Phonons II - Thermal Properties (Kittel Ch. 5)

Heat Capacity $C$ vs. Temperature $T$

- $T^3$ behavior
- Approaches classical limit $3Nk_B$
Heat capacity

- **Heat capacity** is the measure of how much energy it takes to raise the temperature of a unit mass of an object a certain amount.

- Two heat capacities: constant volume, $C_V$, and constant pressure, $C_P$. For a gas $C_P > C_V$. For a solid $C_P \approx C_V$.

- The contribution of the phonons (lattice vibrations) to the heat capacity of a crystal is called the **lattice heat capacity**.

- Classical result: $C \approx 3N N_{\text{cell}} k_B$, where $N$ is the number of atoms in a unit cell and $N_{\text{cell}}$ is the number of cells in the crystal.
Lattice heat capacity

- The heat that goes into a solid to raise its temperature shows up as internal vibrational energy $U$ (phonons).
- Determine $U(T)$, then we can calculate $C_V = (\partial U/\partial T)_V$.

- In calculating $U$ we need to consider the following:
  - (1) what is the average energy of each phonon;
  - (2) what is the average number of phonons existing at any $T$ for each type (mode) of vibration;
  - (3) how many different types (modes) of vibration are there.
Quantization of vibration waves

- Vibrations in a crystal are independent waves, each labeled by \( k \).
- There are \( 3N \) wave types in a 3D crystal with \( N \) atoms per cell.

- Each independent harmonic oscillator has quantized energies:
  \[
  E_n = (n + 1/2) \hbar \nu = (n + 1/2) \hbar \omega
  \]
- Quanta are called phonons, each phonon carries energy \( \hbar \omega \).
- These can be viewed as particles.
- For each independent oscillator (i.e., for each independent wave in a crystal), there can be any integer number of phonons.
- Need to find out the average number of phonons and the average energy associated with each independent oscillator (mode).
Thermal Properties - Key Points

- **Fundamental law of 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 $P_1 / P_2 = \exp \left(-\frac{(E_1 - E_2)}{k_B T}\right)$ where $k_B$ is the Boltzmann constant.

- Larger probability of smaller energy

- **Applies to all systems** - whether classical or quantum and whether the particles are bosons (like phonons) or fermions (like electrons)
Thermal Properties - Phonons

- **Phonons** are examples of bosons.
- There can be any number \( n \) phonons for each oscillator, i.e., the energy of each oscillator can be \( E_n = (n + \frac{1}{2}) \hbar \omega \), \( n = 0, 1, 2, \ldots \).

The probability of finding an oscillator with \( n \) phonons (and not another value)

\[
P_n = \exp \left( - \frac{E_n}{k_B T} \right) / \sum_{n' = 0}^{\infty} \exp \left( - \frac{E_{n'}}{k_B T} \right)
\]

and the average phonon occupation is

\[
<n> = \sum_{n = 0}^{\infty} P_n \, n \\
= \sum_{n = 0}^{\infty} n \exp \left( - \frac{E_n}{k_B T} \right) / \sum_{n' = 0}^{\infty} \exp \left( - \frac{E_{n'}}{k_B T} \right)
\]
Planck Distribution

• Using the formulas:
\[
\frac{1}{1 - x} = \sum_{s=0}^{\infty} x^s \quad \text{and} \quad \frac{x}{(1 - x)^2} = \sum_{s=0}^{\infty} s x^s
\]

\[
\langle n \rangle = \frac{1}{\left[ \exp \left( \frac{\hbar \omega}{k_B T} \right) - 1 \right]}
\]

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

• At high T, \( U \to \frac{\hbar \omega}{\left[ \frac{\hbar \omega}{k_B T} \right]} \to k_B T \) which is the classical result
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 $\mathbf{k}$ and an index $m = 1, ..., 3N$. Therefore, the total energy of the crystal is:

$$U = U_0 + \sum_{\mathbf{k},m} \hbar \omega_{\mathbf{k},m} \left( \frac{1}{\exp \left( \frac{\hbar \omega_{\mathbf{k},m}}{k_B T} \right) - 1} + \frac{1}{2} \right)$$

**Question:** How to do the sum over $\mathbf{k}$??
Sum over vibration modes of a crystal

• The sum over $k$ and the index $m = 1, ..., 3N$ can be thought of as follows:
  One $k$ point for each unit cell
  The index $m$ counts the atoms per unit cell $N$ multiplied by the number of independent ways each atom can move (3 in 3D).

• The entire crystal has $3N N_{\text{cell}}$ degrees of freedom (i.e. number of ways the atoms can move). This must not change when we transform to the independent oscillators.
1D, two boundary conditions

• Demonstration that the sum over \( k \) is equivalent to one \( k \) point for each unit cell

• \( N \) atoms at separation \( a \), \( u_s = u \exp(ik(sa) - i\omega_{k,m} t) \)

• Fixed boundary conditions: \( u_0 = u_N = 0 \)
  – Standing waves only
  – Possible \( k \) values: \( k = \frac{\pi}{Na}, \frac{2\pi}{Na}, \ldots \frac{n\pi}{Na}, \frac{(N-1)\pi}{Na} \)
  – One \( k \) value per mobile atom, one \( k \) value per cell

• Periodic boundary conditions: \( u_s = u_{N+s} \)
  – Traveling waves, need \( kNa = \pm 2n\pi \)
  – Possible \( k \) values: \( k = 0, \pm \frac{2\pi}{Na}, \pm \frac{4\pi}{Na}, \ldots \frac{2n\pi}{Na} \)
  – One \( k \) value per mobile atom, one \( k \) value per cell
Density of states

• All we need is the number of states per unit energy, and we can integrate over energy to find the thermal quantities

• Total energy

\[ U = \sum_{k=1}^{N_{\text{cell}}} \sum_{m=1}^{3N} \frac{\hbar \omega_{k,m}}{\exp(\hbar \omega_{k,m}/k_B T) - 1} \]

• We know that there are \( N_{\text{cell}} \) possible k values

• In a large crystal one can replace the sum over k with an integral

• Since \( \omega \) and k are related by the dispersion relation we can change variables

\[ U = \sum_m \int d\omega \, D_m(\omega) \frac{\hbar \omega}{\exp(\hbar \omega / k_B T) - 1} \]

• \( D_m(\omega)d\omega \) – number of modes (states) in frequency range \( \omega \) to \( \omega + d\omega \)
Relation between $k$ and $\omega$

- Total energy
  \[
  U = \sum_m \int d\omega \, D_m(\omega) \frac{\hbar \omega}{\exp(\hbar \omega/k_B T) - 1}
  \]

- $D_m(\omega)d\omega$ – number of modes (states) in frequency range $\omega$ to $\omega+d\omega$ for branch $m$
  
  Dispersion relation: $\omega_k = 2 \left( \frac{C}{M} \right)^{1/2} | \sin(ka/2) |$

- Modes in interval $(\omega, k, E)$ to $(\omega+\Delta \omega, k+\Delta k, E+\Delta E)$
  \[
  \Delta N = D(\omega) \Delta \omega = N(k) \Delta k = N(E) \Delta E
  \]
  
  
  \[
  D(\omega)d\omega = N(k) \frac{dk}{d\omega} d\omega = \frac{N(k)}{v_g} d\omega
  \]
  
  Group velocity
Density of states in 1D

- $D_m(\omega)d\omega$ – number of modes (states) in frequency range $\omega$ to $\omega+d\omega$

$$D(\omega)d\omega = \frac{N(k)}{v_g} d\omega$$

- $N(k)$ - number of modes per unit range of $k$
- number of modes between $-\pi/a < k < \pi/a = N = L/a$ (the number of atoms)

- $N(k)=N/(2\pi/a)$

$$D(\omega)d\omega = \frac{Na}{2\pi} \frac{1}{v_g} d\omega = \frac{L}{2\pi} \frac{1}{v_g} d\omega$$
Possible wavevectors in 3D

• Assume $N_{\text{cell}} = n^3$ primitive cells, each a cube of side $a$
• volume of the crystal $V = (na)^3 = L^3$
• vibrations: $\vec{u}_s = \vec{u} \exp(i\vec{k} \cdot \vec{r} - i\omega_{k,m} t)$

$$\vec{r} = xi + yj + zk \quad \vec{k} = k_xi + k_yj + k_zk$$

• periodic boundary conditions:

$$\exp[i(k_x x + k_y y + k_z z)] = \exp[i(k_x(x+L) + k_y(y+L) + k_z(z+L))]$$

$k_x$, $k_y$, $k_z = 0, \pm 2\pi/L, \pm 4\pi/L, .. \quad 2m\pi/L$

na = L

• There is one allowed value of $\vec{k}$ in each volume

$(2\pi/L)^3 = 8\pi^3/V$

$V$ - volume of the crystal
Density of states in 3D

- one allowed value of \( \mathbf{k} \) per volume \( 8\pi^3/V \)
- \( D(\omega)d\omega \) – number of modes (states) in frequency range \( \omega \) to \( \omega+d\omega \)

\[
\Delta N = D(\omega) \Delta \omega = N(\mathbf{k}) \Delta \mathbf{k}
\]

In a cubic lattice the 1D dispersion relation holds - \( \omega \) only depends on \( k \) - spherical symmetry

\[
D(\omega)d\omega = N(\mathbf{k}) 4\pi k^2 \frac{dk}{d\omega} d\omega
\]

\[
N(\mathbf{k}) = V/8\pi^3
\]

- \( D(\omega) = k^2V/2\pi^2 \frac{dk}{d\omega} \)
Heat Capacity

• The internal energy is found by summing over all modes

\[ U = \sum_m \int d\omega \, D_m(\omega) \frac{\hbar \omega}{\exp(\hbar \omega/k_BT) - 1} \]

• The heat capacity is found by differentiating U with respect to temperature, \( C = dU/dT \)

\[ C = k_B \sum_m \int d\omega \, D_m(\omega) \frac{x^2 \exp(x)}{[\exp(x) - 1]^2} \quad x = \frac{\hbar \omega}{k_BT} \]

• Need to express \( D(\omega) \) and \( d\omega \) as a function of \( x \) to do the integral
Debye Approximation

- Approximate crystal with an elastic continuum,
- \( \omega = \nu k \) \((\nu = \text{sound velocity})\)
- In 3D cubic crystal \( D(\omega) = k^2 V / 2\pi^2 \frac{dk}{d\omega} \)
- \( D(\omega) = V \omega^2 / 2\pi^2 \nu^3 \)
- In this approximation the maximum \( \omega \) is not known, we need to determine it from the fact that there are \( N_{\text{cell}} \) modes in each branch
  \[
  \int_{\omega=0}^{\omega_D} d\omega \, D(\omega) = N_{\text{cell}}
  \]

- \( \omega_D^3 = 6\pi^2 \nu^3 N_{\text{cell}} / V \)
- \( N_{\text{cell}} / V = 1 / V_{\text{cell}} \)
- maximum wavevector \( k_D = \omega_D / \nu = (6\pi^2 N_{\text{cell}} / V)^{1/3} \)
Debye temperature

- Thermal energy (3 polarizations)

\[ U = 3 \int_0^{\omega_D} d\omega \, D(\omega) \frac{\hbar \omega}{\exp(h\omega/k_B T) - 1} = \frac{3V k_B^4 T^4}{2\pi^2 \sqrt{3} \hbar^3} \int_0^{x_D} dx \frac{x^3}{\exp(x) - 1} \]

\[ x_D = \frac{\hbar \omega_D}{k_B T} = \frac{\theta}{T} \]

- Characteristic Debye temperature \( \theta = \hbar \nu / k_B (6\pi^2 N_{\text{cell}} / V)^{1/3} \)

\[ U = 9 N_{\text{cell}} k_B T \left( \frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{\exp(x) - 1} \]

\[ C_V = 9 N_{\text{cell}} k_B \left( \frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} \]
Ex. Debye temperature $\theta = \frac{\hbar \nu}{k_B} (6\pi^2 N_{\text{cell}} / V)^{1/3}$

What material characteristics does the Debye temperature depend on?
Limits of heat capacity in the Debye appr.

\[ C_V = 9N_{cell}k_B \left( \frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} \]

- For \( T >> \theta \), \( x_D \to 0 \), \( \exp(x) \sim 1 + x \)
  \[ C_V \sim 3N_{cell}k_B \] - equal to classical limit

- For \( T << \theta \), \( x_D \to \infty \),
  \[ C_V = 9N_{cell}k_B \left( \frac{T}{\theta} \right)^3 \int_0^\infty dx \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} = 9N_{cell}k_B \left( \frac{T}{\theta} \right)^3 \frac{4\pi^4}{15} \]
  \[ C_V \sim T^3 \]
Debye Approximation

\[ C_v = 9N_{_{\text{cell}}} k_B \left( \frac{T}{\theta} \right)^3 \int_0^\infty dx \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} \]

\( C_v \) has correct general behavior that must be found in all crystals. For 3 dimensions
Einstein Approximation

- The Debye approximation is valid for acoustic modes.
- For optic modes one can assume a constant frequency-Einstein approximation.

\[ \omega \sim k \text{ at small } k \]

\[ 3 (N - 1) \text{ Optic Modes} \]

\[ 3 \text{ Acoustic modes} \]

Each has \( \omega \sim k \) at small \( k \)
Einstein Approximation

- Assume each oscillator has $\omega = \omega_0$
- $D(\omega) = N_{\text{cell}} \delta(\omega - \omega_0)$

$$U = 3N_{\text{cell}} \frac{\hbar \omega_0}{\exp(\hbar \omega_0 / k_B T) - 1}$$

$$C_V = 3N_{\text{cell}} k_B \left( \frac{\hbar \omega_0}{k_B T} \right)^2 \frac{\exp(\hbar \omega_0 / k_B T)}{(\exp(\hbar \omega_0 / k_B T) - 1)^2}$$

- For $T \to 0$, $C_V \sim \exp(-\hbar \omega / k_B T)$
- For $T >> 0$, $C_V \sim 3N_{\text{cell}} k_B$ - equal to classical limit
General expression for $D(\omega)$

- In 1D \[ D(\omega) = \frac{N(k)}{v_g}, \quad v_g = \text{group velocity} \]

- In 3D \[ \Delta N = D(\omega) \Delta \omega = N(k) \Delta k \] \[ D(\omega) d\omega = N(\vec{k}) \int d^3k \]

  integral over the volume of the shell in $k$ space bounded by the surfaces with $\omega$ and $\omega + d\omega$

  \[ \int d^3k = \int dS_\omega dk_\perp = \int dS_\omega \frac{d\omega}{v_g} \quad v_g = |\Delta_k\omega| \]

  \[ D(\omega) = \frac{V}{(2\pi)^3} \int dS_\omega \frac{d\omega}{v_g} \quad \text{integral over } \omega=\text{const surface} \]

- $v_g=0$ - Van Hove singularities
Plot the density of states as a function of $\omega$ for a Debye solid, $D(\omega) = V \frac{\omega^2}{2\pi^2 v^3}$.

How does this plot change for an actual crystal structure?
Energy & Force due to Displacements

- The energy of the crystal changes if the atoms are displaced.
- The change in energy can be written as a function of the positions of all the atoms:

$$E(R_1, R_2, R_3, \ldots) = E(R_1^0 + \Delta R_1, R_2^0 + \Delta R_2, \ldots)$$

- To lowest order in the displacements the energy is quadratic - Hooke’s law - harmonic limit

$$E = E_0 + (1/2) \sum_{ij} \Delta R_i \cdot D_{ij} \cdot \Delta R_j + \ldots$$

(There are no linear terms if we expand about the equilibrium positions)
Consequences of anharmonicity

• If we expand the energy beyond the harmonic order:
  \[ E = E_0 + \frac{1}{2} \sum_{ij} \Delta R_i \cdot D_{ij} \cdot \Delta R_j + \frac{1}{6} \sum_{ijk} D_{ijk} \cdot \Delta R_i \cdot \Delta R_j \cdot \Delta R_k + \ldots \]

• The problem is fundamentally changed:
  No longer exactly solvable

• Consequences:
  There is thermal expansion and other changes with temperature
  The heat capacity is not constant at high T
  Phonons decay in time
  Two phonons can interact to create a third
  Phonons can establish thermal equilibrium and conduct heat like a “gas” of particles

Difficult and Messy
Inelastic Scattering and Fourier Analysis

Inelastic diffraction occurs for:

\[ k_{\text{in}} - k_{\text{out}} = G \pm k_{\text{phonon}} \]
\[ \omega_{\text{in}} - \omega_{\text{out}} = \pm \omega_{\text{phonon}} \text{ or } E_{\text{n}} - E_{\text{out}} = \pm \hbar \omega_{\text{phonon}} \]
Scattering of Phonons - I

- The same idea applies to phonons. One phonon can scatter to create two.

- Scattering can occur for

\[
\begin{align*}
\mathbf{k}_{\text{in phonon}} &= \mathbf{k}_{\text{out phonon 1}} + \mathbf{k}_{\text{out phonon 2}} \pm \mathbf{G} \\
\omega_{\text{in phonon}} &= \omega_{\text{out phonon 1}} + \omega_{\text{out phonon 2}}
\end{align*}
\]
Scattering of Phonons - II

- Two phonons can interact to create one.
- This is called “up conversion (umklapp)”, which can be done with intense phonon beams and occurs for

\[ \mathbf{k}_{\text{out phonon}} = \mathbf{k}_{\text{in phonon 1}} + \mathbf{k}_{\text{in phonon 2}} \pm \mathbf{G} \]

\[ \omega_{\text{out phonon}} = \omega_{\text{in phonon 1}} + \omega_{\text{in phonon 2}} \]
Thermal expansion

• The energy of a pair of atoms depends on the displacement $x$ from their equilibrium separations, $U(x) = cx^2 - gx^3 - fx^4$

• The average displacement $\langle x \rangle$ is determined by the condition that the average force vanishes.

• In the harmonic approximation $F = cx$. Therefore $\langle x \rangle = 0$, $\langle F \rangle = 0$, and there is no thermal expansion.

• Anharmonicity adds additional terms:
  
  $F = cx - \frac{1}{2} g x^2 - ...$, $\langle F \rangle = 0 \Rightarrow \langle x \rangle = \frac{1}{2} \frac{(g/c)}{c} \langle x^2 \rangle$

• In general, this means thermal expansion.
Thermal expansion

Energy of Crystal vs. Distance Between Atoms

Thermal Expansion - Average distance increases as vibration amplitude increases

Absolute Minimum
Characterizing thermal dilation

• Average displacement of atoms, \(<x>\)

\[
<x> = \frac{\int_{-\infty}^{\infty} dx \ x \ exp\left[-U(x)/k_B T\right]}{\int_{-\infty}^{\infty} dx \ exp\left[-U(x)/k_B T\right]} \approx \frac{3g}{4c^2} k_B T
\]

• \(U(x)\) – potential energy of a pair of atoms.
• Thermal expansion of a crystal or cell: \(\delta = \frac{dV}{V}\)
• For cubic crystals \(\frac{dV}{V} = 3 \ \frac{dx}{x}\)

From the theory of elastic media:

• Potential energy of a unit cell due to dilation:

\(U_{cell}(T)=V_{cell} \ B \ \delta^2/2\), where \(B\) is the bulk modulus
Transport of heat in an ordinary gas

- Molecules move in all directions and scatter so that they come to local thermal equilibrium in each region.
- How can random motion cause heat flow in one direction?
- On average, in hotter regions molecules have more kinetic energy. A molecule that moves from a hotter region to a colder one brings energy above the local average. The opposite for a molecule moving from a colder to a hotter region. Either way, there is transport of energy from hotter to colder regions.

![Diagram of heat flow](image-url)
Phonons also act like a gas

- A phonon is a particle - a quantum of vibration
- It carries energy just like a molecule.
- Phonons can come to equilibrium by scattering just like molecules (phonon scattering is due to defects and to anharmonicity).
- What is different?
  Phonons can be **created and destroyed**. But we will see that we can treat them exactly like gas.
Thermal conductivity of phonons

• Definition: \( j = \text{heat flow (energy per unit area per unit time)} = -K \frac{dT}{dx} \); \( K \) – thermal conductivity

• If a phonon moves from a region with local temperature \( T \) to one with local temperature \( T - \Delta T \), it supplies excess energy \( c \Delta T \), where \( c = \text{heat capacity per phonon} \). (Note \( \Delta T \) can be positive or negative).

• Temperature difference between the ends of a free path: \( \Delta T = (dT/dx) v_x \tau \), where \( \tau = \text{mean time between collisions} \).

• Then \( j = -n v_x c v_x \tau dT/dx = -n c v_x^2 \tau dT/dx \)
Phonon Heat Transport - continued

- This can be simplified in an isotropic case, since averaging over directions gives \( \langle v_x^2 \rangle_{\text{average}} = \frac{1}{3} v^2 \)
- This leads to \( j = - \frac{1}{3} n c v^2 \tau \frac{dT}{dx} \)
- Finally we can define the mean free path:
  \[ L = v \tau \text{ and} \]
  \[ C = nc = \text{total heat capacity} \]
- Then \( j = - \frac{1}{3} C v L \frac{dT}{dx} \)
  and
  \[ K = \frac{1}{3} C v L = \text{thermal conductivity} \]
  (just like an ordinary gas!)
Phonon Heat Transport - continued

- What determines mean free path $L = v \tau$?
- At **low temperature**, the thermal phonons are sound waves that have long mean free paths -
  
  $$L \sim \text{sample size}$$

- At **high temperature**, phonons scatter from other phonons.
- ONLY **Umklapp** scattering limits the energy flow. The density of other phonons is $\sim T$, so
  
  $$L \sim 1/T$$

- At **intermediate temperature**, phonon scatter from defects and other phonons.
Phonon Heat Transport - continued

- Low T - $K$ increases with $T$ because density of phonons increases with roughly constant $v$ and $L$
- High T - $K$ decreases with $T$ as Umklapp scattering increases
Phonon Heat Transport - continued

• Behavior in an excellent quality crystal:

- Low T: $K$ increases as density of phonons increases ($v$ and $L$ are ~ constant)
- Approaches high T limit $1/T$
- Maximum controlled by defects
- $K$ decreases because Umklapp scattering increases rapidly

[Diagram showing thermal conductivity $K$ as a function of temperature $T$.]
**Umklapp Scattering**

- Scattering that changes total crystal momentum by a reciprocal lattice vector.

- $\mathbf{k}_{\text{in phonon}} = \mathbf{k}_{\text{out phonon 1}} + \mathbf{k}_{\text{out phonon 2}} \pm \mathbf{G}$

- $\omega_{\text{in phonon}} = \omega_{\text{out phonon 1}} + \omega_{\text{out phonon 2}}$

> Unless $\mathbf{G} \neq 0$, the scattering does **not** change the total phonon momentum or energy. Therefore only Umklapp scattering limits the heat flow. It also leads to thermal equilibrium.
• Vibrations of atoms
  **Harmonic approximation**
  Exact solution for waves in a crystal
  Labeled by $k$ and index $m = 1, \ldots, 3N$

• Quantization of vibrations
  **Phonons act like particles**
  Can be created or destroyed by inelastic scattering experiments

• Thermal properties
  Fundamental law of probabilities
  **Planck distribution** for phonons
  Heat Capacity $C$
  Low $T$: $C \sim T^3$  --  High $T$: $C \sim \text{constant}$
  Thermal conductivity $K$
  Maximum as function of $T$