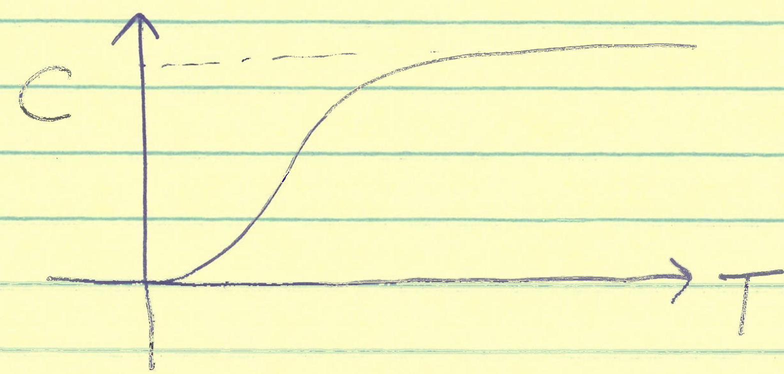
Wed. Aug. 29

- last time we discussed the heat capacity (per atom) for a solid
- at high T, we get the classical Dulong-Petit law

$$C = 3k_B \text{ (per atom)}$$

- at low T, we find non-linearity



- We discussed that quantum effects begin to dominate at low T
- this arises from the quantized energy levels of the harmonic oscillators & the theory models the measured behavior quite well

- let's take a closer look at how this works

- a quantum harmonic oscillator (QHO) only has energy levels

$$E_n = \hbar\omega\left(\tfrac{1}{2}+n\right)$$

- it is important to note that ω is assumed to be the same "Einstein freq."

- For 1D, the partition function

$$Z_{1D} = \sum_{n\geq 0} \exp\left(-\beta\hbar\omega[n+\tfrac{1}{2}]\right)$$

- Compare to classical : $\int \rightarrow \sum$

$$\int \frac{d\vec{p}}{(2\pi\hbar)^3} \int d\vec{x}\, e^{-\beta H(\vec{p},\vec{x})}$$

- Before moving forward, let's recall what the partition function is:

- probability the system is in state 'n'

$$P_n = \frac{1}{Z} e^{-\beta E_n}, \quad Z = \sum_n e^{-\beta E_n}$$

- What do we expect for $\sum_n' P_n$?

$$\sum_n' P_n = \frac{1}{Z}\sum_n' e^{-\beta E_n} = \frac{1}{Z} Z = 1$$

$\langle E \rangle \equiv$ expectation value of energy

$$\langle E \rangle = \sum_n' E_n P_n = \frac{1}{Z}\sum_n E_n e^{-\beta E_n}$$

- $$\frac{\partial}{\partial \beta}\left(e^{-\beta E_n}\right) = -E_n e^{-\beta E_n} \qquad \langle E \rangle = \frac{-1}{Z}\sum_n\left(\frac{\partial}{\partial\beta}e^{-\beta E_n}\right)$$

$$\langle E \rangle = -\frac{1}{Z}\sum_n E_n e^{-\beta E_n} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

- For the QHO, we then have

$$\langle E \rangle = \frac{1}{Z}\sum_n E_n e^{-\beta E_n} \qquad n_B(x) = \frac{1}{e^x - 1}$$

for $E_n = \hbar\omega(n + 1/2) \Rightarrow \langle E \rangle = \hbar\omega\left(n_B(\beta\hbar\omega) + \frac{1}{2}\right)$

- $$C = \partial\langle E \rangle / \partial T = k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

- let's look at the limits

$$C = 3k_B (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

- for high T, $\frac{\hbar\omega}{k_B T} << 1$
- let $x = \beta\hbar\omega$ (so $x << 1$)
- $e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2} + \ldots$
- for small x, $e^x \simeq 1 + x$

$$\hat{C} = 3k_B x^2 \frac{e^x}{(e^x-1)^2} \cong 3k_B \frac{x^2(1+x)}{(1+x-1)^2}$$

$$= 3k_B \frac{x^2}{x^2} \underbrace{(1+x)}_{\text{small } x \simeq 1}$$

$C \simeq 3k_B$ for high T ✓

- let's return to the probability
- what is the probability of finding our oscillators in the grand state

$$E_n = \hbar\omega(n + 1/2)$$

$$E_0 = \hbar\omega/2$$

$$P_n = \frac{1}{Z} e^{-\beta E_n} \Rightarrow P_0 = \frac{1}{Z} e^{-\beta\hbar\omega/2}$$

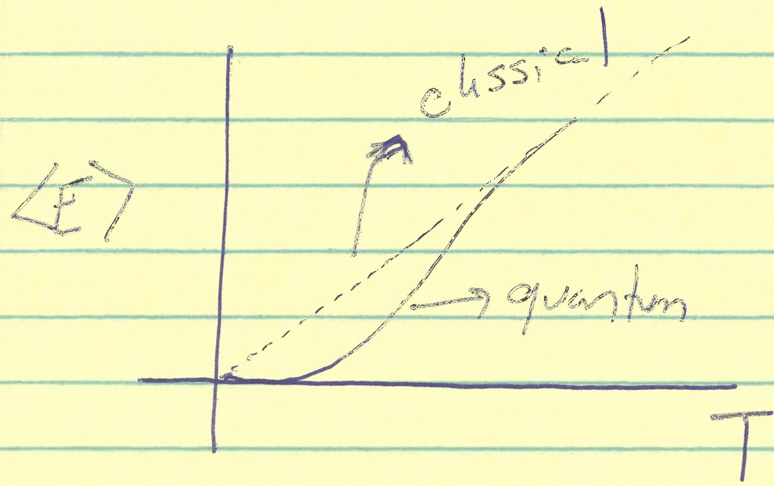
$$P_0 = \frac{e^{-\beta\hbar\omega/2}}{\left(e^{-\beta\hbar\omega/2} + e^{-3\beta\hbar\omega/2} + \dots e^{-\infty}\right)} = \frac{e^{-\beta E_0}}{e^{-\beta E_0} + \dots e^{-\infty}}$$

$$= \frac{e^{-\beta\hbar\omega/2}}{e^{-\beta\hbar\omega/2}}\left[\frac{1}{1 + e^{-\beta\hbar\omega} + \dots}\right]$$

- very low T, $T \ll \hbar\omega/k_B$, $\beta \gg 1 \rightarrow e^{-\beta\hbar\omega} \rightarrow 0$

- $P_0 \rightarrow 1$, for low T (all H.O.'s in grand state) ✓

- the expectation value $\langle E \rangle \to \hbar\omega/2$ (grand state)



- one parameter we have not diswssed is ω, the frequency
- We assume it is the same for all oscillators & is sometimes called the "Einstein" frequency
- Correspondingly, the Einstein temp.

$$T_E = h\omega/k_B$$

- we adjust this parameter to best fit the C vs. T curve
- Eg. $T_E = 240K$ for Cu