so

$$U = 3\left(\frac{L}{\pi}\right)^3\left(\frac{1}{8}\right) 4\pi \int_0^{k_D} k^2 dk \ \langle \varepsilon_n \rangle$$

Since $k_n = n\frac{\pi}{L}$, $n_D = (6N/\pi)^{1/3}$ $dk = dn\frac{\pi}{L}$

$$U = 3\left(\cancel{\frac{L}{\pi}}\right)^3\left(\frac{1}{\cancel{2}\cancel{8}}\right)\cancel{4}\pi \int_0^{n_D} n^2 \left(\cancel{\frac{\pi}{L}}\right)^2 dn \left(\cancel{\frac{\pi}{L}}\right) \langle \varepsilon_n \rangle$$

$$U = \frac{3\pi}{2}\int_0^{n_D} dn\, n^2 \frac{\hbar\omega_n}{\exp(\hbar\omega_n/\tau)-1}$$ KK Eq. 4.40

Assume $\omega = vk = vn\pi/L$,

$$U = \frac{3\pi}{2}\int_0^{n_D} dn\, n^2 \frac{\hbar v n\pi/L}{\exp(\hbar v n \pi/L\tau)-1} = \frac{3\pi^2\hbar v}{2L}\int_0^{n_D} dn \frac{n^3}{\exp\left(\frac{\hbar v n\pi}{L\tau}\right)-1}$$

As before,

let $x = \frac{\hbar v n \pi}{L\tau}$, then $n = \frac{x\tau L}{\hbar v \pi}$; $dn = \frac{\tau L}{\hbar v \pi}dx$,

$$U = \frac{3\pi^2\hbar v}{2L}\int_0^{n_D} \frac{\tau L}{\hbar v\pi}dx\left(\frac{\tau L}{\hbar v \pi}\right)^3 \frac{x^3}{\exp(x)-1}$$

$$\cancel{U = \frac{3\pi^2\hbar v L^3\tau^4}{2L\hbar^4 v^4\pi^4}\int_0^{n_D} dx \frac{x^3}{\exp(x)-1} =}$$

$$U = \left(\frac{3\pi^2 \hbar v}{2L}\right)\left(\frac{\tau L}{\pi \hbar v}\right)^4 \int_0^{x_D} dx \, \frac{x^3}{\exp x - 1}$$ KK Eq. 4.41

Since $x = \dfrac{\hbar v n \pi}{L\tau}$, $x_D = \dfrac{\hbar v n_D \pi}{L\tau}$

and since $n_D = \left(\dfrac{6N}{\pi}\right)^{1/3}$ KK Eq. 4.38, derived before

KK Eq. 4.42
$$x_D = \frac{\hbar v \pi}{L\tau}\left(\frac{6N}{\pi}\right)^{1/3} = \frac{\hbar v}{\tau}\left(\frac{6\pi^3 N}{L^3 \pi}\right)^{1/3} = \frac{\hbar v}{\tau}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

Usually, this is written as $x_D = \theta/T$ Eq. 4.43

Since $\tau = k_B T$, $x_D = \dfrac{\theta k_B}{\tau}$ $\cancel{= \frac{\theta k_B}{\tau} = \frac{\hbar v}{\tau}\left(\frac{6\pi^2 N}{V}\right)^{1/3}}$

$\tau / k_B = T$

$$x_D = \frac{\theta k_B}{\cancel{\tau}} = \frac{\hbar v}{\cancel{\tau}}\left(\frac{6\pi^2 N}{V}\right)^{1/3} \Rightarrow \theta = \left(\frac{\hbar v}{k_B}\right)\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$ KK Eq. 4.44

θ is called the <u>Debye temperature</u>

Units:
$$\left(\frac{\frac{J \cdot s \cdot m}{s}}{\frac{J}{K}}\right)\left(\frac{1}{m^3}\right)^{1/3} = \frac{\cancel{J} \cdot \cancel{s} \cdot \cancel{m} \cdot K}{\cancel{J} \cdot \cancel{s} \cdot \cancel{m}}$$

if you don't divide by k_B, the units are energy, but by convention it is used as a temperature. Notice that the two quantities that determine the Debye temperature:

the speed of sound v and the density N/V are easily measured in the lab. You can determine a microscopic quantity: the energy of the most energetic phonon in a material, by measuring macroscopic quantities.

~~A Several~~

The Debye temperatures of several elements are given in Fig. 4.1. ☆ What element has the most energetic phonons? The least?

The energy of the Debye solid is more complicated that that of the box of electromagnetic waves because the limit of the integral is not ∞. But consider the case $T \ll \theta$, $T \to 0$. $x_D = \theta/T \to \infty$. So in the low temperature limit,

$$U = \left(\frac{3\pi^2 \hbar v}{2L}\right)\left(\frac{\tau L}{\pi \hbar v}\right)^4 \int_0^\infty dx \, \frac{x^3}{\exp x - 1}$$

$\frac{\pi^4}{15}$, as before

$$U = \frac{3\pi^2 \cancel{\hbar}\cancel{v}\, \tau^4 L^{\cancel{4}3} \cancel{\pi^4}}{2\cancel{L}\, \cancel{\pi^4}\, \hbar^{\cancel{4}3} v^{\cancel{4}3}\, 15} = \frac{3\pi^2\tau^4 V}{\cancel{30}_{10}\, \hbar^3 v^3} = \frac{\pi^2\tau^4}{10\hbar^3 v^3/V}$$

Now, $\theta^3 = \frac{\hbar^3 v^3}{k_B^3} \frac{6\pi^2 N}{V} \Rightarrow \frac{\hbar^3 v^3}{V} = \frac{\theta^3 k_B^3}{6\pi^2 N}$, so

$$U = \frac{\pi^2 \tau^4 \, \overset{3}{\cancel{6}}\pi^2 N}{5 \, \cancel{10} \, \theta^3 k_B^3} = \frac{3\pi^4 N \tau^4}{5(k_B\theta)^3}$$

Since $\tau = k_B T$,

$$U = \frac{3\pi^4 N k_B^{\cancel{4}} T^4}{5 \cancel{k_B^3} \theta^3} = \frac{3\pi^4 N k_B T^4}{5\theta^3}$$

KK Eq. 4.46

At low ~~energ~~ temperature, the high energy phonon modes are not occupied because of the Boltzmann distribution.

Since all the existing phonons are of low frequency $\leftrightarrow$ long wavelengnt, the fact that there is a maximum frequency does not matter.

wavelength much larger than the interatomic distance.

The heat capacity at constant volume is

$$C_V = \left(\frac{\partial U}{\partial \tau}\right)_V = \frac{\partial}{\partial \tau} \frac{3\pi^4 N \tau^4}{5(k_B\theta)^3} = \frac{12\pi^4 N}{5} \left(\frac{\tau}{k_B\theta}\right)^3$$

KK Eq. 47

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T} \frac{3\pi^4 N k_B T^4}{5\theta^3} = \frac{12\pi^4 N k_B}{5} \left(\frac{T}{\theta}\right)^3$$

This result is known as the Debye T^3 law.

what happens at high temperature, $T >> \theta$,

$T \to \infty$. $x_D = \theta/T \to 0$. Before that,

$$x = \frac{\hbar v n \pi}{L\tau} \to 0, \qquad e^x \approx 1 + x$$

$$u = \left(\frac{3\pi^2 \hbar v}{2L}\right)\left(\frac{\tau L}{\pi \hbar v}\right)^4 \int_0^{x_D} dx \frac{x^{\cancel{3}2}}{\cancel{1} + x \cancel{- 1}}$$

$$u = \frac{\cancel{3}\cancel{\pi^2}\cancel{\hbar}\cancel{v}\,\tau^4 L^{\cancel{4}3}}{2\cancel{\mathcal{L}}\,\pi^{\cancel{2}4}\hbar^{\cancel{3}4} v^{\cancel{4}3}} \frac{x_D^{\,3}}{\cancel{3}} = \frac{\tau^{4} \cancel{L^3}}{\cancel{2}\pi^2 \cancel{\hbar^3}\cancel{v^3}} \frac{\cancel{\hbar^3}\cancel{v^3}\cancel{\pi^3}\, \cancel{6}3N}{\cancel{L^3}\cancel{\tau^3}\,\cancel{\pi}}$$

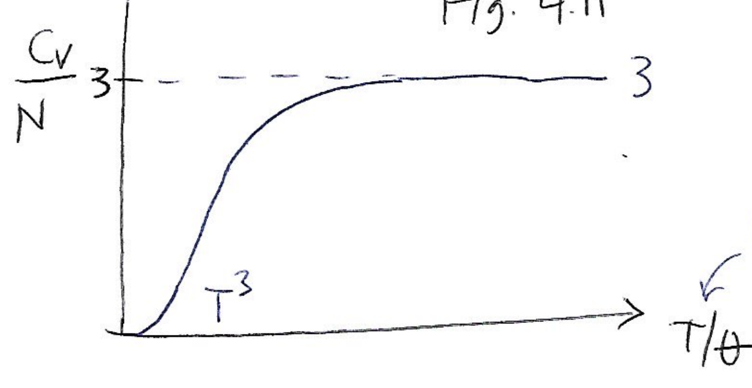
$$u = 3N\tau$$

$$C_V = \left(\frac{\partial u}{\partial \tau}\right)_V = \frac{\partial}{\partial \tau} 3N\tau = 3N$$

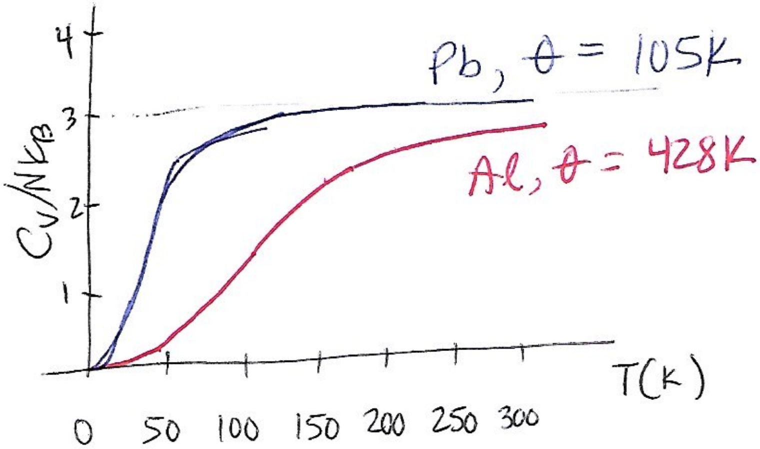
The heat capacity at high temperature is a constant, called the Dulong-Pettit limit.

~~At~~ At high temperature, all the modes are occupied, according to Boltzmann distribution. Because of this, the equipartition theorem holds.

Fig. 4.11



Heat capacity looks pretty much the same for all solids, but it's scaled by the inverse of the Debye temperature



The high T, low T regimes depend on the Debye temperature

The Dulong and Petit law was well known at high T, but experiments started to show that as the Temp. decreases, the heat capacity decreases. Einstein borrowed Planck's quantization assumption and showed that this accounted for the experimental trends. Einstein knew that his theory, the Einstein solid, was not completely correct because he assumed independent harmonic oscillators, but decided to publish the results becaused they showed the importance of quantization.

Planck $\longrightarrow$ radiation

Einstein $\longrightarrow$ matter