
- Specific Heat of Crystal Lattice
  - Boltzmann model
  - Einstein model
  - Debye Model
- The concept of Density of States
So far we considered crystals at $T = 0$. The ideal periodic structure is the ground state of this complex quantum system. It is a non-trivial problem to find a ground state of a system of strongly interacting particles, but we’ll ignore this for now. Anyway, if $T$ increases, we expect to observe excitations.

Since exact calculations are impossible (zillions of interacting particles!), statistical methods and approximations become of primary importance. A very powerful method – to identify a sub-system whose excitations can be treated as weakly interacting quasiparticles or collective excitations. Then the energy of this sub-system is its ground-state energy + the energy of its excitations.

Two types of elementary excitations:

1. Excitations which are transformed into the “ideal gas” of particles if the interactions are turned off. They are called quasiparticles (“dressed” particles). Example – electronic excitations near the Fermi energy.

2. Excitations that exist only because of interactions, and vanish if the interactions are turned off. They are called collective excitations. Example – phonons which involve collective motion of many ions.

The quasiparticle excitations are related to fermions (e.g. electrons and holes), collective excitations - to bosons (e.g. phonons).
The first sub-system to be considered is ions in a crystal lattice. At low energies that we consider in the solid state physics the internal degrees of freedom in ions are not excited, so we’ll treat them as point-like masses without internal degrees of freedom. The ground state ($T = 0$) - only quantum fluctuations. Non-zero $T$ generates excitations which disrupt the order.

Examples of related phenomena: lattice specific heat, lattice thermal conductivity, electron scattering by the lattice.

**Approaches:**

- Continuum $\Leftrightarrow$ Discrete ($\text{period} \leftrightarrow \lambda$)
- Classical $\Leftrightarrow$ Quantum ($k_B T \leftrightarrow \hbar \omega$)

**Quantum Correspondence:**

Classical harmonic system with a single normal mode $\omega$  $\leftrightarrow$ Quantum system with eigenstates $E_n = \hbar \omega \left( n + \frac{1}{2} \right)$
Specific Heat of Crystal Lattices – our first goal

\[ C \equiv \frac{\partial Q}{\partial T} \]

- We don’t distinguish between \( C_V \) and \( C_P \) - solids, in contrast to gases, do not expand/contract much with \( T \).
- The electron contribution to \( C \) is typically small at \( T \gtrsim 10K \) – we’ll discuss this later in the course.

\( C \) goes to 0 as \( T \to 0 \)

\[ C \text{ approaches } 3R \approx 25 \text{ J/K} \cdot \text{mol} \text{ at high } T \]
The high-$T$ limit $C_{ph} = 3Nk_B T = 3R$, which is known as the Dulong-Petit Law (1819).

Boltzmann (1897) explained this fact by considering $N$ independent atoms trapped in potential wells formed by interactions with other atoms. The atoms/ions are in thermal equilibrium with thermostat. $N$ independent atoms have $6N$ degrees of freedom ($3N$ 1D oscillators, each has two degrees of freedom). According to the equipartition theorem, each quadratic degree of freedom will possess an average energy $\frac{1}{2}k_B T$.

This is a classical result ($k_B T \gg \hbar \omega$). The low-$T$ behavior remained a puzzle.
The low-$T$ value of $C$ is quite different from $3R$, it approaches 0 at $T \to 0$. **Einstein** (1907) replaced classical oscillators with quantum ones.

In general, interactions between atoms (ions) in crystals are not harmonic. However, at low $T$ (think small amplitude), harmonic approximation works well.

$N$ atoms $\Rightarrow$ $3N$ normal modes.

The energy of each quantum oscillator $E_n = \hbar \omega (n + 1/2), \quad n = 0, 1, 2 \ldots$
Energy of Einstein solid:

$$E = \sum_{i=1}^{3N} \hbar \omega \left( n_i + \frac{1}{2} \right)$$

where $n_i$ - the number of energy quanta in the $i^{th}$ oscillator.

Planck distribution:

$$\langle n(\omega) \rangle = \frac{1}{\frac{\hbar \omega}{e^{\frac{\hbar \omega}{k_B T}} - 1}}$$

Temperature dependence:

$$E(T) = 3N\hbar \omega \left( \frac{1}{\frac{\hbar \omega}{e^{\frac{\hbar \omega}{k_B T}} - 1} + \frac{1}{2}} \right)$$
Heat Capacity in the Einstein Model

\[ E(T) = 3N\hbar \omega \left( \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} + \frac{1}{2} \right) \]

\[ C = \frac{\partial E(T)}{\partial T} = 3Nk_B (\beta \hbar \omega)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \]

\[ \beta \equiv \frac{1}{k_B T} \]

**Limits:**

- **high** \( T \) \( (k_B T \gg \hbar \omega) \): \( C(T) = 3Nk_B = 3R \)
  - Equipartition, the Dulong-Petit law

- **low** \( T \) \( (k_B T \ll \hbar \omega) \)
  \[ C(T) = 3Nk_B (\beta \hbar \omega)^2 e^{-\beta \hbar \omega} \propto e^{\frac{\hbar \omega}{k_B T}} \]

**Experiment vs. Einstein’s theory.**

\( T_E = 1320K \) – the only fitting parameter.

A. Einstein, *Annalen der Physik* 22, 180 (1907)
The Einstein model predicts much too low a heat capacity at low $T$!

(Experiment: $C \propto T^3$ rather than $C \propto e^{-\frac{h\omega}{k_B T}}$)

Einstein’s model ignores the fact that the ions are coupled together – *coupled oscillators*.

For coupled oscillators, the calculation of the partition function may look rather difficult. But a system of *$N$ coupled* 3D oscillators is equivalent to a system of *$3N$ independent* 1D oscillators. The price to be paid is that the independent oscillators are not of the same frequency; the normal modes of vibration of a solid have a wide range of frequencies. These modes are not related to the motion of single atoms, but to the collective motion of all atoms in the crystal – *vibrational modes* or *sound waves*.

Now we deal with a *broad spectrum of $\omega$* and not a single characteristic frequency as in the Einstein’s model:

$$E(T) = \sum_i \langle n_i \rangle \hbar \omega_i$$
Debye’s Theory of the Heat Capacity of Solids

Debye’s model (1912) treats the solid as a continuum, i.e., the atomic structure is ignored. A continuum has vibrational modes of arbitrary low frequencies, and at sufficiently low $T$ only these low-$\omega$ modes are excited. The low-$\omega$ modes are simply standing sound waves, they should be quantized the same way as Planck had quantized light waves in 1900.

The continuum model works well at low $T$ (the characteristic energy of excitations is $\sim T$), where the wavelength is much greater than the inter-atomic distance $a$:

$$\omega = ck$$

all sound waves propagate with the same speed $c$ (not the speed of light) (a linear dispersion law)

$$\omega = ck \quad \times \hbar$$

$$E = c \frac{h}{\lambda} \sim k_B T$$

(note “ultra-relativistic” $E = cp$)

$$\lambda = \frac{hc}{k_B T} = [T = 1K] \sim \frac{6.6 \cdot 10^{-34} \times 2 \cdot 10^3}{1.4 \cdot 10^{-23} \times 1} \sim 10^{-7} m = 0.1 \mu m >> a$$

- the discreteness can be ignored
Continuum Approximation

Isotropic medium:  \( u_n = u_{n0} e^{i(k \cdot \vec{r} - \omega t)} \)

Dispersio

Dispersion relation is linear  \( \omega = ck \)

One longitudinal mode:  \( \vec{u}_n \parallel \vec{k} \)

Two transverse modes:  \( \vec{u}_n \perp \vec{k} \)

We neglect the difference in the speed of propagation of longitudinal and transverse modes. In reality the phase velocity of traverse vibrations is always smaller than that for longitudinal ones - smaller restoring force (in many metals the longitudinal waves travel approx. twice as fast as the transverse ones).

In anisotropic lattices, elastic waves are combinations of longitudinal and transverse oscillations (except for a few directions of \( k \), such as [100] in simple cubic lattice).
The average energy in a mode:

$$\langle \varepsilon_i \rangle = \langle n_i \rangle \hbar \omega_i = \frac{\hbar \omega_i}{\frac{\hbar \omega_i}{e^{\frac{k_B T}{\hbar}} - 1}}$$

$$\langle \varepsilon \rangle = k_B T$$ in the classical limit $k_B T \gg \hbar \omega$.

$$\langle E \rangle = \sum_i \frac{\hbar \omega_i}{\frac{\hbar \omega_i}{e^{\frac{k_B T}{\hbar}} - 1}}$$

The modes with the same $\omega_i$ can have different wave vectors $k$ — waves with the same $\omega$ can propagate in different directions (degeneracy).

In both cases $\omega = v \sqrt{5 \frac{\pi}{L}}$ so these two modes are degenerate.
Phonon Density of States in $\mathbf{k}$-space

Since in macroscopic objects there is an almost continuous spectrum of sound waves, it’s convenient to replace summation by integration.

\[
\sum_i \rightarrow \int d\omega
\]

The sound wave: \( A(r, t) = A e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \)

Dispersion relation: \( \omega(k) = ck \)

Assumption: \( c \) is independent of \( k \) and polarization.

To avoid complications at the boundaries, let’s introduce periodic (Born – von Karman) boundary conditions:

\[
A(x, y, z) = A(x + L_x, y, z) = A(x, y + L_y, z) = A(x, y, z + L_z).
\]

\[
e^{ik_x L_x} = e^{ik_y L_y} = e^{ik_z L_z} = 1
\]
Density of States in $k$-space

$$e^{ik_x L_x} = e^{ik_y L_y} = e^{ik_z L_z} = 1$$

$$k_x = \frac{2\pi n_x}{L_x}, \quad k_y = \frac{2\pi n_y}{L_y}, \quad k_z = \frac{2\pi n_z}{L_z} \quad n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots$$

to simplify, assume $L_x = L_y = L_z = L$

The states in the $k$-space represent a grid. Each $k$-state occupies volume

$$\frac{2\pi}{L} \frac{2\pi}{L} \frac{2\pi}{L} = \frac{(2\pi)^3}{V}$$

Density of states (DoS): the number of different $k$-states within the interval $k \leftrightarrow k + \delta k$ per unit volume:

$$g(k) \equiv \frac{dG(k)}{dk}$$

$$G(k) = 3 \frac{4}{3} \frac{\pi k^3}{(2\pi)^3} = \frac{k^3}{2\pi^2}$$

$$g_{3D}(k) = \frac{3}{2\pi^2} k^2$$

three polarizations (two transverse and one longitudinal)

DoS in 1D and 2D?

$$g_{1D}(k) \propto \text{const}$$

$$g_{2D}(k) \propto \omega$$
The number of states in the frequency interval $d\omega$ is proportional to the volume in $k$-space between the surfaces $\omega(k) = \text{const}$ and $\omega(k) + d\omega(k) = \text{const}$. 

\[ G(\omega) = \int_{0}^{k(\omega)} g(k) \, dk \] 

\[ g(\omega) d\omega = \int_{k(\omega)}^{k(\omega+d\omega)} g(k) \, dk = \frac{3}{2\pi^2} \int_{k(\omega)}^{k(\omega+d\omega)} k^2 \, dk = \frac{k^3}{2\pi^2} \bigg| k = (\omega + d\omega)/c \] 

\[ k = \omega/c \] 

\[ = \frac{3}{2\pi^2} \frac{\omega^2 d\omega}{c^3} \]

\[ g_{3D}(\omega) d\omega = g_{3D}(k) dk \] 

\[ g_{3D}(\omega) = g_{3D}(k) \frac{dk}{d\omega} \] 

\[ g_{3D}(\omega) = \frac{3}{2\pi^2} \frac{\omega^2}{c^3} \]

DoS in Einstein model? DoS in 1D and 2D?

\[ g_{1D}(\varepsilon_{ph}) \propto \text{const} \]

\[ g_{2D}(\varepsilon_{ph}) \propto \omega \]
Effective Dimensionality (with respect to $\lambda = 2\pi/k$)

Dimensionality of electrons, phonons, etc. is the effective dimensionality of their $k$-space.

**Example:** phonons in a thin film

Low $T \left( < \frac{\hbar}{k_B} \frac{c}{t} \right)$: 2D phonons

High $T \left( \gg \frac{\hbar}{k_B} \frac{c}{t} \right)$: 3D “anisotropic” phonons

Thus, the effective dimensionality of phonons can change with $T$. 
Consider a metal film with \( c = 3\text{km/s} \). How thin should be this film to be able to consider the phonons in the film as two-dimensional at \( T = 1\text{K} \)?

\[
k_B T \sim \hbar c k \quad k \sim \frac{k_B T}{\hbar c}
\]

Phonons can be considered as 2D if

\[
k \leq \frac{\pi}{t} \quad \text{or} \quad t \leq \frac{\pi}{k}
\]

\[
t \leq \frac{\pi}{k} \sim \frac{\pi \hbar c}{k_B T} \approx 70\text{nm}
\]
For an \textit{arbitrary} dispersion relation $\omega(k)$ (not necessarily linear):

\begin{align*}
    g_{3D}(k) &= \frac{3}{2\pi^2} k^2 \\
    g_{3D}(\omega) d\omega &= g_{3D}(k) dk \\
    \frac{d\omega(k)}{dk} &\equiv v_g(k) \quad \text{- the group velocity} \\
    \frac{\omega(k)}{k} &\equiv v_{phase} = c(k) \quad \text{- the phase velocity}
\end{align*}

\begin{align*}
    g_{3D}(\omega) &= \frac{3k^2}{2\pi^2} \frac{dk}{d\omega} \\
    g_{3D}(\omega) &= \frac{3\omega^2}{2\pi^2 [c(\omega)]^2} \frac{1}{v_g(\omega)}
\end{align*}

\textbf{DoS} $g(\omega)$ \textbf{depends on (a) dimensionality and (b) the dispersion relation} $\omega = c(k)k$. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{dispersion_relation.png}
\caption{Dispersion relation and DoS diagram.}
\end{figure}
continuous
discrete

the boundary of the first Brillouin zone

standing wave

\( v_g = 0 \)
Specific Heat in the Debye’s Theory

\[ E(T) = \sum_i \langle n_i \rangle \hbar \omega_i \]

\[ \langle n_i \rangle = \frac{1}{e^{\beta \hbar \omega_i} - 1} \]

\[ E(T) = \int_0^\infty \langle n(\omega) \rangle \hbar \omega \, g(\omega) \, d\omega \]

\[ = \int_0^\infty \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \frac{3}{2\pi^2} \frac{\omega^2}{c^3} \, d\omega = \frac{3\hbar}{2\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta \hbar \omega} - 1} \, d\omega = \frac{3\hbar}{2\pi^2 c^3} \frac{1}{(\beta \hbar)^4} \int_0^\infty \frac{x^3}{e^x - 1} \, dx \]

\[ = \frac{3\hbar}{2\pi^2 c^3} \frac{1}{(\beta \hbar)^4} \frac{\pi^4}{15} = \frac{1}{10} \left( \frac{\pi}{\hbar c} \right)^3 (k_B T)^4 \]

\[ C \equiv \frac{\partial \langle E \rangle}{\partial T} = \frac{2\pi^2 k_B^4}{5 (\hbar c)^3} T^3 \]

- correct result at low \( T \), but should be modified at high \( T \)
Figure 9  Low temperature heat capacity of solid argon, plotted against $T^3$. In this temperature region the experimental results are in excellent agreement with the Debye $T^3$ law with $\theta = 92.0$ K. (Courtesy of L. Finegold and N. E. Phillips.)

$T_D = 92K$

Low-Temperature Heat Capacities of Solid Argon and Krypton*

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High-$T$ Limit: in Search for High-$\omega$ Cut-off

Because of a finite distance between atoms in a crystal, it does not make sense to consider arbitrary large $k$ (i.e. arbitrary small $\lambda$) – should be a **high-$k$ ($\omega$) cut-off**.

\[
\omega_{cutoff} \sim c \frac{\pi}{a}
\]

$c \sim 3 \text{ km/s}, a \sim 0.2 \text{ nm}, \omega_{cutoff} \sim 5 \cdot 10^{13} \text{ rad}^{-1}
\]

Compare with the max. sound $\omega \sim 2\pi \cdot 10^4 \text{ rad}^{-1}$
Debye introduced an *ad hoc* cut-off: at high $T$ the average energy $\langle E \rangle$ should be $3n k_B T$ (the total number of modes times the energy per mode).

$$\langle E \rangle = \int_0^{\omega_D} \langle n(\omega) \rangle \hbar \omega g(\omega) d\omega$$

Total number of modes (per unit volume) $n = N/L^3$ is the density of atoms

$$3n = \int_0^{\omega_D} g(\omega) d\omega$$

- condition for the cut-off

High-$T$ limit:

$$\frac{1}{e^{\beta \hbar \omega} - 1} \approx (\beta \hbar \omega)^{-1}$$

All $3N$ modes are excited, the energy of each mode ($\propto$ its amplitude squared) $\approx k_B T$.

$$\omega_D = (6\pi^2 n)^{1/3} c$$

- the *Debye frequency*, $\omega_D$

The cut-off value of $k = (6\pi^2 n)^{1/3}$ is on the order of $\frac{\pi}{a} \sim n^{1/3}$, as it should be.
Specific Heat in the Debye Theory

Low $T \ (T \ll T_D)$ \hspace{1cm} \[ C = \frac{2 \pi^2 k_B^4}{5 \ (hc)^3} T^3 = \frac{12 \pi^4}{5} R \left( \frac{T}{T_D} \right)^3 \]

High $T \ (T \geq T_D)$ \hspace{1cm} \[ C = 3R \]

$T_D$ is usually determined by fitting the exp. data on specific heat.
Debye Temperature

\[ T_D \equiv \frac{\hbar \omega_D}{k_B} = \frac{\hbar}{k_B} (6\pi^2 n)^{1/3} c \]

The greater the sound speed and the density of ions, the higher the Debye temperature. If the temperature is normalized by \( T_D \), the data for different materials collapse onto a universal dependence.

\( T_D \) varies from \( \sim 105 K \) for lead (soft, low \( c \)) to \( \sim 2200 K \) for diamond (hard, high \( c \)) .

\( T_D \) plays similar role for phonons as \( T_F \) plays for electrons: it separates the high-\( T \) (classical) and the low-\( T \) (quantum) regime. In the case of electrons in metals, \( T_F \sim 10^4 K \) so only quantum regime is encountered. For phonons \( T_D \sim 10^2 − 10^3 K \) , and both classical and quantum behavior can be observed.
Limitations of the Debye Theory

- The dependence $g_{3D}(\omega) \propto \omega^2$ was obtained by ignoring the discreteness of matter. In reality, $g(\omega) \propto \omega^2$ holds only for low $\omega$ ($\lambda \gg a$). At $\omega \sim \omega_D$ we will need to modify the dispersion relation $\omega(k)$ and the corresponding density of states.

- The speed of sound is assumed to be the same for all polarizations of acoustic waves, which is not true.

The real phonon spectra are very complicated, and $T_D$ is treated as an experimental fitting parameter.

Our goal will be to (qualitatively) understand the spectra.
Summary

Classical ⇔ Quantum \( (k_B T \leftrightarrow \hbar \omega) \)

Continuum ⇔ Discrete \( (period \leftrightarrow \lambda) \)

Several models that describe the energy stored in the lattice vibrations:

- **Boltzmann**: classical approach (no energy quantization), works well at \( k_B T \gg \hbar \omega_D \);

- **Einstein**: quantum \( (k_B T \gtrsim \hbar \omega_D) \), independent oscillators, oversimplified DoS (just one \( \omega_E \)) and, as a result, underestimation of \( E \) and \( C \) at low \( T \);

- **Debye**: quantum, coupled oscillators = broad range of \( \omega \), DoS is more realistic but still not quite right because discreteness is not treated consistently.

**Density of States**: important concept which will be used extensively in the course.

Today: Simon Ch. 2. Next time: Simon Ch. 9.