Topic 6-2: Heat Capacity with the Debye Model
Kittel Pages: 112-114

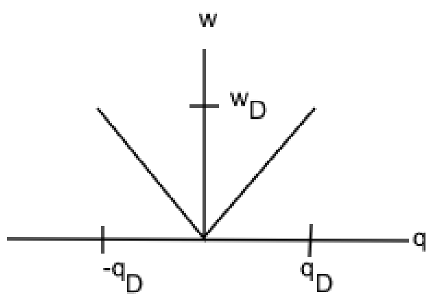
Summary: We now move from the Einstein model to the Debye model, which accounts for multiple phonon frequencies. After deriving the heat capacity equation using the Debye model we discover that the Debye model is inaccurate at intermediate temperatures.

Recall Approach 2: Einstein model

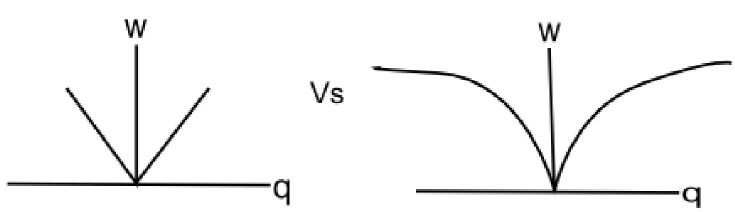
- Einstein assumed all atoms vibrate at the same frequency and are isolated
  - No dispersion or wave vectors

Approach 3: Debye model in 3D

- Debye model invokes a linear, isotropic phonon dispersion (in all q directions)



- Even less accurate than the ball and spring model we derived earlier; however, the Debye model does have multiple phonon frequencies, instead of Einstein's single ω_o, so it should still be an improvement….



- Debye system energy

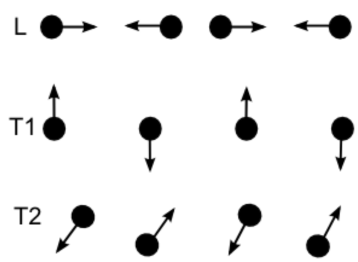
$$U_D = \int_0^{\omega_D} d\omega\, D(\omega) U_n(n,\omega,T) \qquad [1]$$

$$U_n = \langle n \rangle \hbar\omega \qquad [2]$$

$$< n >= \frac{1}{e^{\frac{\hbar\omega}{\tau}}-1} \qquad [3]$$

- $\tau = k_B T$

- **Talking through equation:** We determine the total system energy U_D by integrated across the entire frequency range within this Debye solid. The integrand is the product of the density of vibrational states at frequency ω with the energy of a single state at ω with phonon occupancy <n> (determined by temperature T).
- Next, we multiply by 3 because we have 2 transverse modes and 1 longitudinal mode in 3D for a given q vector. In image below, all the q vectors are left to right (or right to left, hard to say…).



- The two transverse modes are orthonormal
- Again, to obtain the heat capacity, we're going to drop the zero point energy because of derivative in heat capacity

$$U_n =< \frac{1}{e^{\frac{\hbar\omega}{\tau}}-1} + \frac{1}{2} > \hbar\omega \qquad [4]$$

$$\frac{\partial U_n}{\partial T} = \frac{\partial}{\partial T}\left(\frac{1}{e^{\frac{\hbar\omega}{\tau}}-1}\right)\hbar\omega + 0 \qquad [5]$$

- Plugging everything into the integral:

$$U_D = 3\int_0^{\omega_D} d\omega\, D(\omega) < n > \hbar\omega \qquad [6]$$

- Know D in 3D is $\frac{V\omega^2}{2\pi^2 {v_s}^3}$ where V is the sample volume and v_s is the speed of sound

$$U_D = \frac{3V\hbar}{2\pi^2 {v_s}^3}\int_0^{\omega_D} d\omega\, \frac{\omega^3}{e^{\frac{\hbar\omega}{\tau}}-1} \qquad [7]$$

- Thus, heat capacity is:

$$C = \frac{\partial}{\partial T}\frac{3V\hbar}{2\pi^2 {v_s}^3}\int_0^{\omega_D} d\omega\, \frac{\omega^3}{e^{\frac{\hbar\omega}{\tau}}-1} \qquad [8]$$

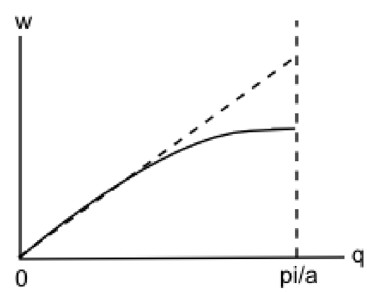
- Need cutoff frequency ω_D
- We know the total number of modes equals 3N·r
  - N is the number of primitive cells
  - r is the number of atoms per cell
  - 3 from the one longitudinal, two transverse
- Can also find number of modes by integrating the density of states from 0 to the cutoff frequency

$$3Nr = \int_0^{\omega_D} d\omega\, D \quad [9]$$

- This gives:

$$\omega_D = \sqrt[3]{\frac{6\pi^2 {v_s}^3 Nr}{V}} \quad [10]$$

- OK, the math is nasty, here are the limits
  - At high temperature we get $3k_B$ per atom. Nice!
  - At the low temperature limit we get $C = \frac{12}{5}\pi^4 N k_B (\frac{T}{\theta})^3$
    - $\theta = \frac{\hbar v_s}{k_B}(\frac{6\pi^2 N}{V})^{1/3}$
- This gives a heat capacity proportional to T^3 which agrees with experiment
- Debye model only has one free parameter which is the slope of the linear dispersion v_s. The low frequency speed of sound can be used to estimate the temperature dependence of the heat capacity, or visa versa



- Debye model has a discrepancy which causes inaccuracy at intermediate temperatures when phonons start to populate the upper part of the dispersion

Questions to Ponder

1. How do you design a solid with really high or really low heat capacity?

2. Why do we care about heat capacity? Are there reasons to think about heat capacity beyond something simple like heat storage?