Lecture 17

Heat Capacity of Solids

The Debye Model

The key difference between Einstein's theory and Debye's is that in the Einstein model, it is assumed that all of the atoms are vibrating about their equilibrium positions independantly with the exact same frequency. The Debye model builds on this by allowing the oscillators within the system to have a distribution of frequencies.

Fortunately, we have already developed part of the framework we need for this task. Recalling the definition of the density of states from Lecture 12, we will modify it to represent the density of vibrational states, $g(\omega)$. We will impose the requirement that if we intergate the density of vibrational states over the entire frequency range, we should get back the total number of phonons in our system, $3N$. That is

$$\int g(\omega) \mathrm{d}\omega = 3N$$

Debye used the following knowledge to determine an appropriate distribution of frequencies - we know that vibrational waves will travel through the solid with a speed equal to the speed of sound of the solid. That is

$$\omega = v_s q$$

where q is the wave vector of the lattice vibrations. The density of these vibrations is given as

$$g(q)\mathrm{d}q = \frac{4\pi q^2 \mathrm{d}q}{(2\pi/L)^3} \times 3$$

where the factor of 3 comes from the allowed polarisations of the wave, and we have assumed the crystal is a cube of side L. Tidying up a bit gives

$$g(q)\mathrm{d}q = \frac{3V q^2 \mathrm{d}q}{2\pi^2}$$

which, in terms of ω, is

$$g(\omega)\mathrm{d}\omega = \frac{3V \omega^2 \mathrm{d}\omega}{2\pi^2 v_s^3}$$

The next assumption Debye allowed for is that, since there is a maximum of $3N$ modes in the crystal, there exists a maximum frequency (the Debye frequency) such that

$$\int_0^{\omega_\mathrm{D}} g(\omega)\mathrm{d}\omega = 3N$$

which, after substituting in for $g(\omega)$, gives

$$\omega_D = \left(\frac{6N\pi^2 v_s^3}{V} \right)^{1/3}$$

which also let's us write

$$g(\omega)d\omega = \frac{9N\omega^2 d\omega}{\omega_D^3}$$

Now, we'll define the Debye temperature as

$$\Theta_D = \frac{\hbar\omega_D}{k_B}$$

So the question we now need to ask is "is the predicted heat capacity versus temperature from this model a better match to our data?". Let's work out an expression for it and see.

Starting with the partition function, we'll have

$$\ln(Z) = \int_0^{\omega_D} d\omega\, g(\omega)\, ln\left[\frac{e^{-\hbar\omega\beta/2}}{1 - e^{-\hbar\omega\beta}} \right]$$

Breaking this integral up gives

$$\ln(Z) = -\int_0^{\omega_D} \frac{1}{2}\hbar\omega\beta g(\omega)d\omega + \int_0^{\omega_D} g(\omega)\ln[1 - e^{-\hbar\omega\beta}]d\omega$$

which in turn gives

$$\ln(Z) = -\frac{9}{8}N\hbar\omega_D\beta - \frac{9N}{\omega_D^3}\int_0^{\omega_D} \omega^2 \ln[1 - e^{-\hbar\omega\beta}]d\omega$$

The internal energy is then

$$U = -\frac{\partial \ln(Z)}{\partial \beta} = -\frac{9}{8}N\hbar\omega_D + \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D} \frac{\omega^2}{e^{\hbar\omega\beta} - 1}d\omega$$

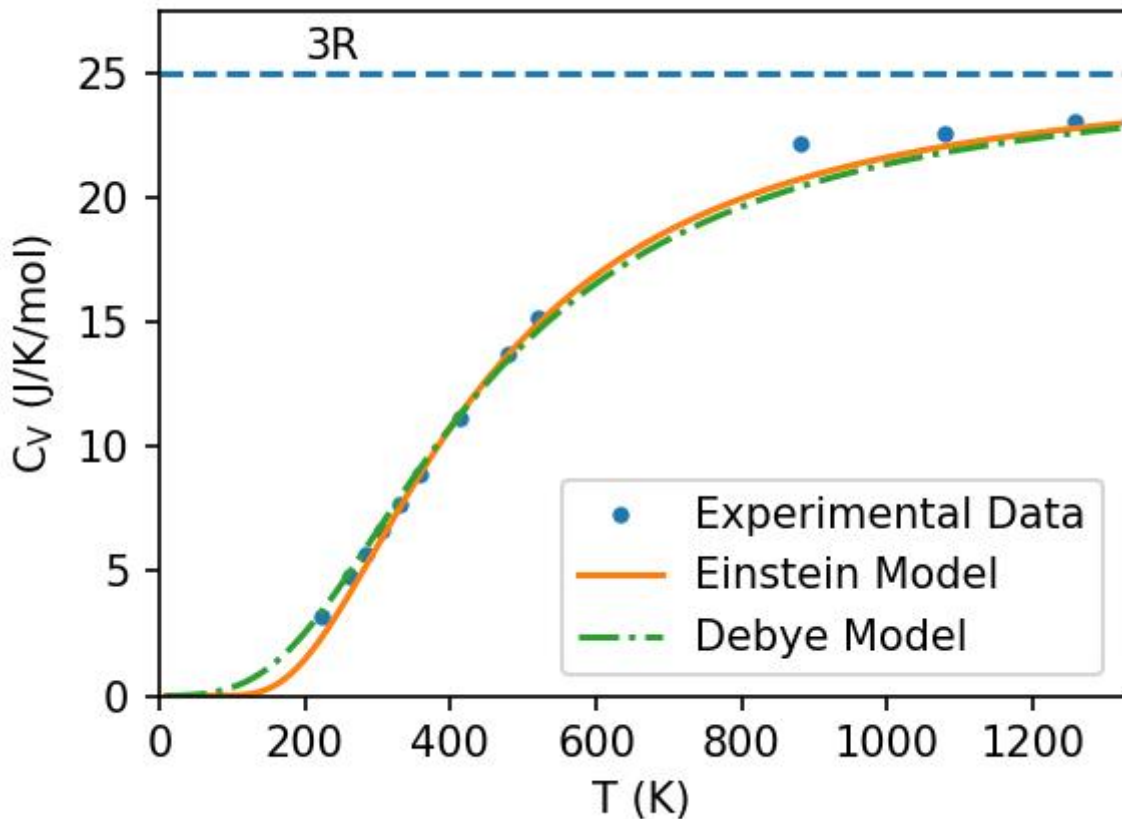Finally, the heat capacity is then

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

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

which simplifies to

$$C_V = \frac{9R}{x_D^3}\int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2}$$

where $x = \hbar\beta\omega$ and $x_D = \hbar\beta\omega_D$.

Real Gases

So, we know of particular cases when gases do not behave like an ideal gas For example as they cool, their heat capacities diverge from the constant that the ideal gas law predicts. So let's look at a few ways in which we can improve on an ideal gas.

Consider again the equation of state of an ideal gas:

$$PV = Nk_{\mathrm{B}}T$$

This equation leads to isotherms as plotted in the left of the below figure. To try and make this equation match the observed behaviour of real gases, we can think of two simple modifications:

1. Allow for non-zero molecule size. In essence, this means that molecules are no longer free to travel anywhere within the gas - instead, the volume they can probe is reduced slightly by the volume taken up by other molecules. We can simply parameterise this as $V \to V - Nb$, where b is somehow related to the molecule size.
2. Allow for molecular attraction. If the density of the gas is given by N/V, then the change in energy related to $\frac{aN^2}{V^2}dV$. This effectively increases the pressure we should see in the gas relative to the ideal pressure by $P = P_{\mathrm{ideal}} + \frac{aN^2}{V^2}$

These modifications then give Van Der Waal's equation of state

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_{\mathrm{B}}T$$

This equation leads to isotherms as plotted on the right of the below figure.

Aside

This same equation can be arrived at in a more formal manner by considering the following. If we let the partition function for our gas be

$$Z_N = \frac{1}{N!} \left(\frac{V - Nb}{\lambda_{\text{th}}^3} \right)^N e^{-\beta(-aN^2/V)}$$

where again we've reduced the volume to account for the volume taken up by other molecules, and included an additional energy term in the partition function related to the interaction energy $-aN^2/V$. We can then calculate the Helmholtz free energy using $F = -k_{\text{B}}T \ln(Z_N)$ and then $P = -\left(\frac{\partial F}{\partial V} \right)_T$ to get the above equation of state.

Ideal Gas   Van Der Waals Gas
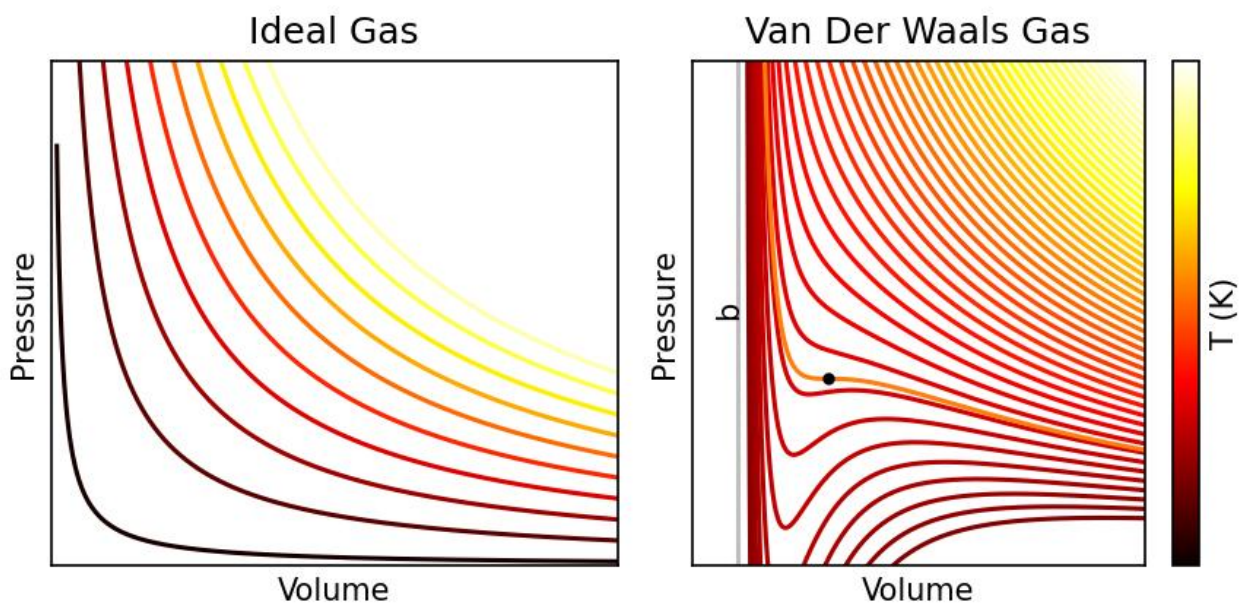
$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

For an ideal gas, this is always positive (as the last term is always negative, as the isoterms always have a negative slope). However, as we can see from the plot of the Van der Waals equation of state, at low temperatures, there are regions where $\left(\frac{\partial V}{\partial P} \right)_T$ is positive, meaning κ_T becomes negative. Under such conditions, increases the pressure exerted on the gas causes the volume to increase rather than decrease. Given that this means work is done on the gas ($W = -PdV$), then energy is provided to further increase the pressure - meaning this configuration is highly unstable!

There is a critical temperature whose isotherm does not have a positive gradient, but which has an inflection point - this is the critical temperature, which we'll discuss in a few lectures time.

Let's now determine the location of this critical point for a Van der Waal's gas. Solving the Van der Waal's equation for P, and assuming we're working with 1 mole, gives:

$$P = \frac{Nk_{\mathrm{B}}T}{V - Nb} - \frac{aN^2}{V^2}$$

The inflection point occurs when

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{Nk_{\mathrm{B}}T}{(V - Nb)^2} + \frac{2aN^2}{V^3} = 0$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2Nk_{\mathrm{B}}T}{(V - Nb)^3} - \frac{6aN^2}{V^4} = 0$$

Solving this both for $Nk_{\mathrm{B}}T$ gives

$$\frac{2aN^2(V - Nb)^2}{V^3} = Nk_{\mathrm{B}}T = \frac{6aN^2(V - Nb)^3}{2V^4}$$

which gives

$$2 = \frac{3(V - Nb)}{V}$$

and thus the critical volume is

$$V_{\mathrm{C}} = 3Nb$$

Using this volume and the above equations then gives

$$T_{\mathrm{C}} = \frac{8a}{27k_{\mathrm{B}}b}$$

and

$$P_{\mathrm{C}} = \frac{a}{27b^2}$$

So what happens at the critical point? Well, let's look at the isothermal compressability:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T_c}$$

We have that

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$$

and so the isothermal compresability diverges!

So, in order to figure out what happens below the critical temperature, let's look at the Gibbs' Free energy. We're choosing this as the Gibb's function is useful for experiments which are carried out under constant temperature and constant pressure.

I'm not going to go into too detailed a discussion about what happens around this critical point. If you are interested, I highly recommend section 26.1 of Blundell & Blundell, or 5.3 of Schroeder.