PHYS 0551 Lecture #14

Title: Heat capacity (C_V) for a gas of phonons.

To calculate C_V, we need to know how many of each possible phonon for all temperatures of interest. For this we need to refer back to our "knowledge" of thermodynamics.

Recall that the change in heat $dQ = dU + pdV$

Heat capacity;

$$C_V \equiv \left(\frac{dQ}{dT}\right)_V \rightarrow \left(\frac{\partial U}{\partial T}\right)_V$$

where U is the change in energy and V is volume.

In general, it is difficult to keep V fixed so that experimentally we have:

$$Cp = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

but if $p \approx 0$, no work is done and thus $PdV = 0$ and C_p and C_V become equivalent.

What is the total internal energy of a vibrating crystal?

$$U = \sum_q \sum_p U_{q,p} = \sum_q \sum_p < n_{q,p} > (\hbar\omega_{q,p}) + \text{zero point energy}$$

where q are the allowed phonon modes, p are the polarizations (2T,1L), and $< n_{q,p} >$ is the number of phonons for a particular mode (q, p).

Note: A regression in order to determine the number of phonons per mode.

For a collection of *harmonic oscillators*, we will show $< n >= \frac{1}{e^{E/k_BT}-1}$ These are Bose-Einstein statistics which are applicable for integer spin "particles". $k_B \equiv$ Boltzman constant.

Recall the Boltzman factor, e^{-E/k_BT}, gives the relative probability that a single "state" (or energy level) will be occupied. You should review an introductory thermodynamics text if necessary (eg., Rief or Kittel & Kroemer) . The absolute occupancy of one state is:

$$\frac{e^{-E_n/k_BT}}{\sum_{\text{all states, } s=0} e^{-E_s/k_BT}}$$

where n is the particular state

Note: the denominator is *not* necessarily $= 1!$

For a collection of harmonic oscillators $E_n = n\hbar\omega;\ n = 1, 2, 3, ...$

Since there is no limit on the number of phonons occupying a particular mode, we need the thermal average $< n >$ to determine how many phonons are present.

$$\text{Fraction of oscillators in the } n^{\text{th}} \text{ state} = \frac{e^{-n\hbar\omega k_B T}}{\sum_s e^{-s\hbar\omega k_B T}}$$

$$\text{Thermal average} =< n >= \frac{\sum_n \; n \; e^{-n\hbar\omega k_B T}}{\sum_s \; e^{-s\hbar\omega k_B T}} \; (n \text{ is an integer})$$

NOTE: This is just a version of the mean value theorem

$$\overline{f(x)} = \frac{1}{b-a}\int_a^b f(x)\, dx, \quad b-a = \int_a^b dx$$

Recall

$$\sum_{m=0}^{N-1} x^m = \frac{1-x^N}{1-x} \quad (x < 1)$$

$$\frac{1}{1-x} \equiv 1+x+x^2+x^3+.... \; \frac{x^N}{(1-x)} \equiv x^N+x^{N+1}+x^{N+2}+.... \text{ so } \frac{1}{1-x}-\frac{x^N}{1-x} = 1+x+....+x^{N-1}$$

Back to $< n >$

Now

$$\begin{aligned}
\sum_s e^{-s\hbar\omega/k_B T} &= \sum_s x^s \text{ if } x = e^{\hbar\omega/k_B T} \\
&= | + x + x^2 + x^3 + x^4 + ... \\
&= \frac{1}{1-x} = \frac{1}{1-e^{-\hbar\omega/k_B T}}
\end{aligned}$$

Now let $y = -\hbar\omega/k_B T$ and examine the numerator

$$\begin{aligned}
\sum_n n \; e^{-n\hbar\omega/k_B T} &= \frac{d}{dy}\sum_n \; e^{ny} \\
&= \frac{d}{dy}\left(\sum_n \; x^n\right) \\
&= \frac{d}{dy}\left(\frac{1}{1-e^y}\right) \\
&= \frac{+e^{+y}}{(1-e^{+y})^2}
\end{aligned}$$

Thus

$$\begin{aligned}
\langle n \rangle &= \frac{e^{+y}(1-e^{y})}{(1-e^{+y})^2} = \frac{+e^{+y}}{1-e^{+y}} = \frac{1}{e^{-y}-1} \\
\langle n \rangle &= \frac{1}{e^{+\hbar\omega/k_BT}-1} \\
\text{and} & \\
\langle E_n \rangle &= \langle n \rangle\hbar\omega + \text{zero point energy}
\end{aligned}$$

Thus now we have determined the occupancy of a single mode, ω, and its total thermal energy. However we still need to find the total energy contained by all modes.

$$U = \sum_k \sum_p \frac{\hbar\omega_{k,p}}{\exp(\hbar\omega_{k,p}/k_BT)-1}$$

Note that we have E vs. ω (and not vs. k). If the crystal is large there is "continuum" of states in dk which can be changed to $d\omega$.

$$U = \sum_p \int d\omega D(\omega) \frac{\hbar\omega}{\exp(\hbar\omega/k_BT)-1} + \text{zero pt.}$$

$$(C_{lattice})_V = k_B \sum_p \int d\omega \frac{D(\omega)x^2 \exp\ x}{(\exp\ x-1)^2}, \quad x = \hbar\omega/k_BT$$

If $D(\omega)$ is known, C_V can be determined.

We know $D(\omega)$ from the previous lecture, but first let us examine a simpler model first proposed by Einstein. All oscillators have the same frequency ω_E. All atoms oscillate independently

Thus

$$\begin{aligned}
D(\omega) &= 3N\ \delta(\omega-\omega_E) \\
U &= \int d\omega\ 3N\ \delta(\omega-\omega_E)\ \frac{\hbar\omega}{\exp(\hbar\omega/k_BT)-1)} + \frac{3N}{2}\ \hbar\omega_E \\
U &= \frac{3N\ \hbar\omega_E}{\exp(\hbar\omega_E/k_BT)-1} + \frac{3N}{2}\hbar\omega_E \\
C_V &= \frac{3Nk_B\left(\frac{\hbar\omega_E}{k_BT}\right)^2}{(\exp(\hbar\omega_E/k_BT)-1)^2}\ \exp(\hbar\omega_E/k_BT)
\end{aligned}$$

if $k_BT >> \hbar\omega_E$ $\quad \exp(\hbar\omega_E/k_BT)-1 \approx \hbar\omega_E/k_BT$

$\exp(\hbar\omega_E/k_BT) \approx 1$

$\boxed{C_V = 3Nk_B}$ $\longrightarrow$ Classical equipartition of energy enumerated by Dulong & Petite with $\frac{1}{2}k_BT$ for each degree of freedom.

If $k_BT << \hbar\omega_E$ U $= \frac{1}{2}\ kr^2 + \frac{1}{2}\ \frac{p^2}{m}$; $V^2 = x^2 + y^2 + z^2$ and $p^2 = m(V_x^2 + V_y^2 + V_z^2)$

$$U \approx \frac{\hbar\omega_E\ 3N}{\exp(\hbar\omega_E/k_BT)} + \frac{3N}{2}\hbar\omega_E$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \approx 3Nk_B\frac{(\hbar\omega_E/k_BT)^2}{exp(\hbar\omega_E/k_BT)}$$

It turns out that this approximation is good for describing the optical modes of vibration. It is also good at high temperature, but fails at low temperatures. Experimentally $C_V \propto T^3$ for insulators. To improve the agreement between theory and experiment, we must use a D(ω) closer to the actual case.

(1) The 1[st] order we can ignore the singularities at the zone boundary.

(2) Assume that a sphere whose volume equals that of the 1st BZ gives the maximum phonon frequency.

$\frac{4}{3}\ \pi\ |k_D|^3 = \left(\frac{2\pi}{a}\right)^3;\ Na^3 = V$ This is the volume of the Debye sphere.

$k = \omega/v_s$ No dispersion in this approximation

$$\frac{4}{3}\ \pi\ \omega_D^3/v_s^3 = \left(\frac{2\pi}{a}\right)^3$$

$$\omega_D^3 = \frac{6\pi^2}{V}\ v_s^3\ N$$

$\omega_D = (6\pi^2 v_s^3 N/V)^{1/3};$ Debye frequency

$$U = \sum_p^3 \int_0^{\omega_D} d\omega \frac{D(\omega)\hbar\omega}{\exp(\hbar\omega/k_BT)-1} + \text{zero pt.}$$

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

$$U = \frac{3V}{2\pi^2 v_s^3} \int_o^{\omega_D} \frac{\hbar\omega^3}{\exp(\hbar\omega/k_BT)-1} + \text{zero pt.}$$

Substitute $x = \hbar\omega/k_BT$ $x_D = \theta_D/T = \hbar\omega_D/k_BT$

$$U = 9Nk_BT\ \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D}\ dx\frac{x^3e^x}{e^x-1} + \text{zero pt.}$$

if $k_BT >> \hbar\omega$ $e^x - 1 \approx x$

and

$$U = 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \int_o^{x_D} x^2\, dx = 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \frac{x_D^3}{3} = 3Nk_BT$$

$U = 3Nk_BT \quad C_V = 3Nk_B \quad \rightarrow$ This is again the classical thermodynamic limit.

If $k_BT < \hbar\omega$:

$$x_D \rightarrow \infty \quad U = 9Nk_BT \left(\frac{T}{\theta_D}\right)^3 \int_0^\infty \frac{dx\, x^3}{e^x - 1}$$

Notice the $C_V \propto T^3$

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

$$C_V \simeq \frac{12\pi^4}{s} Nk_B \left(\frac{T}{\theta_D}\right)^3$$

Thus the "simple" Debye approximation contains all the basic physics.