Lecture 08

Thursday, January 28, 2010

How do we know phonons?

- Specific heat puzzle in the early part of the 20th century -- solved by phonon model.
- Spectroscopy "sees" phonons. Inelastic neutron/light/electron scattering (INS/IXS/IES) is sensitive to phonons among other things.

Waves in crystal III (**Crystal momentum Conservation**)

In the case of the scattering experiment, we re-call the general property of waves in crystal. Namely, the wave vector in a crystal is ambiguous up to a reciprocal wave vector. This is true not only for an elastic process such as X-ray/neutron/electron diffraction that we discussed at length, but also for any scattering process, including inelastic ones.

Diffraction	$\vec{k}_f = \vec{k}_i + \vec{G}$
Absorption of one phonon	$\vec{k}_f = \vec{k}_i + \vec{k}_{ph} + \vec{G}$
Emission of one phonon	$\vec{k}_f + \vec{k}_{ph} = \vec{k}_i + \vec{G}$
...	...
Any scattering in a crystal (p, q: particle index)	$\sum_p \vec{k}_{f,p} = \sum_q \vec{k}_{i,q} + \vec{G}$

For each equation, $\vec{G}$ is an *arbitrary* reciprocal vector.

The above equations collectively go by the name of "**crystal momentum conservation**" equation. The last one is the most general form.

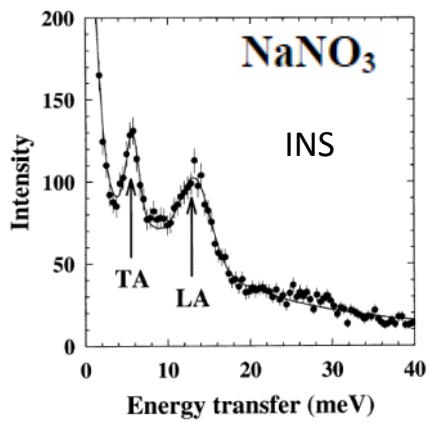
Crystal momentum

- A conserved quantity associated with a discrete translational symmetry of a crystal.
- For a given wave vector, **crystal momentum** is $\hbar\vec{k} + \vec{G}$, where $\vec{G}$ is an arbitrary reciprocal lattice vector.
- Usually, we take the crystal momentum $\hbar\vec{k}$ to be defined in a standard cell, most often the 1st BZ, keeping in mind that adding any arbitrary reciprocal vector to it does not do a thing.
- In free space, $\hbar\vec{k}$ would be the momentum. For a wave in crystal, $\hbar\vec{k}$ is not the

momentum, and it is not useful to talk about the momentum since it is not a conserved quantity. In fact, if people say "momentum" in the context of waves (that is, particles) in a crystal, then what they mean is probably "crystal momentum."

Observation of phonons in an inelastic scattering experiment

Here is a generic example of how inelastic phonon peaks are observed in an INS experiment, alongside a giant elastic peak at zero energy transfer.

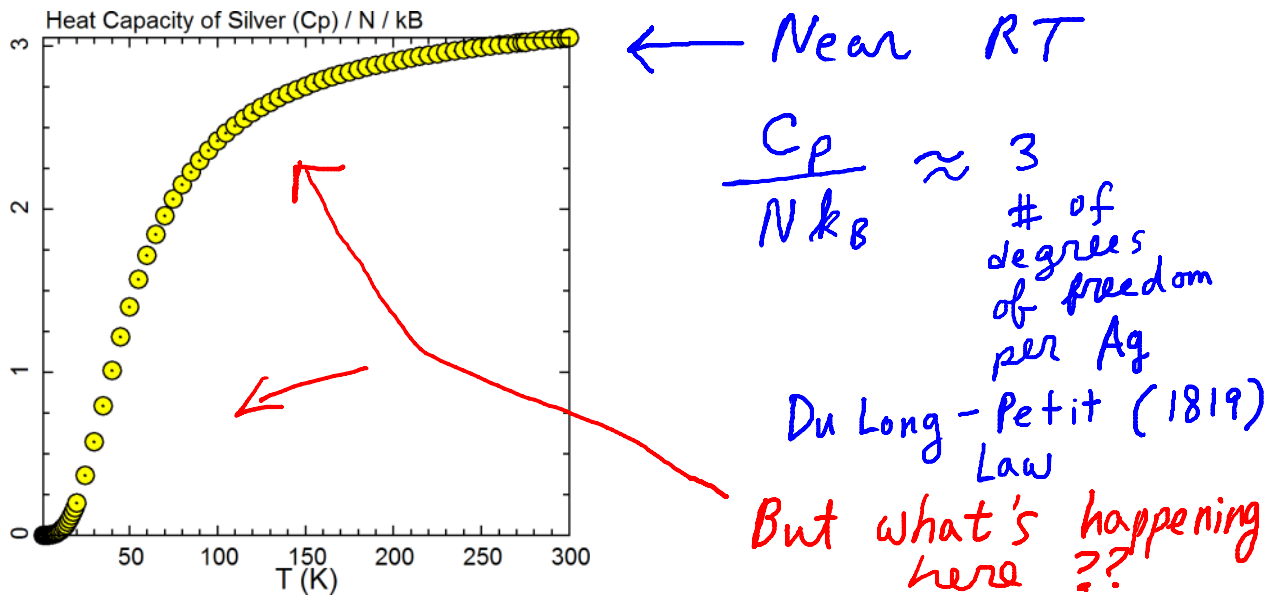


M J Harris†, M E Hagen‡, M T Dove§ and I P Swainson‖
J. Phys.: Condens. Matter 10 (1998) 6851–6861.

This example corresponds to one $\vec{k}$ value for the phonon. By rotating the sample and the spectrometer one can sweep different $\vec{k}$ values, and obtain full $\omega_{\vec{k}}$ curves as a function of $\vec{k}$. How the crystal momentum conservation and the energy conservation principles can explain this type of measurement is explained well in, e.g. A&M chapter 24.

Einstein Model

At the dawn of the last century, the heat capacity of ordinary substances presented a great puzzle in that it did not admit a good explanation by Classical Mechanics.



Data from G. T. Furukawa, W. G. Saba, and M. L. Reilly, Natl. Stand. Ref. Data Series 18, Natl. Bur. Stand. (U.S) (1968)

Einstein came along and suggested a simple model for this. The model was **not successful**. But it did *not* mean that the model was incorrect. More about this below. So, to this day, we consider the Einstein model or "Einstein phonons" when we consider certain problems in solid state physics.

Einstein proposed that each atom vibrates independently at its natural frequency, and atoms do not interact with each other at all.

So, in this model, all you need is to consider the thermodynamics of a single harmonic oscillator with the frequency ω_0. Thus, the partition function $Z = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n}$, where $\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega_0$ and $\beta = \frac{1}{k_B T}$. $\varepsilon = \frac{\sum_n \epsilon_n e^{-\beta\epsilon_n}}{Z} = -\,\partial \log Z\,/\partial\beta$. From this, $c_v = -\partial\varepsilon/\partial T$ gives the heat capacity for the single oscillator. Multiply by the number of atoms, N, and the degrees of freedom per atom, 3, then we get C_v for the whole crystal. Note that usually what is measured is C_p which is the heat capacity at constant pressure. What is theoretically calculated more easily is C_v. For a solid, these two usually do not differ much at all. See Appendix A at the course web site.

Z is basically a sum over a geometric series, and so the above calculations are rather plain. Here they go.

$$Z = e^{-\frac{1}{2}\beta\hbar\omega_0}\frac{1}{1-e^{-\beta\hbar\omega_0}},$$

$$\varepsilon = \frac{1}{2}\hbar\omega_0 + \frac{e^{-\beta\hbar\omega_0}}{1-e^{-\beta\hbar\omega_0}}\hbar\omega_0 = \frac{1}{2}\hbar\omega_0 + \frac{1}{e^{\beta\hbar\omega_0}-1}\hbar\omega_0$$

The result for ε is simple: $\varepsilon = \frac{1}{2}\hbar\omega_0 + n(\hbar\omega_0)\hbar\omega_0$, where $n(x)$ is the Bose-Einstein distribution function for energy x.

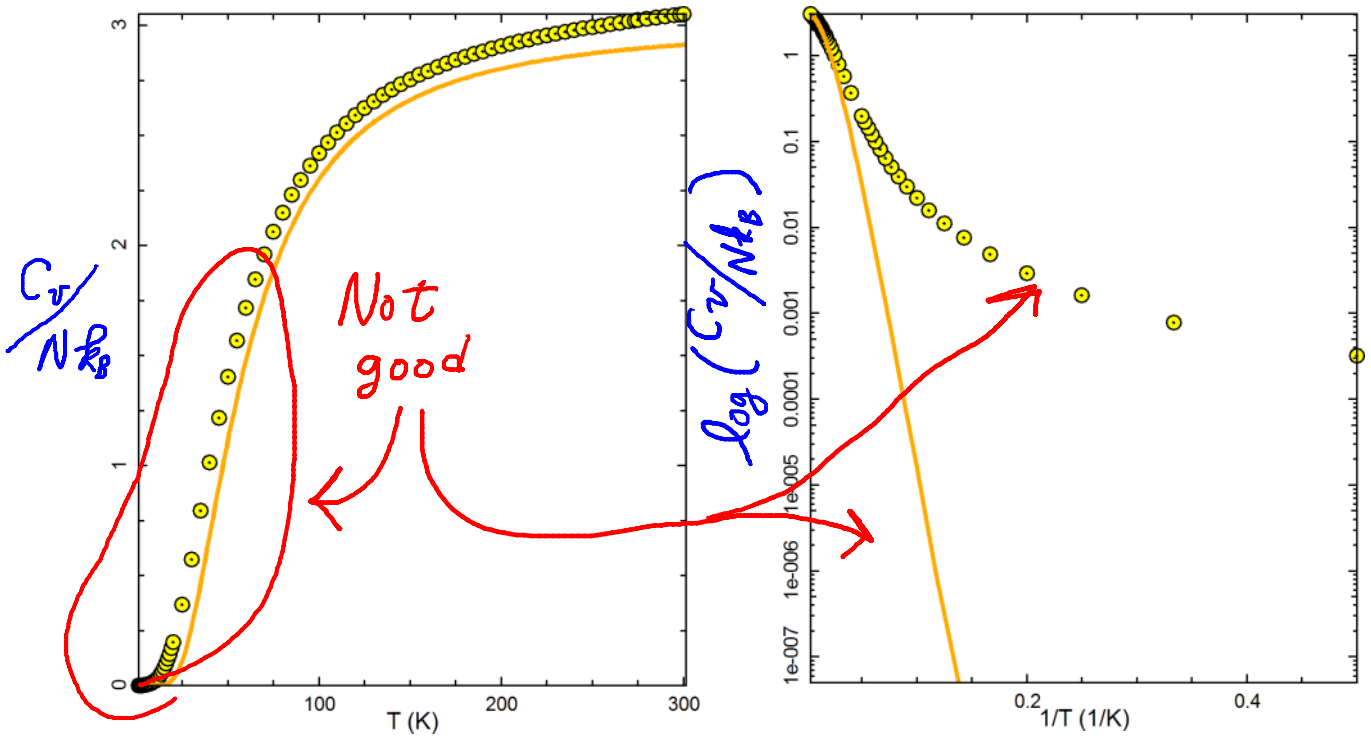
$$C_v = 3N\frac{\partial\varepsilon}{\partial T} = 3N\frac{e^{\beta\hbar\omega_0}}{(e^{\beta\hbar\omega_0}-1)^2}\left(\frac{\hbar\omega_0}{k_B T}\right)^2 k_B = \frac{(\beta\hbar\omega_0)^2}{4\sinh^2\left(\frac{\beta\hbar\omega_0}{2}\right)}3Nk_B$$

It is very instructive to examine the high and low temperature behavior of this function.

When $T \gg \hbar\omega_0$ $(\beta\hbar\omega_0 \to 0)$, $C_v \approx 3Nk_B$ (Du Long - Petit law).

When $T \ll \hbar\omega_0$ $(\beta\hbar\omega_0 \to \infty)$, $C_v \approx e^{-\beta\hbar\omega_0}(\beta\hbar\omega_0)^2 3Nk_B \ll 3Nk_B$.

That we recover the Classical Mechanics result when $T \gg \hbar\omega_0$ can be easily understood since the number of phonons $\gg 1$. The triumph of Einstein's theory is showing the existence of the quantum suppression of the heat capacity at low temperature. The failure of the theory is that this suppression, an exponential one, is in disagreement with the much weaker suppression of the data. The following fit of the above data with the Einstein model shows this problem.



Density of States

Before we go on to discuss the Debye model of phonons, let us discuss the density of states (DOS), $D(\omega)$.

$$D(\omega) = \frac{dN_m}{d\omega}$$

N_m is the number of phonon modes.

Consider a 1D problem first. For a given dispersion relation ω_k we have the following

$dN_m = \frac{dk}{\frac{2\pi}{L}} \times 2$ ($\frac{2\pi}{L}$ is the length per k point, and 2 accounts for negative and positive k) $= \frac{L}{\pi} dk = \frac{\frac{L}{\pi} d\omega}{\left|\frac{d\omega}{dk}\right|}$. And thus,

in case $\frac{d\omega}{dk} < 0$

$$D(\omega) = \frac{L}{\pi} \frac{1}{\left|\frac{d\omega_k}{dk}\right|} = \frac{L}{\pi} \frac{1}{v_g}$$ 1D, for one branch

v_g is the group velocity. At the BZ boundary, where the group velocity goes to 0, DOS diverges! This is the so-called **van-Hove singularity**.

In 3D, the general expression is $D(\omega) = \frac{V}{(2\pi)^3}\int \frac{dS_\omega}{v_g}$ where $v_g = \left|\nabla_{\vec{k}}\omega_{\vec{k}}\right|$ and S_ω is the constant energy surface in the $\vec{k}$ space that satisfies $\omega_{\vec{k}} = \omega$. This general expression should be easy to understand since (1) the gradient is perpendicular to S_ω and (2) the volume per $\vec{k}$ point is $\frac{(2\pi)^3}{V}$.

Another useful expression is $D(\omega) = \frac{V}{(2\pi)^3}\int d\vec{k}\delta\left(\omega - \omega_{\vec{k}}\right)$. This can be understood as follows: the number of modes in the energy range between ω and ω+$d\omega$ = dN_m = $\sum_{\vec{k}} \delta_{\omega<\omega_{\vec{k}}<\omega+d\omega} = D(\omega)d\omega$ where this delta is a Kronecker delta. In the continuum limit $\sum_{\vec{k}} = \frac{V}{(2\pi)^3}\int d\vec{k}$. Also, note that $\delta_{\omega<\omega_{\vec{k}}<\omega+d\omega}/d\omega$ is a square spike function with a total area of 1. I.e., as $d\omega$ goes to zero, $\delta_{\omega<\omega_{\vec{k}}<\omega+d\omega}/d\omega$ becomes the Dirac delta function $\delta\left(\omega_{\vec{k}} - \omega\right) = \delta\left(\omega - \omega_{\vec{k}}\right)$. QED.

So, in 3D, we have a situation where $v_g = 0$ gives rise to divergence in the integrand. The difference here from the 1D case is that $D(\omega)$ does not necessarily diverge, but if it doesn't then its derivatives do, and this singularity is again called **van-Hove singularity**.

Let us take a simple case when $\omega_{\vec{k}} = \omega(k)$ where $k = \left|\vec{k}\right|$. Then, $D(\omega)$ can be obtained without using the above general formulae. Number of modes per volume $d\vec{k} = \frac{Vd\vec{k}}{(2\pi)^3} = \frac{Vk^2dkd\Omega}{(2\pi)^3}$. Since $d\omega = \frac{d\omega}{dk}dk$, we can integrate over the solid angle to get $dN_m = \frac{Vk^2dk4\pi}{(2\pi)^3} = \frac{Vk^2dk}{2\pi^2} = \frac{Vk^2}{2\pi^2}\left(\frac{d\omega}{dk}\right)^{-1}d\omega$. So,

$$D(\omega) = \frac{Vk^2}{2\pi^2}\left(\frac{d\omega}{dk}\right)^{-1} \quad \text{if} \quad \omega_{\vec{k}} = \omega(k),\ \text{3D}$$

in case $\frac{d\omega}{dk} < 0$

Debye model

$\omega = vk$ (v is the speed of sound)

$$D(\omega) = \frac{V\omega^2}{2\pi^2v^3}$$

For N primitive lattice points (or primitive bases) in the sample, we require

$\int_0^{\omega_D} D(\omega)d\omega = N$ (per polarization). The spirit here is to do a good job at low energy.

Thus, $\omega_D^3 = \frac{6\pi^2 v^3 N}{V}$ -- **Debye frequency**: $\omega_D = v\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$

$$D(\omega) = \frac{3N\omega^2}{\omega_D^3}$$

Debye wave vector: $k_D = \frac{\omega_D}{v}$

Debye temperature: $\theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$

Total energy: $E = E_0 + 3\int_0^{\omega_D} d\omega D(\omega) n(\hbar\omega)\hbar\omega$ (3 for the three polarizations)

E_0 is the total zero point energy, which is temperature independent. The thermal energy part (the 2nd term) is

$$E - E_0 = \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} = \cdots = 9Nk_B T\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} dx \frac{x^3}{e^x - 1}$$

$\frac{\pi^4}{15}$ if $T \to 0$

$$C_v = \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D} d\omega \frac{\omega^3}{(e^{\beta\hbar\omega} - 1)^2}\hbar\omega\frac{1}{k_B T^2} = \cdots$$

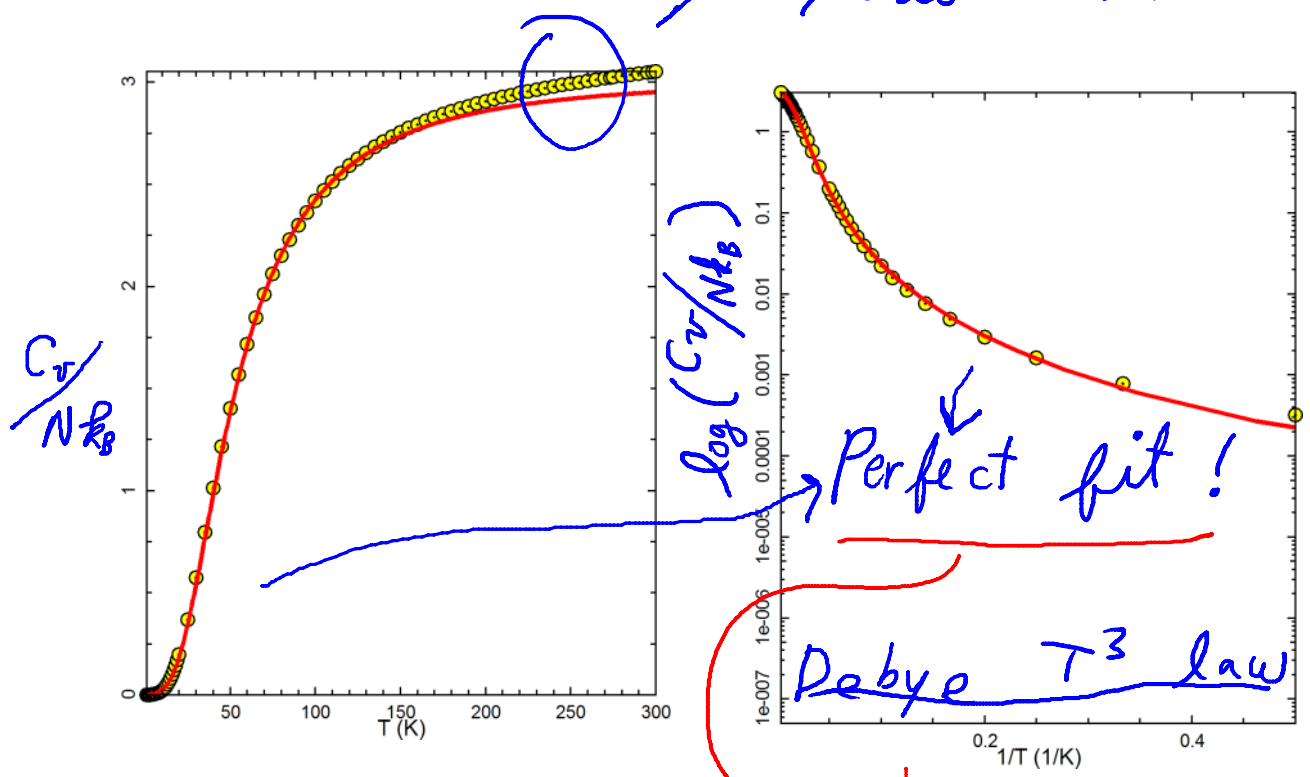
$$= 9Nk_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

If $T \gg \theta_D$, $C_v \approx 3Nk_B$ (Du Long - Petit), as it should.

If $T \ll \theta_D$, $C_v \approx \frac{12\pi^4}{5} Nk_B\left(\frac{T}{\theta_D}\right)^3$ (**Debye-T^3 law**) .

The big triumph of Debye's model is the explanation of the important low energy behavior, which is deeply connected to the emergence of acoustical phonons in a crystal.

Will discuss later.



Perfect fit!

Debye T^3 law

but also see free electron theory later

Note on notation

C_V, C_P — used in later lecture notes.

C_v, C_p — used here and appendix A