

Day 8: Wednesday – 50 minutes

The specific heat of a solid in the low- and high-temperature limits:

The specific heat of an insulator generally is constant at high temperatures and varies as T^3 at low temperatures. The high temperature behavior is readily understood as follows. Write down the expression for the total energy (let's use ω as a variable this time for practice):

$$E_{tot} = \int_{\omega=0}^{\omega_{max}} \hbar\omega f(\omega, T) D(\omega) d\omega = \int_{\omega=0}^{\omega_{max}} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} D(\omega) d\omega$$

Now if the temperature is high enough so that $k_B T \gg \hbar\omega_{max}$, then the exponential can be expanded and the integral becomes

$$E_{tot} = \int_{\omega=0}^{\omega_{max}} \frac{\hbar\omega}{1 - \hbar\omega / k_B T} D(\omega) d\omega = k_B T \int_{\omega=0}^{\omega_{max}} D(\omega) d\omega.$$

This hasn't assumed any particular density of states (or dispersion relation), except that there is a maximum frequency. Now note that the integral simply gives the total number of states (or modes) in the system. (If you take the number of states per unit frequency, multiply by the frequency interval and add up, you get the number of states!) This number is N if our system is N atoms in a 1-D chain, or $3N$ if our N atoms form a 3-D system.

Thus the phonon contribution to the specific heat of a solid at high temperature is

$$C = \frac{\partial E_{tot}}{\partial T} = \frac{\partial}{\partial T} k_B T N = N k_B \text{ in 1-D and}$$

$$C = \frac{\partial E_{tot}}{\partial T} = \frac{\partial}{\partial T} k_B T 3N = 3N k_B \text{ in 3-D, and}$$

k_B per mode in any dimension.

Now at low temperatures, we need a new scheme. At low temperatures, only the lowest vibrational modes are excited. For the lowest vibrational modes, the dispersion relation reduces to

$$\omega_q = \omega_{\max} \sin\left(\frac{k_q a}{2}\right) \approx \omega_{\max} \frac{k_q a}{2}.$$

Note that the dispersion is linear and the slope $\frac{d\omega}{dk} = \frac{\omega_{\max} a}{2} = v_{\text{sound}}$ gives the sound velocity in the crystal (low frequency phonons are sound waves). We can rewrite the dispersion relation as $\omega_q \approx v_{\text{sound}} k_q = v_{\text{sound}} \frac{q\pi}{Na}$. Thus when we find the density of states (now in ω space) or the number of states per unit frequency interval, we get (again in 1 dimension):

$$D(\omega) = \frac{dq}{d\omega} = \frac{Na}{\pi v_{\text{sound}}}.$$

Let's start again from our expression for the total energy:

$$E_{\text{tot}} = \int_{\omega=0}^{\omega_{\max}} \hbar \omega f(\omega, T) D(\omega) d\omega = \int_{\omega=0}^{\omega_{\max}} \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} D(\omega) d\omega$$

and substitute the low-temperature density of states (for a 1-dimensional system):

$$E_{\text{tot}} = \int_{\omega=0}^{\infty} \frac{Na}{\pi v_{\text{sound}}} \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} d\omega.$$

Notice that the upper limit of integration has been extended to infinity. Provided the temperature is low enough, this doesn't matter, because the lower the temperature, the lower the frequency at which the exponential kills the integral.

Change variables: $E_{\text{tot}} = \frac{Na}{\pi v_{\text{sound}}} (k_B T)^2 \int_{\eta=0}^{\infty} \frac{\eta}{e^{\eta} - 1} d\eta$. The integral you can look up – it is

$\frac{\pi^2}{6}$. Take the derivative to get the phonon contribution to the specific heat for a 1-dimensional

chain at low temperatures: $C = \frac{\pi N a k_B^2 T}{3 v_{\text{sound}}}$. Note that it varies linearly with T and not as the

cube as we said earlier. The cubic term arises in 3 dimensions as we shall see shortly.

So we have the high and low temperature limits correct. To deal with the intermediate temperatures requires a little more effort, but it is not difficult. The most common procedure is called the Debye interpolation scheme, and it is described in the Hook and Hall notes. It essentially requires taking the density of states as constant at the low frequency value up to a particular frequency called the Debye frequency, and zero thereafter. The Debye frequency is chosen to make the number of modes in the crystal come out correctly, even with the incorrect DoS.

Density of states in two and three dimensions:

As remarked earlier, we have to be a little careful about the interpretation of dq in 2 and 3 dimensions. Instead of modes being labeled by one integer or a length on a 1-D line, imagine them being labeled by pairs of integers or an area on a 2-D grid (in 2 dimensions) or by a triplet of integers or a volume in 3 dimensions. Then there are two (three) quantum numbers to define a state: q_x and q_y (and q_z).

So now we rethink $D(E) = \frac{dq}{dE}$ in 2D. dq now represents an area that contains all the states in energy interval dE , so we'll relabel it dA_q . (Need to reserve the use of q for something else). Thus

$$D_{2D}(E) = \frac{dA_q}{dE}$$

Now we can count modes like this:

$$N = \int_{E(q=q_{\min})}^{E(q=q_{\max})} D_{2D}(E) dE$$

Or we can count them like this:

$$N = \frac{1}{4} \int_{q_{\min}}^{q_{\max}} 2\pi q dq$$

Here we note that q now represents the distance from the origin in q -space to the integer pair that labels the mode. $q^2 = q_x^2 + q_y^2$. All points the same distance from the origin have the same q and therefore the same energy. Thus modes in an energy range dE live in a thin annulus of radius $2\pi q$ and width dq . The factor of $1/4$ out front prevents us from overcounting modes (we need only the first quadrant for unique modes). Note also that we have assumed that the integers make up a quasi-continuous variable set, which is OK provided the energy differences between states with different q are small.

Equating the two, we find that $D_{2D}(E)dE = \frac{1}{4}2\pi q dq \Rightarrow D_{2D}(E)dE = \frac{\pi q dq}{2 dE}$

As an exercise, find the result for $D_{3D}(E) = \frac{\pi q^2}{2} \frac{dq}{dE}$

Our specific heat problem at low temperature in 3 dimensions then goes like this:

It turns out that in 3 dimensions, the only difference in the dispersion relations for a monatomic collection of coupled oscillators is that we get three dispersion relations, not one! One corresponds to longitudinal oscillations, and two correspond to transverse oscillations. Transverse and longitudinal vibrations have different velocities, but the dispersion is still linear at low frequencies. (Let's neglect the sound velocity differences for the moment). When we calculate the DoS we have to sum over all branches of the dispersion relations.

So we still have $\omega_q \approx v_{\text{sound}} k_q = v_{\text{sound}} \frac{q\pi}{Na}$, and $\frac{dq}{d\omega} = \frac{L}{\pi v_{\text{sound}}}$.

$$D(\omega) = \frac{\pi q^2}{2} \frac{dq}{d\omega} = \frac{\pi q^2}{2} \frac{Na}{\pi v_{\text{sound}}} = \frac{\omega^2 (Na)^3}{2\pi^2 v_{\text{sound}}^3} = \frac{\omega^2 V}{2\pi^2 v_{\text{sound}}^3}$$

where V is the volume of the solid.

Now comes the integral:

$$E_{tot} = \int_{\omega=0}^{\infty} \frac{\omega^2 V}{2\pi^2 v_{sound}^3} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} d\omega$$

Clean up and change variables:

$$E_{tot} = \frac{V}{2\pi^2 v_{sound}^3 \hbar^3} (k_B T)^4 \int_{\omega=0}^{\infty} \frac{\eta^3}{e^{\eta} - 1} d\eta$$

Look up the integral – it is $\frac{\pi^4}{15}$. Now differentiate with respect to T and

$$C = \frac{2V\pi^2 k_B^4}{15v_{sound}^3 \hbar^3} T^3 \text{ with the "Debye } T\text{-cubed" dependence as advertised.}$$

If we add the contributions from all three dispersion relations, we get:

$$C = \frac{2V\pi^2 k_B^4}{15\hbar^3} \left(\frac{1}{v_{long}^3} + \frac{2}{v_{trans}^3} \right) T^3$$

So now we've obtained the high temperature and low temperature phonon contributions to the specific heat in one and three dimensions. The Debye interpolation scheme mentioned earlier is used as a means to interpolate between the two temperature regimes.

The extent to which the specific heat experimentally measured agrees with the model we've presented here is a measure of our understanding of the interatomic forces. It is well known that this particular model is very simplistic, and that real phonon dispersion relations are not so nicely sinusoidal. Nonetheless it is remarkable how far such a simple model can get us.