Topic 6-1: Planck Distribution and Einstein Heat Capacity

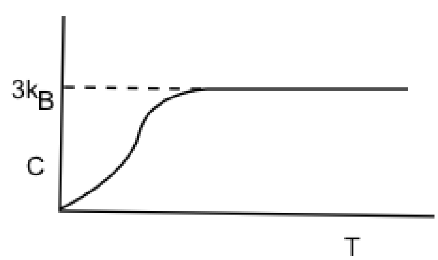
Kittel Pages: 107,108,114-117

Summary: In this video we discuss heat capacity. Firstly, we discuss the Dulong-Petit experimental observation of heat capacity in solids. Then we focus on the Einstein model of heat capacity which treats atoms as isolated harmonic oscillators and uses the Planck distribution to develop an expression for heat capacity. This model works well at high temperatures but fails to describe experimental behavior at low temperatures.

- Heat capacity (C): energy required to change some body by some δT: $C_v = (\frac{\partial U}{\partial T})_V$
    - Body: anything from a mole to a gram to a cm^3 of a material
- For an ideal gas $C = \frac{3}{2} k_B$ per atom
    - K_B is the Boltzmann constant

Approach 1: Dulong-Petit experimental observation

- Law of Dulong-Petit: experimentally solids at high temperature were found to have $3k_B$ per atom
    - Model totally fails at low temperature



Approach 2: Einstein's isolated harmonic oscillator model

- In the early 20th century Einstein proposes to treat each atom as an *isolated* harmonic oscillator where all atoms vibrate at the same frequency, ω_o
- Energy of each vibrational mode in an atom is $U_n = (n + \frac{1}{2})\hbar\omega_o$
- Total energy is $U_n = 3N < n(\omega_o) > \hbar\omega_o$
    - N is the total number of atoms in the solid
    - 3 indicates that each atom has vibrational modes in 3 dimensions, each at ω_o

- We're dropping the zero point energy term (+1/2) because later, when we take the derivative to get heat capacity, it would drop out on its own anyway
- <n(ω)> is the phonon occupancy at frequency ω

- Since phonons act like bosons, we will use the **Planck distribution** for the population distribution

$$< n(\omega) > = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad [1]$$

- Plugging this back into our expression for *U* we get:

$$U = \frac{3N\ \hbar\omega_O}{e^{\frac{\hbar\omega}{\tau}} - 1} \quad [2]$$

  - where τ is $k_B T$

- Since $C_v = (\frac{\partial U}{\partial T})_V$ we can take the derivative, yielding

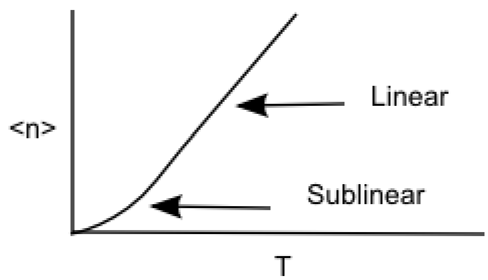
$$C_v = k_B (\frac{\hbar\omega_O}{\tau})^2 \frac{e^{\frac{\hbar\omega_O}{\tau}}}{(e^{\frac{\hbar\omega_O}{\tau}} - 1)^2} \quad [3]$$

- Can define a new variable $x = \frac{\hbar\omega}{k_B T}$
- This gives $C_v = 3Nk_B x^2 \frac{e^x}{(e^x - 1)^2}$
- At high temperature, x goes to 0 and heat capacity goes to $3Nk_B$. Awesome, agrees w/ experiment ($3k_B$ per atom)
- At low temperature, x goes to infinity, so heat capacity rises *exponentially* with T.
  - Not exactly right compared to experiment: measured heat capacities are proportional to T^3 at low temperature
  - *C* still drops from $3k_B$ per atom down to zero at 0K, so the model is capturing some of the underlying physics.

- **Concept question:** In a harmonic oscillator, the energy spacing is constant. So why are the high and low temperature limits of heat capacity different (dropping to zero vs remaining at $3k_b$/atom)?
- When we're talking about heat capacity, we're thinking about the *change* in phonon number <n> with temperature. If a small change in temperature requires the addition of many new phonons (aka, the amplitude of vibration increases significantly), this will be

energetically costly and the heat capacity at that temperature will be large. Below, we'll see it's the opposite case: At low temperature, the change in <n> is small with *dT*, thus the energy required to increase the temperature is small and the heat capacity is likewise minimal.

- Let's start by visualizing how <n> changes with temperature



- <n> is linear at high temperature and sublinear at low temperatures
- <n> is the only thing in the energy expression that changes with temperature so this temperature dependence is reflected in the heat capacity expression
  - **At high T**, the derivative of <n> is constant, which is to say, the number of modes increases linearly with T. Recall that the amplitude of the vibrations is connected to the mode occupancy <n>
  - **At low T,** you can see that <n> barely increases w/ T. Thus, increasing temperature is not energetically costly.

Questions to Ponder

1. Why did Einstein’s model fail at low temperature?