Lecture 10 - Phonons II - Thermal Properties

### Phonons II - Thermal Properties (Kittel Ch. 5)

![Graph](C)\(C \propto T^3\)

**Outline**

- What are thermal properties?
  - Fundamental law for probabilities of states in thermal equilibrium

- Planck Distribution
  - Start of quantum mechanics
  - Applied to solids in early days of q. m.
  - Bose-Einstein statistics - Planck distribution

- Density of states, Internal energy, Heat capacity
- Normal mode enumeration
- Debye Model -- \(C \propto T^3\) law at low \(T\)
- Einstein Model
  - (Read Kittel Ch 5)

### Highlights

- **Keys Today**
  - Fundamental laws
  - How to make good approximations

- **Beginnings of quantum mechanics**
  - Max Planck - 1901
  - Observations and experimental facts that showed problems with classical mechanics
  - One was radiation – the laws of classical mechanics predicted that light radiated from hot bodies would be more intense for higher frequency (blue and ultraviolet) – totally wrong!
  - Planck proposed that light was emitted in “quanta” – units with energy \(E = h\nu = nh\)
  - One key result is the distribution of the frequencies of waves as a function of temperature
  - Applies to all waves!

### Thermal Properties - Key Points

- **Fundamental law a system in thermal equilibrium:**
  - If two states of the system have total energies \(E_1\) and \(E_2\), then the ratio of probabilities for finding the system in states 1 and 2 is:
  \[
P_1 / P_2 = \exp \left( -\frac{(E_1 - E_2)}{k_BT} \right)
  \]
  where
  \(k_B\) is the Boltzman constant

- **Applies to all systems** - whether treated as classical or as quantum and whether the particles are bosons (like phonons) or fermions (like electrons)
- **Quantum Mechanics makes the problem easier**, with final formulas for thermal energy, etc., that depend upon whether the particles are bosons or fermions

- **Thermal Properties - Phonons**
  - Phonons are examples of bosons that do not obey an exclusion principle. There can be any number \(n\) phonons for each oscillator, i.e., the energy of each oscillator can be \(E_n = (n + \frac{1}{2})\hbar\nu\), \(n = 0, 1, 2, \ldots\)
  - Thus the probability of finding the oscillator with \(n\) phonons:
    \[
P_n = \exp \left( -\frac{E_n}{k_BT} \right) / \sum_{n=0}^{\infty} \exp \left( -\frac{E_n}{k_BT} \right)
    \]
  - Note: \(\sum_{n=0}^{\infty} P_n = 1\) as it must for probabilities

  - And the average phonon occupation is
    \[
    \langle n \rangle = \sum_{n=0}^{\infty} P_n n = \sum_{n=0}^{\infty} n \exp \left( -\frac{E_n}{k_BT} \right) / \sum_{n=0}^{\infty} \exp \left( -\frac{E_n}{k_BT} \right)
    \]

  - See next slide
Planck Distribution

- Using the formulas:
  \[ \frac{1}{1 - x} = \sum_{s=0}^{\infty} s x^s \]
  \[ \frac{x}{1 - x^2} = \sum_{s=0}^{\infty} s x^s \]
  (simple proof in class)

  it follows that:
  \[ \langle n \rangle = \text{Planck Distribution} \]

- Average energy of an oscillator at temperature T:
  \[ U = \langle n \rangle + \frac{1}{2} \]
  \[ = \frac{\hbar \omega}{1 - \exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} + \frac{1}{2} \]

- At high T, \[ U \rightarrow k_B T \]
  which is the classical result

Mean square displacement

- Homework problem to estimate the root mean square displacement
  \[ \Delta x_{\text{rms}} = \left[ \langle (x - x_0)^2 \rangle \right]^{1/2} \]
- One can use typical values for C and M
- Result – for most cases \( \Delta x_{\text{rms}} \ll \) near neighbor distance at T=0
- \( \Delta x_{\text{rms}} \) increases and it is \( \sim \) near neighbor distance when the solid melts (Lindeman criterion)

Total thermal energy of a crystal

- The crystal is a sum of independent oscillators (in the harmonic approximation). The independent oscillators are waves labeled by \( k \) and an index \( m = 1, \ldots, 3N \). Therefore, the total energy of the crystal is:
  \[ U = U_0 + \sum_{k, m} \hbar \omega_{k,m} \left( \frac{1}{\exp\left(\frac{\hbar \omega_{k,m}}{k_B T}\right) - 1} + \frac{1}{2} \right) \]

  **Fixed atoms**
  **3 dimensions**
  **Added thermal energy**
  **Zero point energy**

  **Question:** How to do the sum over \( k \)?

Counting \( k \) points

- We can derive this and we can also see that it MUST be true without doing any work!
  - 1. A crystal in 3 dimensions with \( N \) cells and \( N_{\text{atom}} \) atoms/cell has \( 3N N_{\text{atom}} \) "degrees of freedom" (i.e. number of ways the atoms can move).
  - 2. This does not change when we transform to the independent oscillators (i.e. the oscillators with frequencies \( \omega_{k,m} \)).
  - 3. Therefore there are \( 3N N_{\text{atom}} \) independent oscillators!

  This can be thought of as follows:
  - There is one \( k \) point for each primitive cell in the crystal (see next slide)
  - For each \( k \) point there are \( 3N_{\text{atom}} \) ways the atoms in the cell can move, i.e., 3 \( N_{\text{atom}} \) dispersion curves labeled by the index \( m \) with frequency \( \omega_{k,m} \)
  - This is a total of \( 3N N_{\text{atom}} \) independent oscillators!
Counting k points
- If we consider the states on a circle (the line wrapped into a circle), it is easier to consider $u_k = u \exp(iksa)$.
- See Kittel, Ch 5, Fig. 4.
- Consider all the possible waves $u_k = u \exp(i ksa)$ that can fit in a circle of circumference $L$.
$$k = -N \pi /L, \ldots -6 \pi /L, -4 \pi /L, -2 \pi /L, 0, 2 \pi /L, 4 \pi /L, 6 \pi /L, \ldots N \pi /L$$

Conclusion: $# k$ points = # cells (same as before).

$\Delta k = 2 \pi /L$ -- approaches a continuum -- smooth curve for $\omega(k)$.

$\int_{BZ} f(k)$

Using $L = Na$

$\int_{BZ} f(k)$

Counting k points
- Final result in any dimension.
- Equivalent to Kittel Ch 5, Eq. 18.
- But I think my version is clearer.

All expressions for total integrated quantities in a crystal involve a sum over the $k$ points in the Brillouin Zone (or any primitive cell of the reciprocal lattice).

We can express the result as a value per cell as the sum over $k$ points divided by the number of cells $N$.

For any function $f(k)$ the integrated value per cell is

$$\bar{f}_{\text{per cell}} = \frac{1}{N} \int_{BZ} f(k) \Rightarrow \bar{f}_{\text{per cell}} = \left( \frac{1}{V_{BZ}} \right) \int_{BZ} f(k)$$

Total thermal energy
- For the total thermal energy we need a sum over states.
- Then the thermal energy per cell is

$$U_{\text{m}} = \frac{1}{V_{BZ}} \int_{BZ} \sum_{\omega} \frac{1}{\exp \left( \frac{\hbar \omega_{k,m}}{k_B T} \right) - 1}$$

Notice that this depends only on the frequency of the phonons $\omega_{k,m}$.

We can use this to simplify the problem.

Density of States
- What is needed is the number of states per unit frequency $D(\omega)$. Then for any function $f(x)$

$$\left( \frac{1}{V_{BZ}} \right) \int_{BZ} \sum_{\omega} \bar{f}(\omega_{k,m}) = \int_{\omega} D(\omega) f(\omega)$$

How do we find $D(\omega)$?
- By finding the number of states in an energy range from $\omega$ to $\omega + \Delta \omega$.
- The key is that the $k$ points are equally spaced. Thus the number of states per unit $k$ is constant.

Example - One dimension (homework).

Next Slide

Density of states for acoustic phonons in 1 dimension
- The key is that the $k$ points are equally spaced.
- In 1 dimension this means that the number of states per unit $k$ is constant.

Thus

$$D(\omega) = \frac{dN_{\text{state}}}{d\omega} = \frac{dN_{\text{state}}}{dk}(dk/d\omega) = \frac{L(2\pi)}{V_{\text{group}}}$$

Homework
Density of states for acoustic phonons in 3 dimensions

\[ D(\omega) = \frac{1}{V} \frac{dN_{\text{states}}}{d\omega} = \frac{V_i}{(2\pi)^3} |k|^2 \frac{d|k|}{d\omega} = \frac{V_i}{(2\pi)^3} |k|^2 \left( \frac{1}{V_{\text{group}}} \right) \]

The k points are equally spaced in each direction. In 3 dimensions this means that the number of states per unit |k| is \( 4\pi|k|^2 \). Thus

\[ D(\omega) = \frac{V_i}{(2\pi)^3} |k|^2 \left( \frac{1}{V_{\text{group}}} \right) \]

\[ \sim \omega^2 \]

Debye Model for density of states for acoustic phonons in 3 dimensions

- For acoustic phonons at long wavelength (small k), \( \omega = v_s k \)
- The Debye model is to assume \( \omega = v_s k \) for all k in the Brillouin zone
- Then

\[ D(\omega) = \frac{V_i}{(2\pi)^3} |k|^2 \left( \frac{1}{V_{\text{group}}} \right) = \frac{V_i}{(2\pi)^3} \frac{1}{V_{\text{cell}}} \]

- Also we define a cutoff frequency by \( \omega_D = v_s k_{\text{max}} \) where \( k_{\text{max}} \) is the radius that would give a sphere with the same volume as the Brillouin zone

\[ \frac{4\pi}{3} k_{\text{max}}^3 = V_BZ = \frac{(2\pi)^3}{V_{\text{cell}}} \]

or

\[ \omega_D^3 = \frac{6\pi^2 v_s^3}{V_{\text{cell}}} \]

Debye Approximation

- Has correct general behavior that must be found in all crystals. For 3 dimensions:

\[ C_T \sim T^3 \]

Heat capacity

- The heat capacity is the change in energy per unit change in temperature

\[ C_v = \frac{dU}{dT} \]

- Thus in the Debye model

\[ U = 9N k_B T \left( \frac{T}{\Theta} \right)^3 \int_0^\infty dx x^3 \left( \frac{1}{\exp(x) - 1} \right) \]

\[ C_v = 9N k_B T \left( \frac{T}{\Theta} \right)^3 \int_0^\infty dx x^4 \frac{\exp(x)}{(\exp(x) - 1)} \]

- See Kittel for details

Oscillations in general 3 dimensional crystal with N atoms per cell

- 3 (N - 1) Optic Modes
- Each has \( \omega = k \) at small k

\[ \omega_0 \]

\[ \frac{\omega_0}{\pi a} \]

\[ 0 \]

\[ \frac{\pi a}{2} \]
Einstein Approximation

- Appropriate for Optic modes
- Use only one frequency – an average frequency for the optic modes
  \[ U = 3(N_{\text{cell}} - 1) \frac{h \omega}{e^{(h \omega / k_B T)} - 1} \]

\[ \omega_k \]

\[ -\pi/a \quad 0 \quad \pi/a \]

3 Acoustic modes
Each has \( \omega \sim k \) at small k

3 (N -1) Optic Modes

See Kittel p. 114 for Einstein model.

Summary

- Fundamental law for probability of finding a system in a state if it is in thermal equilibrium
- Only need energies of possible states of the system
- Phonons are particles that obey Bose statistics
- Result is Planck Distribution
- Expression for internal energy and heat capacity
- Limits for heat capacity at low T and high T
- Debye approximation
- Debye temperature used as a characteristic measure for vibrational properties of solids
- Einstein Approximation
- How to make useful approximations!

Next time

- Thermal Heat Transport
  Phonon Heat Conductivity
- Anharmonicity
  Crucial for Transport
- Gruneisen Constant
- (Read Kittel Ch 5)