Chapter 5

Phonons

5.1 Introduction

- so far: we considered mainly a static crystal with the atom $s$ at fixed position $\vec{x}_s^0$

- now: consider elastic vibrations of a crystal, with atom $s$ at position $\vec{x}_s(t) = \vec{x}_s^0 + \vec{u}_s(t)$, i.e. we consider (small) displacements $\vec{u}_s(t)$ that depend on time and which are correlated to displacements of other atoms nearby.

Note:
Deformation of solids can be treated by the classical theory of linear elasticity$^2$. \(\Rightarrow\) gives both the energies and dynamics associated with small deformations, provided the wavelength of the deformations is large in comparison with the lattice constants.

However, this (continuum) theory fails when the wavelength of deformations becomes comparable to$^3$ interatomic distances in the crystal lattice.

- results:

  - collective excitations/vibrations of the atoms (at frequency $\omega$) \(\Rightarrow\) formation of waves (with wave vector $\vec{K}$) propagating through the crystal

  → important questions:

    * what are the vibrating modes in a crystal lattice ?
    * what is the relation $\omega(\vec{K})$ ?
    * how do the lattice vibrations interact with mechanical, electromagnetic or other forces ?

$^1$in contrast to uncorrelated vibrations, e.g. due to thermal fluctuations, which was considered for the derivation of the Debye-Waller factor that enters into the expression for the intensity of the Bragg peak for x-ray diffraction

$^2$see e.g. Kittel Introduction to solid state physics (1966) at the end of chapter 3

$^3$or smaller than
lattice vibrations have **particle-like character**
quantum mechanical treatment (particle-wave-dualism):
propagating waves ↔ **phonons** with energy \( h\omega \)  
(*analogy to photons*)

- **importance of phonons:**
  * determine many thermodynamic properties of a crystal  
    (e.g. specific heat)
  * contribution to thermal conductivity
  * interaction with electrons
    → large contribution to resistivity in metals
    → formation of ('Cooper pairs') in ('conventional') superconductors
  * absorption/emission of light in semiconductors
  * ...

- **How many modes of oscillations** can exist in a crystal with \( N \) atoms?

  - 1 atom: 3 degrees of freedom (translation in \( x, y, z \) direction\(^4\))
  - 2 uncoupled atoms: \( 2 \times 3 \) degrees of freedom
  - 2 coupled atoms: also 6 degrees of freedom:
    3 \( \times \) translation
    2 \( \times \) rotation (perpendicular to the line connecting the atoms)
    1 \( \times \) oscillation
  - \( N \) uncoupled atoms: \( 3N \) degrees of freedom (translation)
  - \( N \) coupled atoms: also have to have \( 3N \) degrees of freedom:
    3 \( \times \) translation (crystal as a whole)
    3 \( \times \) rotation (crystal as a whole)
    \( \Rightarrow \) \( 3N - 6 \times \) oscillation

  One finds: the \( 3N - 6 \) degrees of freedom for oscillations can be classified into relatively simple modes of oscillations characterized by their dependence \( \omega(\vec{K}) \) ('dispersion relation')

\(^4\)neglecting rotational motion of the single atoms
Most simple situation is obtained in the [100], [110] and [111] propagation directions of cubic crystals (correspond to directions along the cube edge, the face diagonal and the body diagonal, respectively).

If a wave is propagating along one of these directions entire planes of atoms move in phase with displacements either parallel ('longitudinal) or perpendicular ('transverse') to the direction of the wavevector $\vec{K}$.

$\Rightarrow$ allows simple description of the displacement of a whole plane $s$ from its equilibrium position.

$\Rightarrow$ 1-dimensional problem

Each wavevector has three 'polarization' modes – one longitudinal (Fig.5.1) and two transverse (Fig.5.2).

Figure 5.1: (Dashed lines) Planes of atoms when in equilibrium. (Solid lines) Planes of atoms when displaced as for a longitudinal wave. The coordinate $u$ measures the displacement of the planes [from Kittel, *Introduction to solid state physics* (1996); Fig.4.2].

Figure 5.2: Planes of atoms as displaced during passage of a transverse wave [from Kittel, *Introduction to solid state physics* (1999); Fig.4.3].
5.2 1-dimensional chain of identical atoms

Chain consists of \( N \) atoms with masses \( M \).

- allow only motion of atoms along \( x \)-direction
  - one degree of freedom corresponds to translation of the whole chain along \( x \)
  \( \Rightarrow \) \( N - 1 \) degrees of freedom for oscillations
- arrangement of atoms:

![Diagram of a 1-dimensional chain with displacement](image)

Figure 5.3: Displacement of atoms in 1-dimensional chain

Atoms located at positions \( x_s = sa + u_s(t) \) with lattice constant \( a \)

- choose for simplicity **periodic boundary conditions:**
  Atom 1 has always same position and momentum as atom \( N + 1 \)
  \( (in \ open \ chain: \ e.g. \ atom \ 1 \ and \ atom \ N \ is \ fixed \ in \ space) \)

Force acting on atom \( s \) due to atom \( s + 1 \):

\[
F_s = C(u_{s+1} - u_s), \quad \text{with force constant } C
\]

(5.1)

\( F_s \) is linear in the displacements \( \rightarrow \) Hooke’s law – is valid if deflection \( u_s \) is not too large

For simplicity we consider only interactions with nearest neighbors \( s + 1 \) and \( s - 1 \);
then the total force acting on atom \( s \) is

\[
F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s)
\]

(5.2)

\( \Rightarrow \) equations of motion of atoms \( (s = 1 \ldots N) \) with mass \( M \):

\[
M \frac{d^2 u_s}{dt^2} = M \ddot{u}_s = C(u_{s+1} + u_{s-1} - 2u_s)
\]

(5.3)

**Ansatz** for time dependence of displacements: \( u_s = u_s^{(0)} e^{-i\omega t} \)

\( \Rightarrow \) \( \ddot{u}_s = -\omega^2 u_s \) in (5.3)

\[
\Rightarrow \quad -M\omega^2 u_s^{(0)} = C(u_{s+1}^{(0)} + u_{s-1}^{(0)} - 2u_s^{(0)})
\]

(5.4)

which is a difference equation in the displacements \( u_s \),

with **travelling wave solutions**

\[
u_s^{(0)} = u e^{iKsa} \]

(5.5)

\( (= \text{longitudinal wave along } x \text{ with wavevector } K) \)

with (5.5) in (5.4) \( \Rightarrow \)

\[
-M\omega^2 u e^{iksa} = Cu(e^{iK(s+1)a} + e^{iK(s-1)a} - 2e^{iKsa})
\]

(5.6)

(divide by \( u \cdot e^{iKsa} \))
\[ M \omega^2 = -C(e^{iKa} + e^{-iKa} - 2) = 2C(1 - \cos Ka) \] (5.7)

This finally yields the dispersion relation \( \omega(K) \)

\[ \omega^2 = \frac{2C}{M} (1 - \cos Ka); \quad \omega = \sqrt{\frac{4C}{M} \sin \left( \frac{Ka}{2} \right)} \] (5.8)

for the travelling wave \( u_s = u e^{i(sKa-\omega t)} \).

- The regime of physically significant values of \( K \) is limited due to \( e^{iKa} \equiv e^{i(Ka+2\pi n)} \), (with \( n = 0, \pm 1, \pm 2, \ldots \))

\[ \rightarrow \text{independent } K \text{ vectors are only specified within the interval} \]

\[ -\pi \leq Ka \leq \pi \quad \Leftrightarrow \quad -\frac{\pi}{a} \leq K \leq \frac{\pi}{a} \quad 1. \text{ Brillouin zone} \]

- connection between \( K \) values within and outside the 1. Brillouin zone:

A vector \( K \) outside the 1. Brillouin zone can be transformed into a vector \( K' \) inside the 1. Brillouin zone by subtracting or adding a multiple of \( 2\pi/a \), i.e. via the transformation \( K' = K + G \) where \( G \) is a reciprocal lattice vector.

The displacement ration of neighboring atoms is

\[ \frac{u_{s+1}}{u_s} = \frac{u e^{i(s+1)Ka}}{u e^{i(s)Ka}} = e^{iKa} \] (5.9)

hence

\[ \frac{u_{s+1}}{u_s} = e^{iKa} = e^{i2\pi n} \cdot e^{i(Ka-2\pi n)} = e^{iK'a} \] (5.10)

i.e. any displacement can always be described by a wavevector within the 1. Brillouin zone.
In other words:
The range of \(-\pi \leq Ka \leq \pi\) covers all independent values of the exponential
\(e^{iKa} = u_{s+1}/u_s\). I.e., saying that two adjacent atoms are out of phase by 0.3\(\pi\) or
2.3\(\pi\) has the same physical meaning, as shown in the figure below.

![Figure 5.5](image)

Figure 5.5: The wave represented by the solid curve conveys no information not given
by the dashed curve. Only wavelengths longer than 2\(a\) are needed to represent the
motion [from Kittel, *Introduction to solid state physics* (1996); Fig.4.5].

- limit of long wavelength:
  if \(K \ll a\) \(\Leftrightarrow\) wavelength \(\lambda \equiv 2\pi/K \gg a\)
  one can approximate in (5.8) \(|\sin(x)| \approx x\), i.e.

\[
\omega \approx \sqrt{\frac{C}{M}} Ka \propto K
\]

this limit corresponds to the *continuum approximation*

- there exists a maximum value for the frequency \(\omega_{\text{max}} = (4C/M)^{1/2}\),
  reached when the \(K\) 'vector' lies on the boundary of the 1. Brillouin zone
  \(\rightarrow K_{\text{max}} = \pm \pi/a \Leftrightarrow \lambda_{\text{min}} = 2a\).
  Typical values are \(\omega_{\text{max}} \sim 10^{13}\) Hz.
  Solution at \(K_{\text{max}} = \pm \frac{\pi}{a}\) (i.e. at the zone boundary): \(K_{\text{max}}sa = \pm s\pi\), hence

\[
u_s = u \cdot e^{\pm i\pi s} e^{-i\omega t} = u \cdot ( -1)^s e^{-i\omega t}
\]

= *standing wave* (due to Bragg reflection at the zone boundary)

compare with Bragg condition \(2d \sin \theta = n \cdot \lambda:\)

\[
d = a,
\theta = \pi/2 \Rightarrow \sin \theta = 1 \Rightarrow 2d \sin \theta = 2a
\]

\[
n = 1
\]

\[
\lambda = 2\pi/K_{\text{max}} = 2\pi/(\pi/a) = 2a \Rightarrow n \cdot \lambda = 2a \quad \text{q.e.d}
\]
5.2 1-dimensional chain of identical atoms

- **group velocity:**
  
The group velocity of a wave packet is given as the slope of the dispersion curve \( \omega(K) \)
  
  \[ v_g = \frac{d\omega}{dK} \quad \text{or} \quad \vec{v}_g = \text{grad}_K \omega(\vec{K}) \tag{5.12} \]
  
  (corresponds to the velocity of energy propagation in a crystal)

  With the dispersion relation (5.8) the group velocity is
  
  \[ v_g = \sqrt{\frac{C_\alpha^2}{M}} \cos \frac{Ka}{2} \tag{5.13} \]

![Figure 5.6: Group velocity vs. \( K \), for monatomic 1-dim. chain. \( v_g = 0 \) at the zone boundary, i.e. there is no transport of energy](image)

  limit of long wavelength:
  
  \[ v_g = \sqrt{\frac{C_\alpha}{M}} \cdot a = \text{const.} \]

  corresponds to sound waves with long wavelength;

- **Distribution of the \( N - 1 \) oscillatory degrees of freedom**

  from periodic boundary conditions \( u_s = u_{s+N} \)

  \[ e^{iKsa} = e^{i[K(s+N)a+2\pi n]} \]

  \[ NKa = 2\pi n \]

  \[ K = \frac{2\pi}{Na} n, \quad n = -N/2 \leq n \leq N/2 \]

  \[ \Rightarrow N \text{ discrete values for } K; \text{ with } K = 0 \text{ corresponding to translation} \]

  \[ \Rightarrow \text{oscillatory degrees of freedom are being } \text{used up} \]

  just within the 1. Brillouin zone.
• **generalization to 3D:**

we used Hooke’s law $F = C \cdot u$ which is valid in that form only in one dimension; in 3D this relation becomes more complex:

- replace force by stress\(^5\) field (‘Spannungsfeld’) $\vec{\sigma}$ (tensor; $3 \times 3$ matrix)
- replace displacement by strain field (‘Dehnungsfeld’) $\vec{\varepsilon}$ (tensor; $3 \times 3$ matrix)
- then: $\vec{\sigma} = C \vec{\varepsilon}$;

$C$ is a tensor (4. Stufe) with 81 components $C_{ikbn}$; hereby: 21 components are independent of each other
(s. Kittel, chapter 3)

• **derivation of force constants from experiment**

So far, we used the approximation of only nearest neighbor interactions, i.e. for the force on atom $s$ from the displacement of atom $s + p$ we only considered $p = \pm 1$.

Particularly in metals the effective forces can be of quite long range, i.e. interactions of lattice planes up to 20 lattice spacings apart from each other (i.e. $p = 20$) can be significant.

For that case one can find a generalization of the dispersion relation (5.7) to $p$ nearest neighbors as

$$\omega^2 = \frac{2}{M} \sum_{p>0} C_p (1 - \cos pKa) \quad (5.14)$$

Solving for the interplanar force constants $C_p$ at range $pa$ yields

$$C_p = \frac{-Ma}{2\pi} \int_{-\pi/a}^{+\pi/a} dK \omega_K^2 \cos pKa \quad (5.15)$$

for a structure with a monatomic basis.

The measurement of the dispersion relation hence allows the determination of the range of the interplanar forces.

\(^5\)stress is defined as force per unit area
5.3 1-dimensional chain of two different atoms

Atoms shall have masses $M_1, M_2$

Atoms with masses $M_1$ are displaced by $u_{s-1}, u_s, u_{s+1}, \ldots$ and atoms with masses $M_2$ by $v_{s-1}, v_s, v_{s+1}, \ldots$

![Diagram of a 1-dimensional chain of two different atoms with displacements $v_s, \ldots$ and $u_s, \ldots$](image)

The force constant shall be again denoted as $C$, i.e. force between two (different) neighboring atoms is $F = C(v_s - u_s)$ (Hook’s law).

⇒ equations of motion:

\[
\begin{align*}
M_1 \ddot{u}_s &= C \cdot (v_s + v_{s-1} - 2u_s) \\
M_2 \ddot{v}_s &= C \cdot (u_{s+1} + u_s - 2v_s)
\end{align*}
\] (5.16)

Ansatz:

traveling waves, now with different amplitudes

\[
\begin{align*}
 u_s &= u \cdot e^{i(sK_a - \omega t)} \\
v_s &= v \cdot e^{i(sK_a - \omega t)}
\end{align*}
\] (5.17)

where the lattice constant $a$ is defined as the distance between nearest neighbors of atoms with same mass (for zero displacement).

Substitution of (5.17) in (5.16) yields

\[
\begin{align*}
-\omega^2 M_1 u &= C v [1 + e^{-iK_a}] - 2C u \\
-\omega^2 M_2 v &= C u [1 + e^{iK_a}] - 2C v
\end{align*}
\] (5.18)

This system of linear equations has a solution only if the determinant of the coefficients of the unknowns $u, v$ vanishes

\[
\det \begin{vmatrix}
2C - M_1\omega^2 & -C \cdot [1 + e^{-iK_a}] \\
-C \cdot [1 + e^{iK_a}] & 2C - M_2\omega^2
\end{vmatrix} = 0
\] (5.19)

hence

\[
M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + 2C^2(1 - \cos K a) = 0
\] (5.20)
• solution for $ka \ll 1$

with $\cos Ka \approx 1 - \frac{1}{2}K^2a^2 + \ldots$ one finds the two solutions

$$\omega^2 \approx 2C \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \quad \text{"optical branch"} \quad (5.21)$$

and

$$\omega^2 \approx \frac{C}{2(M_1 + M_2)} K^2a^2 \quad \text{"acoustical branch"} \quad (5.22)$$

• solution at the zone boundary $K_{\text{max}} = \pm \frac{\pi}{a}$

$\cos Ka = -1$, hence

$$\omega^2 = \frac{2C}{M_1} \quad \text{and} \quad \omega^2 = \frac{2C}{M_2} \quad (5.23)$$

The full dispersion relatione, including the discussed limiting cases is shown below for the case $M_1 > M_2$.

Figure 5.8: Optical and acoustical branches of the dispersion relation for a diatomic linear lattice, showing the limiting frequencies at $K = 0$ and $K = K_{\text{max}} = \frac{\pi}{a}$. The lattice constant is $a$ [from Kittel, Introduction to solid state physics (1996); Fig.4.7].
The figure below shows the atom displacements transverse to the \( K \) vector.

![Diagram of atom displacements](image)

**Figure 5.9:** Transverse optical and transverse acoustical waves in a diatomic linear lattice, illustrated by the particle displacements for the two modes at the same wavelength. [from Kittel, *Introduction to solid state physics* (1996); Fig.4.10].

- For the transverse optical (TO) branch at \( K = 0 \) one finds on substitution of (5.21) in (5.18)

\[
\frac{u}{v} = -\frac{M_2}{M_1}
\]

(5.24)

The minus sign means that the atoms vibrate against each other.

If the two atoms have opposite charges one can excite this type of vibration by the electric field of an incident light wave \( \Rightarrow \) *optical* mode.

- In the \( K = 0 \) limit of (5.21) one finds as a solution for the transverse acoustical branch \( v = u \).

This means that the atoms move together, as in long wavelength acoustical vibrations \( \Rightarrow \) *acoustical* mode.

- **Frequency gap:**

  For certain frequencies – here for \( (2C/M_1)^{1/2} < \omega < (2C/M_2)^{1/2} \) – there are no wavelike solutions.

  \( \Rightarrow \) characteristic for polyatomic lattices

  Solutions for real \( \omega \) yield a complex wavevector
  
  \( \Rightarrow u_s = u \cdot e^{-iK|u|} \cdot e^{-i\omega t} \rightarrow \) damping in space!

**Note:** the \( 2N \) degrees of freedom "fit" again into the 1. Brillouin zone.
5.4 Generalization and examples

- extension to \( p \) atoms in the basis: \( p \) branches in 1D
- extension to 3D:
  - one longitudinal ("L") and two transverse ("T") 'polarization' modes
    E.g. for NaCl or diamond with \( p = 2 \) atoms in the primitive cell:
    for each of the three polarization modes (1L and 2T) one gets two branches
    (acoustical and optical)
    \( \Rightarrow 2 \times 3 = 6 \) branches
    The figures below show examples for germanium and KBr also with \( p = 2 \)
    atoms per primitive cell.
  - \( p \) atoms in primitive cell \( \Rightarrow 3p \) branches:
    3 acoustical branches (1LA, 2TA)
    \( 3p - 3 \) optical branches \( \rightarrow (p - 1)LO, 2(p - 1)TO \)
    (valid for each direction \( \vec{K} \))

![Figure 5.10: Phonon dispersion relations in the [111] direction: Left in germanium at 80 K. The two TA phonon branches are horizontal at the zone boundary position \( K_{\text{max}} = \frac{2\pi}{a} \cdot \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right) \). The LO and TO branches coincide at \( K = 0 \); this also is a consequence of the crystal symmetry of Ge. The results were obtained with neutron inelastic scattering by G. Nielsson and G. Nelin. Right in KBr at 90 K, after A.D.B. Woods et al. The extrapolation to \( K = 0 \) of the TO and LO branches are called \( \omega_T \) and \( \omega_L \). [from Kittel, *Introduction to solid state physics* (1996); Fig.4.8].](image-url)
Example: Silicon

Si crystallizes in the diamond lattice with \( p = 2 \) atoms per cell. The figure below shows the Brillouin zone of such a cubic crystal.

Due to \( p = 2 \), silicon has 6 phonon branches which are degenerate along the lines \( \Delta \) and \( \Lambda \).

\[ \text{Figure 5.11: Brillouin zone of cubic crystals. Some points and lines of high symmetry are drawn.} \]
\[ \Gamma \text{ denotes the center (0,0,0), the point } X \text{ is given by } \frac{2\pi}{a}(0,1,0), \]
\[ \text{the point } L \text{ by } \frac{\pi}{a}(1,1,1) \text{ and the point } K \text{ by } \frac{3\pi}{2a}(0,1,1) \text{ [from Bergmann-Schaefer, Lehrbuch der Experimentalphysik, Bd. 6 Festkörperphysik (1992); Abb.1.18].} \]

\[ \text{Figure 5.12: Dispersion of phonons in Si. Shown is the phonon energy } \hbar \omega, \text{ with phonon frequency } \omega. \Gamma, X, K \text{ and } L \text{ denote different points and } \Delta, \Sigma \text{ and } \Lambda \text{ different lines in the Brillouin zone, as defined in fig. 5.4. Extending the line } \Gamma K \text{ outside the Brillouin zone one reaches a point which is equivalent to } X. L \text{ and } T \text{ means longitudinally and transversely polarized wave, respectively, } A, \text{ acoustical wave, and } O \text{ optical wave.} \]
\[ \text{[from Bergmann-Schaefer, Lehrbuch der Experimentalphysik, Bd. 6 Festkörperphysik (1992); Abb.1.19].} \]
**Example: Tl$_2$Ba$_2$CaCu$_2$O$_8$ (high-$T_c$ superconductor)**

The figures below show the Brillouin zones of a body-centered tetragonal (bct) and a simple tetragonal (st) lattice of a complex cuprate superconductor, together with the calculated phonon dispersion relations of the bct structure.

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**Figure 5.13:** **Left:** Brillouin zones of the body-centered tetragonal (top) and simple tetragonal (bottom) lattices. The symmetry directions along which the dispersion curves are displayed are indicated with heavy lines. For the body-centered tetragonal lattice, $X = (1, 1, 0) \frac{\pi}{a}$, $G_1 = (1, 0, 0) \left(1 + \frac{a^2}{c^2}\right) \frac{\pi}{a}$, and $Z = (0, 0, 2) \frac{\pi}{c} = (2, 0, 0) \frac{\pi}{a}$. For the simple tetragonale lattice, $X = (1, 0, 0) \frac{\pi}{a}$, $M = (1, 1, 0) \frac{\pi}{a}$ and $Z = (0, 0, 1) \frac{\pi}{c}$. $a, a, c$ are the sides of the conventional unit cells of both lattices. **Right:** Phonon dispersion curves of bct Tl$_2$Ba$_2$CaCu$_2$O$_8$ (2:1:2:2:8) along symmetry directions of the bct Brillouin zone. [from Kulkarni et al., Physical Review B 43, 5451 (1991); Fig. 1 and 3].
5.5 Quantized lattice vibrations: Phonons

Quantum mechanics: Energy of a wave with frequency $\omega$:

$$E = \left( n + \frac{1}{2} \right) \hbar \omega$$

with $n$: number of quantum 'particles'; $n = 0, 1, 2, \ldots$

electromagnetic (light) wave: "Quantum particle" = Photon
lattice vibrations: "Quantum particle" = Phonon

here:

$E = \left( n + \frac{1}{2} \right) \hbar \omega$ is the energy of an elastic mode of frequency $\omega$ when the mode is excited to the quantum number $n$,
i.e. the mode is occupied by $n$ phonons.

For $n = 0 \rightarrow E = \hbar \omega / 2$ = zero point energy of the mode.

Occurs for both – phonon and photon – due to their equivalence to a quantum mechanical harmonic oscillator of frequency $\omega$

Phonon momentum:

A phonon of wavevector $\vec{K}$ can interact with particles as if it had a momentum $\vec{p} = h \vec{K}$

However, a phonon does not carry a physical momentum
(except for $\vec{K} = 0$, corresponding to the translation of a crystal as a whole)

Note: $\vec{K}$ is only defined modulo a reciprocal lattice vector $\vec{G}$.

Explanation (in the 'particle picture'):

the crystal as a whole can change its momentum by $h \vec{G}$ during Bragg reflection (recoil);
Recoil energy $E_{\text{recoil}} = (h \vec{K})^2 / 2M_{\text{crystal}}$ very small, since $M_{\text{crystal}}$ very large

• possible interactions of phonons with:
  - electrons, neutron, photons, \ldots
  - other phonons (due to anharmonic terms in the elastic energy)

selection rules in a crystal:
govern allowed transitions between quantum states,
e.g. for elastic scattering of an x-ray photon by a crystal we found

$$\vec{k}' = \vec{k} + \vec{G}$$  \hspace{1cm} (5.25)

where $\vec{G}$ is a reciprocal lattice vector, $\vec{k}$ is the wavevector of the incident photon and $\vec{k}'$ is the wavevector of the scattered photon.
inelastic scattering by phonons:

scattering of a photon with a phonon involved can be described by either

\[ \vec{k}' + \vec{K} = \vec{k} + \vec{G} \]  

(5.26)

i.e. the creation (emission) of a phonon of wavevector \( \vec{K} \) or by

\[ \vec{k}' = \vec{k} + \vec{K} + \vec{G} \]  

(5.27)

i.e. the absorption of a phonon \( \vec{K} \) during the scattering process.

• interaction with neutrons:

Inelastic scattering of neutrons by absorption or emission of a phonon is a widely used method for the determination of the phonon dispersion relation \( \omega(\vec{K}) \). Kinematics are described by

\[ k_{\text{neutron}} + \vec{G} = k_{\text{neutron}}' \pm K_{\text{ph}} \]  

(5.28)

(“±”: creation/annihilation of a phonon)

Here, \( \vec{G} \) is chosen such that \( \vec{K} \) lies in the 1. Brillouin zone.

\[ \frac{\hbar^2 k_{\text{neutron}}^2}{2m_n} = \frac{\hbar^2 k_{\text{neutron}}'^2}{2m_n} \pm \hbar \omega_{\text{ph}} \]  

(5.29)

(“±”: creation/annihilation of a phonon)

Experimental determination of \( \omega(\vec{K}) \) is based on the two conservation laws (5.28), (5.29).

Then in the experiment, one needs to find the energy gain or energy loss of the scattered neutrons as a function of the scattering direction \( \vec{k} - \vec{k}' \).

Advantage of using neutrons:

\[ E_{\text{neutron}}, \lambda_{\text{neutron}} \] are comparable to \( E_{\text{ph}}, \lambda_{\text{ph}} \)
Figure 5.14: Phonon dispersion in GaAs as obtained from neutron scattering (after Strauch and Dorner). The different points and lines on/along the wave vector axis are defined in Fig.5.11; $\nu$ is the frequency [from Bergmann-Schaefer, *Lehrbuch der Experimentalphysik, Bd. 6 Festkörperphysik* (1992); Abb.1.30].
5.6 Thermal properties of phonons

5.6.1 Contribution to the heat capacity

Heat capacity is very sensitive to elementary excitations and ordering phenomena in
crystals (electrons, phonons, magnetic order, spin waves, superconductivity etc.).

Each phenomenon has very specific properties (e.g. $T$ dependence)
$\Rightarrow$ heat capacity is a well suited probe;
- particular advantage: detects volume properties

In general one defines the heat capacity either as

$$ C_V \equiv \left( \frac{\partial U}{\partial T} \right)_V $$

at constant volume or

$$ C_p \equiv \left( \frac{\partial U}{\partial T} \right)_p $$

at constant pressure;

$T$ is the temperature and $U$ is the energy.

The phonon contribution to the heat capacity of a crystal is called the
lattice heat capacity $C_{\text{lat}}$.

some results from quantum statistics (without proof):

A system of quantum particles (e.g. vibrations) shall be characterized by energies $E_n$
($n$: index number)

- question: What is the probability $f(E_n)$ of finding a quantum particle
  at the energy $E_n$?
- answer: depends on the nature of the particle and on temperature:
  - particles with semi-integer spin (e.g. $\frac{1}{2} \hbar$) = fermions,
    e.g. electrons:

$$ f(E_n) = \frac{1}{e^{(E_n-\mu)/k_B T} + 1} \quad \text{Fermi-Dirac distribution function} \quad (5.30) $$

Here, $\mu$ is the chemical potential, which has to be determined in such a way that the number of particles in the system (e.g. all electrons in the crystal) is conserved.

- particles with integer spin (e.g. $0 \hbar, 1 \hbar$) = bosons,
  e.g. photons, phonons:

$$ f(E_n) = \frac{1}{e^{(E_n-\mu)/k_B T} - 1} \quad \text{Bose-Einstein distribution function} \quad (5.31) $$

particular property of photons, phonons:
there is no conservation of the number of particles $\Rightarrow \mu = 0$

classical statistics (for distinguishable particles) yields probability

$$ f \propto e^{-(E-\mu)/k_B T} \quad \text{Boltzmann distribution function} \quad (5.32) $$
Back to the phonon heat capacity:

- internal energy of a vibrating crystal:

\[
U = \sum_p \sum_K \frac{1}{e^{\hbar \omega(K)/k_B T} - 1} \hbar \omega(K)
\]  

(5.33)

= energy \( \hbar \omega(K) \) multiplied by the probability to have a state occupied at this energy – and with summation over all wave vectors \( \vec{K} \) and polarization states \( p \).

- there do exist a lot of states \( \vec{K} \)

\[ \sum_{\vec{K}} \text{ can be transformed into an integral } \int d\omega \cdot D(\omega), \]

with \( D(\omega) \): number of states within the frequency interval \( d\omega \)

(= "density of states or "Zustandsdichte")

- determination of \( D(\omega) \):

  - consider cube with length \( L \), plus periodic boundary conditions

  \( \rightarrow \) possible vibrating states

  (compare to linear chain with \( L = Na \) where we found \( K = 2\pi n/Na \)):

  \( K_x = 0, \pm 2\pi /L, \pm 4\pi /L, \ldots ; K_y, K_z \) analog

  \( \rightarrow \) 1 state per

\[
\left( \frac{2\pi}{L} \right)^3 = \frac{8\pi^3}{V}
\]  

(5.34)

\( \rightarrow \) number of states in \( \vec{K} \) space within a sphere with radius \( K \):

\[
N_K = \frac{4\pi}{3} K^3 \cdot \frac{V}{8\pi^3}
\]  

(5.35)

(for each polarization \( p \)

The density of states for each polarization type is hence given by

\[
D(\omega) = \frac{dN_K}{d\omega} = \frac{dN_K}{dK} \cdot \frac{dK}{d\omega} = \frac{VK^2}{2\pi^2} \cdot \frac{dK}{d\omega}
\]  

(5.36)

- next task: determine \( dK/d\omega \)
Debye model of density of states:

Assumption:
The velocity of sound is taken as constant for each polarization type (like in classical elastic continuum).

Gives simple dispersion relation
\[ \omega = v_s K \]  (5.37)
with sound velocity \( v_s \).

Hence, the density of states is given as
\[ D(\omega) = \frac{V \omega^2}{2\pi^2 v_s^3} \]  (5.38)

Remark:
Debye model is o.k. for acoustical phonons; at sufficiently low temperature \(^6\) mainly those phonons are excited (energy of the optical phonons is large for all \( \vec{K} \))

With \( N \) primitive cells in the crystal volume \( V \):
The total number of acoustic phonon modes is \( N \)

From (5.35) we know then that all \( N \) vibrating states are located within the volume (in \( K \) space)
\[ N = \frac{V}{8\pi^3} \frac{4\pi}{3} K^3 = \frac{V}{8\pi^3} \frac{4\pi}{3} \left( \frac{\omega}{v_s} \right)^3 \]  (5.39)

This relation defines a maximum frequency, or 'cutoff' frequency
\[ \omega \equiv \omega_D = \left( \frac{6\pi^2 v_s^3 N}{V} \right)^{\frac{1}{3}} \]  ("Debye frequency") (5.40)

With the dispersion relation one gets the corresponding cutoff wavevector
\[ K_D = \frac{\omega_D}{v_s} = \left( \frac{6\pi^2 N}{V} \right)^{\frac{1}{3}} \]  ("Debye wave vector") (5.41)

Note: \( \omega_D \) and \( K_D \) depend only on the density \( N/V \), which is physically reasonable.

\(^6\) compare distribution function
Thermal energy for each polarization type:

Now we can use the obtained density of state to make the transformation from the summation over all $K$ vectors in (5.33) to the integration over all possible frequencies up to the maximum frequency $\omega_D$

$$ U = \int d\omega D(\omega) \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1} = \int_0^{\omega_D} d\omega \cdot \frac{V \omega^2}{2\pi^2 v_s^3} \cdot \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1} \quad (5.42) $$

If $v_s$ is identical for all three polarizations

$$ \Rightarrow U = 3 \cdot \frac{V \hbar}{2\pi^2 v_s^3} \int_0^{\omega_D} d\omega \cdot \frac{\omega^3}{e^{\hbar \omega/k_B T} - 1} = \frac{3V k_B^4 T^4}{2\pi^2 v_s^3 \hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1} \quad (5.43) $$

with $x \equiv \frac{\hbar \omega}{k_B T}$ and

$$ x_D \equiv \frac{\hbar \omega_D}{k_B T} = \frac{\Theta}{T} \quad (5.44) $$

Here we defined $\Theta = \hbar \omega_D/k_B$ as the "Debye temperature"

$$ \Theta = \frac{\hbar v_s}{k_B} \left( \frac{6\pi^2 N}{V} \right)^{\frac{1}{3}} \quad (5.45) $$

With this definition we can express the thermal energy as

$$ U = 9Nk_B T \left( \frac{T}{\Theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1} \quad (5.46) $$

with $N$ atoms in the specimen. Thus, the heat capacity (plotted in Fig.5.15)) is

$$ C_v = \frac{\partial U}{\partial T} = 9Nk_B \left( \frac{T}{\Theta} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2} \quad (5.47) $$
For low temperature: \( x_D \to \infty \)
(Debye approximation is anyway only a good approximation at low temperature)

Then:
\[
\int_0^{x_D} dx \frac{x^3}{e^{x^2} - 1} \to \int_0^{\infty} dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}
\]

\[
U = \frac{3\pi^4 N k_B T^4}{5 \Theta^3} \quad \text{and} \quad c_v = \frac{12\pi^4 N k_B T^3}{5 \Theta^3} \approx 234 N k_B \left( \frac{T}{\Theta} \right)^3
\]

\[
c_v \propto T^3 \quad \text{(Debye’s } T^3 \text{ law)}
\]

'simple’ explanation:
We have \( 3N \) possible modes (\( N \): number of primitive cells).
Only those modes having \( \hbar \omega < k_B T \) will be excited at low temperature to an energy close to \( k_B T \).

Hence, from the available volume in \( K \) space only a fraction \( (\omega_T/\omega_D)^3 = (T/\Theta)^3 \) will be occupied by excited modes.
⇒ number of excited phonons \( \approx 3N \left( \frac{T}{\Theta} \right)^3 \);
each phonon has energy \( k_B T \)
⇒ energy \( \sim 3N k_B T (T/\Theta)^3 \), and \( C_V \sim 12N k_B (T/\Theta)^3 \)

The range of validity of the \( T^3 \) is below \( 0.1 \Theta \).

For \( T \gg \Theta \) the heat capacity approaches the classical value \( 3N k_B \).

Typical values for \( \Theta \):
- Li: 334 K
- C: 2230 K
- Au: 165 K
- K: 91 K

![Figure 5.16: Heat capacity of silicon and germanium. Not the decrease at low temperatures. To convert a value in cal/mol·K to J/Mol·K, multiply by 4.186. [from Kittel, Introduction to solid state physics (1996); Fig.5.8].](image-url)
Einstein model of the density of states:

consider \( N \) oscillators at the same frequency \( \omega_0 \)
(o.k. for many \textbf{optical phonons})

Density of states:

\[
D(\omega) = N\delta(\omega - \omega_0) \tag{5.51}
\]

Thermal energy:

\[
U = 3N\frac{\hbar\omega_0}{e^{\hbar\omega_0/k_BT} - 1} \quad "3" \text{ due to polarization} \tag{5.52}
\]

heat capacity:

\[
C_v = 3Nk_B \left( \frac{\hbar\omega_0}{k_BT} \right)^2 \frac{e^{\hbar\omega_0/k_BT}}{(e^{\hbar\omega_0/k_BT} - 1)^2} \tag{5.53}
\]

as plotted in the figure below

![Figure 5.17: Comparison of experimental values of the heat capacity of diamond with values calculated on the earliest quantum (Einstein) model, using the characteristic temperature \( \Theta_E = \hbar\omega/k_B = 1320 \text{ K} \). To convert to J/Mol\cdot K, multiply by 4.186. [from Kittel, \textit{Introduction to solid state physics} (1996); Fig.5.11].](image)

For low temperature: \( C_v \propto e^{-\hbar\omega_0/k_BT} \)
(not as good as Debye model which is in better agreement with experimental data)

For high temperature: \( C_v \rightarrow 3Nk_B \)
(reproducing the "\textbf{Dulong-Petit value}", as the Debye model does)
**General expression for the density of states:**

A general expression for $D(\omega)$ – the number of states per unit frequency range – requires the knowledge of the phonon dispersion relation $\omega(\mathbf{K})$.

The number of allowed $K$ values for which the phonon frequency is between $\omega$ and $\omega + d\omega$ is

$$D(\omega)d\omega = \frac{V}{8\pi^3} \int_{\text{shell}} d^3K$$

(We found earlier that we have one state per $V/(8\pi^3)$);

The integral goes over the volume of the shell in $\mathbf{K}$ space bounded by the two surfaces on which the phonon frequency is constant and either $\omega$ or $\omega + d\omega$.

**Problem:**

evaluate the volume of this shell!

We consider a surface of constant $\omega$ in $\mathbf{K}$ space as shown in the figure below.

Here, we denote $dS_\omega$ an element area on this surface

![Figure 5.18: Element of area $dS_\omega$ on a constant frequency surface in $\mathbf{K}$ space. The volume between two surfaces of constant frequency at $\omega$ and $\omega + d\omega$ is equal to $\int dS_\omega d\omega/|\nabla_K \omega|$ [from Kittel, *Introduction to solid state physics* (1996); Fig.5.12].](image)

With the perpendicular distance $dK_\perp$ between the surfaces of constant $\omega$ and constant $\omega + d\omega$ (see next figure) one gets:

$$\int_{\text{shell}} d^3k = \int dS_\omega dk_\perp$$

(5.55)
5.6 Thermal properties of phonons

Figure 5.19: The quantity $dK_\perp$ is the perpendicular distance between two constant frequency surfaces in $K$ space, one at frequency $\omega$, the other at frequency $\omega + d\omega$ [from Kittel, *Introduction to solid state physics* (1996); Fig.5.13].

Furthermore $|\nabla_K \omega| dK_\perp = d\omega$; here $\nabla_K$ is the gradient in $K$ space

$$dS_\omega dK_\perp = dS_\omega \frac{d\omega}{|\nabla_K \omega|} = dS_\omega \frac{d\omega}{v_g}$$

$$\Rightarrow \quad D(\omega) = \frac{V}{8\pi^3} \int_{\omega=\text{const.}} dS_\omega \frac{1}{v_g}$$

Note:

- Integral goes over area of constant $\omega$ in $K$ space
- $D(\omega)$ can contain singularity points = "Van-Hove singularities", if the group velocity $v_g = 0$
  (this is e.g. the case at Brillouin zone boundary)

Figure 5.20: Density of states as a function of frequency for (a) a solid according to the Debye model and (b) an actual crystal structure. The spectrum for the crystal starts as $\omega^2$ for small $\omega$, but discontinuities develop at singular points [from Kittel, *Introduction to solid state physics* (1996); Fig.5.14].
5.6.2 Thermal expansion of solids

So far, we only considered a linear force-displacement relation to describe lattice vibrations (Hook’s law).

This leads to a potential energy which is quadratic in the interatomic displacements (*harmonic theory*).

As one of its consequences there should be no thermal expansion which we will consider now:

**Naive view:** solid expands, while atoms oscillate
about their equilibrium position.

**but:** if one considers only harmonic oscillations, the average position of
the atom remains unchanged, no matter how large the amplitude
of oscillation is.

⇒ thermal expansion of solids results from **anharmonic** potential

**Quantitatively:**

- Taylor expansion of the potential energy of an atom in the crystal potential
  (equilibrium position shall be at $x = 0$)
  (consider 1-dim. solid)
    
    \[
    U(x) = cx^2 - gx^3 - fx^4 \ldots
    \]  
    
    - only 1. term: "harmonic approximation"
    - additional terms: "anharmonic"
      
      * term $-gx^3$: Asymmetry in mutual repulsion of neighboring atoms
      * term $-fx^4$: Softening of the vibrations (attenuation of the "spring constant" at large amplitudes

- average displacement of the atom:

  - use Boltzmann distribution which weights all possible values of displacement
    $x$ with the factor $e^{-U(x)/k_B T}$ (classical statistics o.k. for high temperatures)

  \[
  \Rightarrow \langle x \rangle = \frac{\int_{-\infty}^{\infty} dx \cdot x \cdot e^{-\beta U(x)}}{\int_{-\infty}^{\infty} dx \cdot e^{-\beta U(x)}}
  \]  

  with $\beta = \frac{1}{k_B T}$. The denominator is a normalization factor; normalizes the total probability to 1.
5.6 Thermal properties of phonons

\begin{align*}
& \int dx \cdot x e^{-\beta U(x)} \approx \int dx \cdot e^{-\beta cx^2}(x + \beta gx^4 + \beta fx^5) = \frac{3\sqrt{\pi}}{4} \frac{g}{c^{5/2}} \beta^{-3/2} \\
& \int dx \cdot e^{-\beta U(x)} \approx \int dx e^{-\beta cx^2} = \sqrt{\frac{\pi}{\beta c}} \\
& \langle x \rangle \approx \frac{3g}{2c^2} k_B T \quad (5.58)
\end{align*}

\( \Rightarrow \) thermal expansion proportional to \( T \) due to 3. order term in the potential

Measurements of the lattice constant \( a \) vs. temperature of solid argon are shown below. The slope \( da/dT \) is proportional to the thermal expansion coefficient (vanishes at low \( T \)), which is significant at high \( T \).

Figure 5.21: Lattice constant of solid argon as a function of temperature [from Kittel, *Introduction to solid state physics* (1996); Fig.5.15].
5.6.3 Phonon contribution to thermal conductivity

consider long slab with temperature gradient $dT/dx$

$\Rightarrow$ there is a steady-state flow of heat

$$j_U = -K_U \cdot \frac{dT}{dx} \quad (5.59)$$

here $K_U$ is the thermal conductivity coefficient (‘Wärmeleitzahl’), and $j_U$ is the flux of thermal energy (or the energy transmitted across unit area per time)

requires:
transfer of thermal energy is a diffusive process, subject to random scattering processes inside the slab;
otherwise $j_U$ would only be determined by the temperature difference $\Delta T$ at the ends of the slab.

$\Rightarrow$ the random nature of the heat transfer is responsible for
(i) the development of a thermal gradient, and
(ii) for the appearance of a mean free path $\ell$ in the expression of the thermal flux.

**Idea for calculation:** consider phonons as a gas of particles

general result of the kinetic gas theory: $K_U = \frac{1}{3} C v \ell$ with:

$C$: heat capacity per volume
$v$: mean particle velocity (here: velocity of sound, few km/s)
$\ell$: mean free path (typically a few nm at 300 K; a few 10 nm at 77 K)

'Derivation':

consider flux of particles $n\langle v_x \rangle$ along $x$ direction ($n$: density of particles)

The associated thermal flux is then given by

$$j_u = -n\langle v_x \rangle \Delta U$$

this is due to the fact that a particle will give up energy $\Delta U = c\Delta T$ at temperature $T$:
(if particle comes from a region with higher temperature $T + \Delta T$;
$c$: heat capacity of the particle)

between end points of a mean free path $\ell$:

$$\Delta T = \frac{dT}{dx} \ell = \frac{dT}{dx} \langle v_x \rangle \tau \quad \text{with } \tau: \text{mean collision time} \quad (5.60)$$

$$\Rightarrow j_u = -n\langle v_x^2 \rangle c \tau \frac{dT}{dx} = -\frac{1}{3} n\langle v^2 \rangle c \tau \frac{dT}{dx} \quad (5.61)$$

with $\ell = v \tau$ and $C = nc$

$$j_U = -\frac{1}{3} C v \ell \frac{dT}{dx} = -\frac{1}{3} C v \ell \frac{dT}{dx} = K_U \frac{dT}{dx} \quad \text{(q.e.d.)} \quad (5.62)$$
Discussion of heat transport mediated by phonon gas

Above, we introduced the mean free path for phonon scattering to derive the heat transport mediated by phonons.

- required: inelastic scattering processes, which restore thermal equilibrium.
- collisions of phonons with lattice defects, or with surface: does not work, because elastic – the phonon frequency remains unchanged
- collisions between phonons:
  (note: in this case anharmonic terms in the potential energy $U(x)$ of the atoms are important!)
  in general: $\vec{K}_1 + \vec{K}_2 = \vec{K}_3 + \vec{G}$
  for $\vec{G} = 0$: Normal processes ($N$ processes)
  for $\vec{G} \neq 0$: Umklapp-Processes ($U$ processes)

$N$ processes:

The total phonon momentum is $\vec{J} = \sum \vec{n}_K h\vec{K}$;
here $n_K$ is the number of phonons with wavevector $\vec{K}$.

The change in total phonon momentum is

$$\Delta \vec{J} = \vec{J}^0 - \vec{J} = h\vec{K}_3 - h\vec{K}_1 - h\vec{K}_2 = h(\vec{K}_3 - \vec{K}_1 - \vec{K}_2) = 0 \quad (5.63)$$

i.e. for $N$ processes the total phonon momentum is conserved

A distribution of hot phonons with $\vec{J} \neq 0$ propagating down a rod will leave $\vec{J}$ unchanged, i.e. $N$ processes will not be able to establish thermal equilibrium.

$\Rightarrow$ no thermal resistance, as illustrated in Fig.5.23(top) for the flow of hot gas molecules in a tube with frictionless walls and in Fig.5.24(top).

$U$ processes:

$\Rightarrow$ $U$ processes are responsible for the thermal conductivity due to phonons as they allow change of the total phonon momentum (Fig.5.23(bottom), 5.24(bottom))

Figure 5.22: (a) Normal ($N$) and (b) Umklapp ($U$) phonon collision processes in the reciprocal lattice of a 2-dim. square lattice. The square represents the 1. Brillouin zone [from Kittel, *Introduction to solid state physics* (1999); Fig.5.17c].
Figure 5.23: (top) Flow of gas molecules in a state of drifting equilibrium down a long open tube with frictionless walls. Elastic collision processes among the gas molecules do not change the momentum or energy flux of the gas because in each collision the velocity of the center of mass of the colliding particles and their energy remain unchanged. Thus energy is transported from left to right without being driven by a temperature gradient. Therefore the thermal resistivity is zero and the thermal conductivity is infinite. (bottom) The usual definition of thermal conductivity in a gas refers to a situation where no mass flow is permitted. Here the tube is closed at both ends, preventing the escape or entrance of molecules. With a temperature gradient the colliding pairs with above-average center of mass velocities will tend to be directed to the right, those with below-average velocities will tend to be directed to the left. A slight concentration gradient, high on the right, will be set up to enable the net mass transport to be zero while allowing a net energy transport from the hot to the cold end. [from Kittel, *Introduction to solid state physics* (1999); Fig.5.16a].
Figure 5.24: **top:** In a crystal we may arrange to create phonons chiefly at one end, as by illuminating the left end with a lamp. From that end there will be a net flux of phonons toward the right end of the crystal. If only $N$ processes ($K_1 + K_2 = K_3$) occur, the phonon flux is unchanged in momentum on collision and some phonon flux will persist down the length of the crystal. On arrival of phonons at the right end we can arrange in principle to convert most of their energy to radiation, thereby creating a sink for the phonons. Just as in Fig.5.23(top) the thermal resistivity is zero. **bottom:** In $U$ processes there is a large net change in phonon momentum in each collision event. An initial net phonon flux will rapidly decay as we move to the right. The ends may act as sources and sinks. Net energy transport under a temperature gradient occurs as in Fig.5.23(bottom) [after Kittel, *Introduction to solid state physics* (1999); Fig.5.16cd].

→ very high temperatures $T > \Theta$:

- all phonon modes are excited and the phonon density $n \propto T$ (compare with Bose-Einstein statistics)
  - $U$ processes will provide relaxation to thermal equilibrium
- mean free path $\ell \propto 1/n \propto 1/T \Rightarrow K_U \propto 1/T$

→ low temperatures:

- number of phonons which are suited to $U$ processes decreases $\propto e^{-\Theta/T}$
  - $K \propto e^{\Theta/T}$

→ very low temperatures:

- mean free paths reaches dimension of the crystal $D$
  - $K_U \rightarrow \frac{1}{3}CvD \propto T^3$, since $C \propto T^3$
example (NaF):

Figure 5.25: Thermal conductivity of a highly purified crystal of sodium fluoride (NaF), after H.E. Jackson, C.T. Walker and T.F. McNelly [from Kittel, *Introduction to solid state physics* (1999); Fig.5.18].

**Final remarks:**

- in metals:
  additional (strong) heat transport due to electrons

- some insulators (e.g. sapphire, Al$_2$O$_3$):
  have nevertheless a thermal conductivity which is comparable to metals,
  e.g. maximum $\sim$200 W/(cmK) at 30 K for sapphire

- for comparison:
  maximum thermal conductivity of copper is 100 W/(cmK)