4. Thermal properties of solids

**Time to study:** 4 hours

**Objective** After studying this chapter you will

- get acquainted with a description of oscillations of atoms
- learn how to express heat capacity for different models
- get acquainted with the quantum and mechanical oscillations of atoms
- learn to understand the relationship between the structure of materials and its mathematical description
- understand phenomenological relations for temperature and thermal conductivity

**Lecture**

4.1. Oscillations of the crystal lattice

We will begin the study of this issue by analysing the interaction between two atoms. The first atom is fixed at the beginning of the coordinates, while the other one moves along the axis x (Figure 4.1).

![Figure 4.1. The course of potential energy of two atoms](image)

The potential energy of the atom can be developed into the Taylor series in the form of

\[
U(R) = U(R_0) + \left( \frac{dU}{dR} \right)_{R_0} (R - R_0) + \frac{1}{2} \left( \frac{d^2U}{dR^2} \right)_{R_0} (R - R_0)^2 + \frac{1}{6} \left( \frac{d^3U}{dR^3} \right)_{R_0} (R - R_0)^3 + \ldots
\]
Pre \( R = R_0 \), the second derivative \((dU/dR)_{R_0} = 0\) in the Taylor series is marked as a positive number \( \beta \) and the third derivative as \(-2\gamma\),

\[ U(R_0) \equiv -R_0, \quad R - R_0 \equiv x. \]

Then the relation 4.1 can be rewritten in the form

\[ U(x) + U_0 = \frac{1}{2} \beta x^2 - \frac{1}{3} \gamma x^3. \quad 4.2 \]

It also applies

\[ F = -\frac{dU}{dx} = -\beta x + \gamma x^2. \quad 4.3 \]

In view of the fact that attractive as well as repulsive forces act in the solid, we can describe the fact qualitatively as the relationship

\[ U(R) = \frac{A}{R^m} - \frac{B}{R^n}. \quad 4.4 \]

Where the exponent \( m \) represents repulsive forces and \( n \) attractive forces. For the equilibrium of atoms in Figure 4.1, you get the relationship

\[ R_0 = (mA/nB)^{1/(m-n)}. \quad 4.5 \]

Now, let us focus our attention to the quantitative estimation of the forces acting between atoms. For this purpose, let us examine the deformation of the molecule in Figure 4.2 under the influence of an external force on the simple classical model of vibrating atoms.

Figure 2.4 The forces acting on the atoms in the molecule are reflected by deformation \( \Delta a \).

For the frequency of vibrating atoms, the relation applies that we know from oscillations of harmonic oscillator in the form
\[ v = \frac{1}{2\pi} \sqrt{\frac{K}{m}}, \]

where \( K \) the spring constant (bond strength) and \( m \) it is the weight. Hooke’s law can then be expressed by Figure 4.3 if \( A \) is the area.

Obviously then the following relations apply

\[ \frac{\Delta a}{a_0} = \frac{1}{Y} \frac{F}{A}, \]

\[ F = K \Delta a, \quad \frac{\Delta a}{a_0} = \frac{1}{Y} \frac{K \Delta a}{a_0^2}, \]

From which we can calculate the “spring constant”

\[ K = a_0 Y. \]

For aluminium, where \( a_0 \) equals \( 2.86.10^{-10} \) m and \( Y(E) \) equals \( 7.10^{10} \) Pa

\( K=20N/m \). The corresponding oscillation frequency is \( 3.4.10^{12} \) Hz, which is approximately consistent with the experimental data (6,4.10^{12} Hz).

\[ \frac{\Delta a}{a_0} = \frac{1}{Y} \frac{F}{A} = \frac{1}{Y} \frac{F}{a_0^2}. \]

Figure 3.4 Hooke’s law
For an average amplitude of oscillations, the following relation applies

$$\bar{A} = \sqrt{\frac{2kT}{K}}.$$  \hspace{1cm} 4.9

After substituting for the appropriate constants we get

$$\bar{A} = \sqrt{\frac{2kT}{K}} = \sqrt{\frac{2 \cdot 1.38 \cdot 10^{-23} \text{ J deg}^{-1} \cdot 300 \text{ deg}}{20 \text{ N/m}}} = 2.0 \cdot 10^{-11} \text{ m} = 0.20 \text{ Å},$$  \hspace{1cm} 4.10

which is a slightly greater value as calculated, but it approximately corresponds to the reality.

Note

Properties of the individual types of relations are given in the table below

<table>
<thead>
<tr>
<th>Typ</th>
<th>Druh vazby</th>
<th>Příklad</th>
<th>Vlastnosti</th>
</tr>
</thead>
<tbody>
<tr>
<td>ionový</td>
<td>elektrostatické přítahování</td>
<td>chlorid sodíku NaCl $E_{\text{vázky}} = 5.28 \text{ eV/atom}$</td>
<td>tvrdé, vysoký bod tání, mohou být rozptýleny v polárních kapalinách, jako je voda</td>
</tr>
<tr>
<td>kovalentní</td>
<td>sídelní elektronů</td>
<td>diamant C $E_{\text{vázky}} = 7.4 \text{ eV/atom}$</td>
<td>velmi tvrdé, vysoký bod tání, nerozptýleně těsně ve všech rozpadlých</td>
</tr>
<tr>
<td>kovový</td>
<td>elektronový plyn</td>
<td>sodík Na $E_{\text{vázky}} = 1.1 \text{ eV/atom}$</td>
<td>kujné, kovový lesk, vysoká elektrická a tepelná vodivost</td>
</tr>
<tr>
<td>molekulární</td>
<td>vázaní molekul</td>
<td>van der Waalsový methan CH₄ sily $E_{\text{vázky}} = 0.1 \text{ eV/atom}$</td>
<td>nízké, nízký bod tání a bod varu, rozptýlené v kovalentních kapalinách</td>
</tr>
</tbody>
</table>
Table 17.1 Types of crystals

<table>
<thead>
<tr>
<th>Type</th>
<th>Type of bond</th>
<th>Example</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>ionic</td>
<td>electrostatic attraction</td>
<td>sodium chloride NaCl</td>
<td>hard, high melting point, may be soluble in polar liquids, such as water</td>
</tr>
<tr>
<td>covalent</td>
<td>sharing of electrons</td>
<td>diamond C</td>
<td>very hard, high melting point, insoluble in almost all solvents</td>
</tr>
<tr>
<td>metal</td>
<td>electron gas</td>
<td>Sodium Na</td>
<td>ductile, metallic gloss, high electrical and thermal conductivity</td>
</tr>
<tr>
<td>molecular</td>
<td>van der Waals forces</td>
<td>Methane CH₄</td>
<td>soft, low melting point and boiling point, soluble in covalent liquids</td>
</tr>
</tbody>
</table>

Now let us focus on a more complicated problem, namely by describing the oscillations of atoms using a model of coupled oscillators. Suppose that the force applied to the plane s, caused by deviation of the plane s+p is proportional to the difference in deviations $u_{s+p} - u_s$. In this case, the equation of motion will have the form

$$M \frac{d^2 u_s}{dt^2} = \sum_p C_p (u_{s+p} - u_s).$$

4.11

$C_p$ is force (spring) depending on the direction of stresses.

The solution of this differential equation for the neighbouring planes has the form

$$\omega^2 = \frac{2C_1}{M} [1 - \cos(Ka)].$$

4.12

$K$ is the wave vector. Solution 4.10 is graphically illustrated in Figure 4.4, where we used trigonometric relationships

$$\omega^2 = \frac{4C_1}{M} \sin^2 \left( \frac{1}{2} Ka \right); \quad \omega = \left( \frac{4C_1}{M} \right)^{1/2} \left| \sin \frac{Ka}{2} \right|.$$

We can see that the values of the wave vector $K$ of the field of so called the first

**Brillouin zone**, it applies

$$- \frac{\pi}{a} \leq K \leq \frac{\pi}{a}.$$

4.13

In these border points, the group velocity of the wave is zero (tangent to the curve at the maximum), and the wave behaves as stagnant (see Figure 4.5).
Legend: the first Brillouin zone

If the crystal is composed of two other atoms of masses $M_1 > M_2$, equations of motion will have the form

$$M_1\frac{d^2u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s),$$

$$M_2\frac{d^2v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s).$$

Graphically, the solution of the equation 4.12 is shown in Fig 4.6. The figure shows that at the Brillouin zone boundary there are prohibited frequencies.
Figure 4.6. Solution of equation 4.12
Legend: optická fonomová větev – optical phonon branch, akustická fonomová větev – acoustic phonon branch

Figure 4.7 shows how the atoms oscillate at optical (it can be excited only by optical, i.e. very high frequencies) and acoustic branches.

Image 4.7. Oscillations of atoms in the optical and acoustic branches
Legend: optický mód – optical mode, akustický mód – acoustic mode

In addition to prohibited frequencies at the Brillouin zone boundary, there are elastic waves in crystals consisting of phonons as energy quanta

\[ E = (n + \frac{1}{2}) \hbar \omega, \]

4.15

4.2. Thermal expansion

Developing the knowledge from the beginning of this chapter, we will express the strength and potential energy in the form
\[ F = - \frac{dU}{dx} = - \beta x + \gamma x^2 \]

\[ U = \frac{1}{2} \beta x^2 - \frac{1}{3} \gamma x^3 \quad 4.16 \]

Then the probability that the atom deviation from equilibrium position is \( x \) can be, based on the knowledge of statistical physics (see Chapter 2), expresses by the relation

\[ f(x) = A \exp \left( - \frac{U}{kT} \right) \approx A e^{-\beta x^2 / 2kT} \left( 1 + \frac{\gamma x^3}{3kT} \right). \quad 4.17 \]

In view of the fact that the atom must exist, the scaling condition applies in the form

\[ \int_{-\infty}^{+\infty} f(x) \, dx = A \int_{-\infty}^{+\infty} e^{-\beta x^2 / 2kT} \left( 1 + \frac{\gamma x^3}{3kT} \right) \, dx = 1. \quad 4.18 \]

After adjustment, we get the following relation for an average deviation value

\[ \bar{x} = \int_{-\infty}^{+\infty} x f(x) \, dx = \left( \frac{\beta}{2\pi kT} \right)^{1/2} \int_{-\infty}^{+\infty} e^{-\beta x^2 / 2kT} \left( x + \frac{\gamma x^4}{3kT} \right) \, dx = \frac{\gamma kT}{\beta^2}. \quad 4.19 \]

For the coefficient of thermal expansion, we get the following relation after adjustments

\[ \alpha = \frac{\bar{x}}{aT} = \frac{\gamma k_T}{\beta a^2}. \quad 4.20 \]

where \( a \) is the interatomic distance and \( k \) is the Boltzmann constant.

Relations of 4.17 and 4.18 shows that if there was not anharmonism of oscillations represented by the coefficient \( \gamma \), thermal expansion of materials would be zero.

4.3. Thermal conductivity

In this section, we will focus on qualitative approach to describe the thermal conductivity. The coefficient of thermal conductivity at high temperatures is inversely proportional to the absolute temperature and proportional to the mean free path of the phonons, which is in turn inversely proportional to the coefficient
of unharmoniousness. The coefficient of unharmoniousness and the coefficient of thermal conductivity are thus inversely proportional to $\gamma^2$ and therefore it applies

$$x \approx \frac{1}{\gamma^2 T},$$

4.21

The overall equation for the coefficient of thermal conductivity at high temperatures can be written in the form

$$x = \text{konst} \frac{M^3 v_0^7}{a^8 \gamma^2 T}.$$  

4.22

$M$ is the mass of the atom, $v_0$ is the speed of sound, and $a$ is the interatomic distance. Again we can see that if there was not anharmonism, thermal conductivity would be infinite.

But let us look at the issue of thermal conductivity in terms of phonon interactions. Pierls showed that in terms of thermal conductivity of the material, the processes for which the following relation applies are not important

$$K_1 + K_2 = K_3,$$  

4.23

but so-called U-processes (umklappen= fold, flip), which also feature a vector of the reciprocal lattice; it is symbolically shown in Figure 4.8.

$$K_1 + K_2 = K_3 + G,$$  

4.24

![Figure 4.8 a vector diagram of the normal dispersion (left) and the U-process (right)](image)

4.4. Heat capacity – a standard model

In this section, we will discuss models of heat capacity. The mean value of the energy of a classical harmonic oscillator modelling the thermal vibrations of atoms in the grid with three degrees of freedom can be expressed by the following relation in the grid with $N_0$ (Avogadro’s number) atoms
Specific heat capacity at a constant volume is defined by the formula

\[ c_v = \left( \frac{\partial U}{\partial T} \right)_v \tag{4.26} \]

and after substituting we get Dulong-Petit law in the form

\[ c_v = 3R = 5.97 \text{ kcal/kmol deg}. \tag{4.27} \]

Figure 4.9 shows that at high temperatures, the heat capacity get close to the value determined by Dulong-Petit law, but this law is not able to explain the temperature dependence of specific heat capacity.

**Figure 4.9 The temperature dependence of specific heat capacity**

Legend: olovo – lead, hliník – aluminium, křemík – silicon, uhlik (diamant) – carbon (diamond), absolutní teplota – absolute temperature

**4.5. Heat kapacity- Einstein model**

Einstein assumed that the energy of the oscillators must be quantized and can be expressed in the relation

\[ E = \frac{hv}{\exp(hv/kT) - 1} \tag{4.28} \]
Where, using a similar thought process as in the above-mentioned case, we express the energy of oscillators in the form

\[ U = 3N_0 \bar{E} = \frac{3N_0 \nu \hbar v}{\exp(hv/kT) - 1} \] 4.29

And then we calculate the specific heat capacity at a constant volume in the form

\[ c_v = \left( \frac{\partial U}{\partial T} \right)_V = 3RT \left( \frac{\nu \hbar v}{kT} \right)^2 \frac{\exp(hv/kT)}{[\exp(hv/kT) - 1]^2} \] 4.30

Einstein’s model clearly describes the temperature dependence of specific heat capacity, but Einstein did not consider the interaction between the individual oscillators, so at low temperatures, its course is different from experimental data, as can be seen in Figure 10.4.

Figure 4.10 The temperature dependence of specific heat capacity according to Einstein’s model.

### 4.6. Heat capacity – Debye model

Debye considered the material not as a collection of independent oscillators, but as a continuum in which two transverse waves and one longitudinal wave can spread. The number of such waves of a given frequency interval is equal to

\[ n(\nu) \, d\nu = 4\pi \left( \frac{1}{\nu^3} + \frac{2}{\nu^3} \right) \nu^2 \, d\nu \] 4.31

Specific heat capacity at constant volume is in the form
\[ c_V = \left( \frac{\partial U}{\partial T} \right)_V = 9R \left[ 4 \left( \frac{T}{\theta} \right)^3 \int_0^{\theta/T} x^3 \exp(x) - 1 - \left( \frac{\theta}{T} \right) \exp(\theta/T) - 1 \right] \] \hspace{1cm} 4.32

where

\[ \theta = \frac{h\nu_m}{k} \] \hspace{1cm} 4.33

is the Debye temperature of the break of the temperature dependence of specific heat capacity at a constant volume, as can be seen in Figure 4.11.

\[ \pi^2 \frac{1}{2} \frac{kT}{u_F} R. \] \hspace{1cm} 4.34

At low temperatures, this contribution is well distinguishable from the lattice contribution, which is proportional to the third power of the absolute temperature.

**4.7. Heat capacity- electron specific heat capacity**

In metals, contribution of the electron gas, which is proportional to the absolute temperature and has the following form, is added to the lattice contribution to specific heat capacity

\[ c_V = \frac{1}{2} \pi^2 \left( \frac{kT}{u_F} \right) R. \] \hspace{1cm} 4.34

Figure 4.11 Debye temperature
Summary of concepts of the chapters (subchapter)

Oscillations of atoms, oscillations of one-dimensional chain with one and two types of atoms, the concept of Brillouin zone, optical and acoustic modes, thermal conductivity and thermal expansion, phonons, standard model of specific heat capacity, Einstein’s model of specific heat capacity, Debye model of specific heat capacity, Debye temperature, specific heat capacity of the electron gas.

Questions on the explained topic

1. Explain classic description of oscillations of atoms.
2. What determines the Brillouin zone in oscillations of atoms?
3. Explain the concept of acoustic and optical branches.
4. What would be the thermal expansion of materials without anharmonic member?
5. What would be the thermal conductivity of materials without anharmonic member?
6. What is a phonon?
7. How do phonon processes affect the thermal conductivity?
8. Explain the models for specific heat capacity.