large L (which is the case for macroscopic objects) we get a *quasi-continuous* mesh. Each point on the k axis represents a mode of vibration. (Notice that in quantizing k , we actually quantize λ , the wavelength of vibration.) The number of modes in a given interval dk is given by:

$$\frac{L}{2\pi} dk = n \quad (8)$$

Usually physicists like frequencies more than wave numbers, so we want to get the number of modes in a given frequency range. How do we get that? Well, we have our dispersion relation so we can relate k with ω .

Def (Density of states , $D(\omega)$) : The density of states $D(\omega)$ is defined s.t. $D(\omega)d\omega$ gives the number of modes lying in the frequency range $[\omega, \omega + d\omega]$.

Thus we have :

$$\frac{L}{\pi} dk = D(\omega)d\omega \quad (9)$$

Note that we have multiplied equation (8) with 2, because the wave travels to the right as well as to the left. This is clearly seen from the figure below.

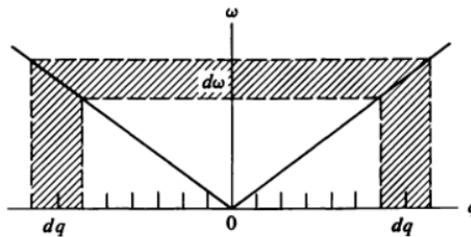


Fig. 3.4 The enumeration of modes. The dispersion curve is composed of two segments: $\omega = v_s q$ and $\omega = -v_s q$. The former represents waves traveling to the right, the latter waves traveling to the left.

Using our *linear* dispersion relation, we rearrange the above to:

$$D(\omega) = \frac{L}{\pi} \frac{1}{d\omega/dk} = \frac{L}{\pi} \frac{1}{v_s} \quad (10)$$

In the three dimensional case, the above is just replicated with minor modifications: In 3D out wave solution reads:

$$u = Ae^{i[k_x x + k_y y + k_z z]} = Ae^{i\vec{q} \cdot \vec{r}} \quad (11)$$

Lets assume our sample is cubic with edge length L . With the boundary conditions we get:

$$e^{i(k_x L + k_y L + k_z L)} = 1 \quad (12)$$

Hence

$$(k_x, k_y, k_z) = \frac{2\pi}{L}(n, m, l), \quad n, m, l \in \mathbb{Z} \quad (13)$$

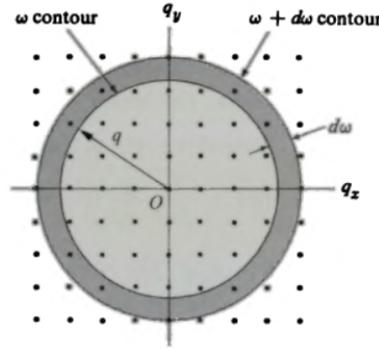


Fig. 3.5 Allowed values of \mathbf{q} for a wave traveling in 3 dimensions. (Only the cross section in the q_x, q_y -plane is shown.) The shaded circular shell is used for counting the modes.

We see that the volume assigned to each point in the \vec{q} space is equal to $(\frac{2\pi}{L})^3$. Every point corresponds to one mode. We now want to find the number of modes inside a sphere whose radius is k . So we divide the volume of that sphere with the volume of one point, and get the number we seek:

$$\left(\frac{2\pi}{L}\right)^3 \frac{4\pi}{3} k^3 = \frac{V}{(2\pi)^3} \frac{4\pi}{3} k^3, \quad (14)$$

where we have set $V = L^3$. Differentiation the above with respect to k (the radius of our chosen sphere) we get :

$$\frac{V}{(2\pi)^3} 4\pi k^2 dk, \quad (15)$$

thus obtaining the number of modes in a spherical shell with width dk . In order to obtain the density of states $D(\omega)$, we again use our dispersion relation to switch from k to ω , and get:

$$D(\omega)d\omega = \frac{V}{(2\pi)^3} 4\pi \left(\frac{\omega}{v_s}\right)^2 \frac{d\omega}{v_s} \quad (16)$$

This gives the number of modes in a spherical shell with the width $d\omega$. Here, however, we have associated with each value of \vec{k} only a single mode. But in this space, for each \vec{k} the wave may be either longitudinal (one mode) or transverse (two modes). So we need to multiply the right hand side of (16) with three to obtain the density of states:

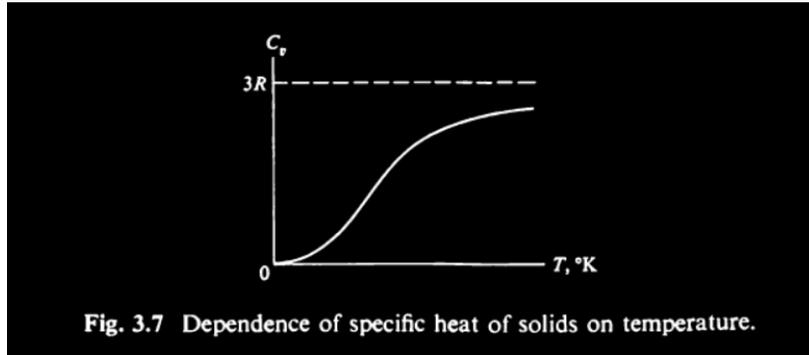
$$D(\omega) = \frac{3V}{2\pi^2} \frac{\omega^2}{v_s^3} \quad (17)$$

3 Specific Heat : Einstein and Debye Models

The specific heat at constant volume is given by:

$$C_v = \left(\frac{\partial E}{\partial T} \right)_V \quad (18)$$

Dulong - Petit Law : $C_V = 3R$ at high temperatures regardless of substance.



It can be observed that near absolute zero $C_v \propto T^3$. To be able to understand why Einstein and Debye had to go through their troubles (god bless), we take on the description as it would be done classically:

Classically the model would be one with harmonic forces that bind the atom to

its site in a solid. From elementary physics the energy average for a 1D oscillator is equal to kT , that is:

$$\bar{\epsilon} = kT. \quad (19)$$

Thus, in 3D we would have three times this and if we wanted it per mole we would get:

$$E = 3N_A kT = 3RT, \quad (20)$$

where N_A is Avogadro's number and $R = N_A k$. Substituting this into our equation for the Specific heat at constant Volume we find:

$$C_V = 3R \quad (21)$$

Thus we have gotten a C_V that is not depending on T , which in experiments is not the case. This is where Einstein and Debye come in.

3.1 The Einstein Model

The difference between Einstein's and the classical model is that Einstein used the energy given by QM for the oscillator. The energy of an isolated oscillator given by QM is:

$$\epsilon_n = n\hbar\omega \quad (22)$$

Note that we have excluded the Zero-point energy, as zero-point motion is not relevant to our present discussion.

However, the atomic oscillators in a solid are not isolated, but exchange energy with the ambient thermal bath surrounding the solid. So we will need some probability calculus. The average energy of the oscillator at thermal equilibrium is given by:

$$\bar{\epsilon} = \frac{\sum_{n=0}^{\infty} \epsilon_n e^{-(\epsilon_n/kT)}}{\sum_{n=0}^{\infty} e^{-(\epsilon_n/kT)}}, \quad (23)$$

where the $e^{-(\epsilon_n/kT)}$ is the Boltzmann factor, giving the probability that the energy state ϵ_n is occupied. The sum in the denominator is inserted for normalization. Substituting the quantized energy and evaluating the series involved we obtain:

$$\bar{\epsilon} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \quad (24)$$

We can now find the energy of the solid by noticing that each atom is actually equivalent to three oscillators (each atom has 3 degrees of freedom), and as there are N_A atoms, in total we've got $3N_A$ oscillators:

$$E = 3N_A \frac{\hbar\omega_E}{e^{\hbar\omega_E/kT} - 1} \quad (25)$$

The C_V is now simply the derivative of this energy with respect to T :

$$C_V = 3R \left(\frac{\hbar\omega_E}{kT} \right)^2 \frac{e^{-\frac{\hbar\omega_E}{kT}}}{e^{-\frac{\hbar\omega_E}{kT}} - 1} \quad (26)$$

or, if we introduce the Einstein temperature θ_E , where $k\theta_E = \hbar\omega_E$, we get:

$$C_V = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{-\theta_E/T}}{e^{-\theta_E/T} - 1} \quad (27)$$

The temperature θ_E is an adjustable parameter, chosen to produce the best fit to the experimental values over the whole temperature range. The Einstein frequency ω_E is calculated once θ_E is determined.

Important remarks regarding Einsteins result:

- 1) $C_V \rightarrow 0$ as $T \rightarrow 0$, a fact that was lacking in the Classical result.
- 2) In the limit $T \gg \theta_E$ (large temperatures) it is found that $C_V \simeq 3R$, thus in agreement with Dulong-Petit.
- 3) In the limit $T \ll \theta_E$, his result becomes:

$$C_V \simeq B(T)e^{-\theta_E/T}, \quad (28)$$

hence drops exponentially, where as it should drop with the third power of T according to experiments.

Conclusion on Einsteins model:

Very good at high temperatures, fails at low temperatures.

3.2 Debye's Model

Debye's approach was somewhat different than Einsteins. The difference was that Debye did consider the atoms in the solid as coupled oscillators in the sense that atoms don't oscillate independent of one another. For this he needed the *collective lattice modes*, for which he used the *density of states* derived previously.

For reasons of mathematical simplicity he used the collective modes of sound waves in solids as the prototype of lattice modes. (Remember : when a sound wave travels through a solid, the atoms move with the same amplitude in a fixed phase relationship to one another.)

Considering the dispersion relation of such sound waves ,eq. (3), immediately

we notice that ω now covers in fact a range of values, where as in Einsteins model it was only one frequency value.

Note This dispersion relation is merely an approximation that works only in the long wavelength range of waves propagating through the solid. It ignores completely the discreteness of the solid, a property, that will cause problems as we shall see shortly.

The total energy of vibration is given by:

$$E = \int \bar{\epsilon} D(\omega) d\omega. \quad (29)$$

Thus the vibration energy is the average energy multiplied with the number of modes in the given frequency range. Substitution of equations (24) and (17) ¹, we obtain:

$$E = \frac{3V}{2\pi^2 v_s^3} \int \omega^2 \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \quad (30)$$

But what are the limits of integration supposed to be? The lower limit is evidently $\omega = 0$. The upper *cutoff* frequency was determined by Debye as to include as much modes as there are degrees of freedom, thus $3N_A$. Mathematically this reads:

$$\int_0^{\omega_D} D(\omega) d\omega = 3N_A, \quad (31)$$

where ω_D is called the **Debye frequency**. Substituting $D(\omega)$ with (17) we obtain:

$$\omega_D = v_s (6\pi^2 n)^{1/3}; \quad n = \frac{N_a}{V}, \quad (32)$$

n being the concentration of atoms in the solid. Now the specific heat reads:

$$C_v = \frac{3V}{2\pi^2 v_s^3} \frac{\hbar^2}{kT^2} \int_0^{\omega_D} \frac{\omega^4 e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2} \quad (33)$$

Note: The integral and derivative were interchanged since $\frac{dE}{dT}$ is integrable and $E(0) = 0$.

Introducing a formal new variable : $x = \hbar\omega/kT$ and the *Debye Temperature* θ_D as $k\theta_D = \hbar\omega_D$ we get:

$$C_v = 9R \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (34)$$

¹The substitution of these is justified : $\bar{\epsilon}$ because we still treat them as oscillators in thermal equilibrium, $D(\omega)$ because here we assumed the lattice to be continuous

The Debye temperature is determined as for (34) to give the best fit over the whole temperature range. It can be easily seen that in Debye's Model at High temperature $C_v \approx 3R$ and at low temperatures $C_v \propto T^3$.

So what's wrong with Debye's Model? It's still just an approximation, and not a very good one for that matter. To see this if we plot θ_D vs T over a wide temperature range, where θ_D has been found and FIXED for each temperature as for (34) to give the best fit to the data. If Debye's Model was exact, the value of θ_D so obtained should not vary with Temperature. However, it has been found that θ_D does indeed vary with T. This is the problem that is caused by the ignoring of the discreteness of the lattice.

Conclusion on Debye's Model:

It's good for the extreme. However it remains an approximation.

4 Closing Remarks

The interest in **specific heat** is certainly huge, as it opens many doors to the use of specific materials to satisfy specific demands. More so, a relation connecting it to **intra-solid properties** would help a great deal to "create" specific materials in order to solve complex problems connected to heat transfer. Using waves we managed to get such a relation. In fact we managed to get two relations : **Einstein's** and **Debye's**, each with its pros and cons. Moreover, we constructed a special function, which is of fundamental importance to the field of Solid State Physics : **The density of states**, $D(\omega)$, which through a given **dispersion relation** connects the **number of modes** with a certain **frequency range**.