Physics 112 : Lecture 12

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel
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1 Heat Capacity

For a simplistic model of solids, like Einstein solids (i.e. a lattice of harmonic oscillators with the same frequency), we can find the partition function of a single harmonic oscillator:

$$Z = \sum_{n=0}^{\infty} e^{-n\hbar\omega/\tau} = \left[\frac{1}{1-e^{-\hbar\omega/\tau}}\right]$$

Then for the whole system, the partition function is given multiplicatively:

$$Z = \left[\frac{1}{1-e^{-\hbar\omega/\tau}}\right]^{3N}$$

where the 3 factor comes from 3 dimensions, (the partition function in the first line is just for a one dimensional harmonic oscillator), and the N factor comes from N particles in total. Now, we can find the energy in the system:

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = 3N\hbar\omega\left[\frac{1}{e^{\hbar\omega/\tau}-1}\right] = 3N\hbar\omega\langle n\rangle$$

Now, we can find the heat capacity:

$$C_v = \frac{\partial U}{\partial T} = 3Nk_B\frac{(\hbar\omega/\tau)^2 e^{\hbar\omega/\tau}}{[e^{\hbar\omega/\tau}-1]^2}$$

Now, we have two limits that we care about. In the first, we have $\tau >> \hbar\omega$, the classical limit, and we have:

$$C_v \approx 3Nk_B$$

In the other limit, $\tau << \hbar\omega$, the quantum effects become more important, and we find that:

$$C_v \approx \left(\frac{\hbar\omega}{\tau}\right)^2 e^{-\hbar\omega/\tau}$$

so the heat capacity becomes exponentially surpressed in the low temperature limit. This is, however, not what we observe in the laboratory. In the laboratory, we actually observe that:

$$C_v \approx T^3$$

So our theory does not match up with experiment. The fundamental flaw in our assumptions is that the particles in our Einstein solid do not interact; which is wrong in reality. We can imagine new, lower energy modes for the system, for instance we can imagine the particles in our Einstein solid washing back and forth in the solid. So now, let's consider the positions of the atoms. Let $\alpha = 1, 2, 3, ...$ dimensions, and i indexes the particles in the solid. Then we define:

$$\delta_{i\alpha} = x_{i\alpha} - x_{i\alpha}^0$$

where δ is the displacement frm the rest position, x is the position, and x^0 is the rest position. Associated with these displacemenets, we have a kinetic energy term:

$$K = \frac{1}{2} \sum_{i=1}^{N} \sum_{\alpha=1}^{3} m_i \dot{\delta}_{i\alpha}^2$$

Now, we also have a potential energy term:

$$V = V_0 + \frac{1}{2} \sum_{i\alpha} \sum_{j\gamma} A_{i\alpha,j\gamma} \delta_{i\alpha} \delta_{j\gamma}$$

where A is the matrix that holds the interactions between the particles and each other. Now, we can find the 'normal modes' of the displacements by essentially diagonalizing the A matrix, and letting:

$$\delta_{i\alpha} = \sum_{n=1}^{3N} B_{i\alpha,n} q_n$$

where q_n is our new basis where A is diagonal presumably. Note that q_n isn't even position of the atoms anymore, but some sort of 'wave' that propogates large numbers of atoms in the Einstein Solid. Now, our Hamiltonian is given by:

$$H = V_0 + \frac{1}{2} \sum_{n=1}^{3N} (\dot{q}_n^2 + \omega_n^2 q_n^2)$$

So we can write more compactly:

$$H = \frac{1}{2}(\dot{q}^2 + \omega^2 q^2)$$

for a single mode. Importantly, the modes are independent, so we can use our old physics to now describe the system without worrying about interaction problems. To proceed, we make three key assumptions/observations. Firstly, the sound waves travel with speed c_s, that is, at the speed of sound (not at the speed of light; though the mathematics are the same).

Secondly, when the modes travel through a solid there are three different polarizations (two transverse one longitudinal), and through a liquid only 1 polarization (longitudinal). Finally, we restrict the wavelength of the travelling waves to be greather than a, the distance between two atoms. Taking these assumptions, we proceed by finding the density of states:

$$D_c(\omega)d\omega = \alpha dn_x dn_y dn_z = \frac{\alpha V}{(2\pi)^3}d^3k = \frac{\alpha V}{(2\pi)^3}4\pi k^2 dk = \frac{\alpha V}{2\pi^2 c_s^3}\omega^2 d\omega$$

where α is the number of polarizations, n_x, n_y, n_z are the quantum numbers, we do a spherical integral in k space. Note that this is the exact same density of states that we had for our blackbody radiation. For reference, everything we've been doing is known as the Debye model. So now, we want to do the same thing we did with the photon case, except we want to truncate the integral that we get, because we have some minimum wavelength given by the spacing of the atoms. So the debye density of states is given:

$$D_D = D_c(\omega) \text{ for } \omega < \omega_D \qquad D_D = 0 \text{ for } \omega > \omega_D$$

where D_c is the continuous density of states from before, D_D is the Debye density of states, ω_D is the cutoff frequency, and we will impose that:

$$\int_0^\infty D_D(\omega)d\omega = 3N$$

that we only count $3N$ total number of modes, which we intuitively guess is the limit where our continuum hypothesis breaks down. Solving this integral, we find that:

$$w_D = c_S\left(\frac{18\pi^2}{\alpha}\frac{N}{V}\right)^{1/3} = \frac{c_s}{\alpha}\left(\frac{18\pi^2}{\alpha}\right)^{1/3}$$

where we substitute in $a^3 = V/N$, recall that a is the distance between neighboring atoms. If we substitute in $\alpha = 3$, we find that we do indeed get $\lambda_D \approx a$, i.e. the wavelength is comparable to the atomic spacing. Now, to find the energy, we have:

$$U = \sum_n \langle \epsilon_n \rangle = \sum \frac{\hbar\omega_n}{e^{\hbar\omega_n/\tau} - 1} = \int_0^{\omega_D} \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} D_c(\omega)d\omega$$

we can introduce a dimensionless constant $x = \hbar\omega/\tau$ to make our lives a bit easier, and let

$$x_D = \frac{\hbar\omega_D}{\tau} = \frac{T_D}{T}$$

where T_D is the 'debye temperature' that we find is:

$$T_D = \frac{\hbar c_s}{k_b a}\left(\frac{18\pi^2}{\alpha}\right)^{1/3}$$

substituing back into our integral, we have:

$$U = \frac{9Nk_bT^4}{T_D^3}\int_0^{T_D/T}\frac{x^3}{e^x - 1}dx$$

We think that the solid is 'perfectly specified' by the debye temperature, that is, we can specify the debye temperature for a variety of solids, and know thermodynamic properties about it. Now, in the limit as $T << T_D$, the integral becomes an integral to infinity, and we get what we had for blackbody radiation:

$$U \approx \frac{3\pi^4 N k_b T^4}{5T_D^3}$$

So, we can easily calculate the heat capacity by differentiating the above with respect to T, and voila, the heat capacity scales with T^3. In the other limit, where $T >> T_D$, we can approximate e^x with a taylor series, and we recover magically,

$$U = 3Nk_BT$$

which is great.