Thermal properties

- Heat capacity
  - atomic vibrations, phonons
  - temperature dependence
  - contribution of electrons

- Thermal expansion
  - connection to anharmonicity of interatomic potential
  - linear and volume coefficients of thermal expansion

- Thermal conductivity
  - heat transport by phonons and electrons

- Thermal stresses
Heat capacity

The heat capacity, \( C \), of a system is the ratio of the heat added to the system, or withdrawn from the system, to the resultant change in the temperature:

\[
C = \frac{\Delta Q}{\Delta T} = \frac{dQ}{dT} \quad [\text{J/deg}]
\]

- This definition is only valid in the absence of phase transitions
- Usually \( C \) is given as specific heat capacity, \( c \), per gram or per mol
- Heat capacity can be measured under conditions of constant temperature or constant volume. Thus, two distinct heat capacities can be defined:

\[
C_v = \left( \frac{\delta q}{dT} \right)_v \quad \text{- heat capacity at constant volume}
\]

\[
C_p = \left( \frac{\delta q}{dT} \right)_p \quad \text{- heat capacity at constant pressure}
\]

\( C_p \) is always greater than \( C_v \) - Why?

Hint: The difference between \( C_p \) and \( C_v \) is very small for solids and liquids, but large for gases.
Heat capacity

Heat capacity is a measure of the ability of the material to absorb thermal energy.

**Thermal energy** = kinetic energy of atomic motions + potential energy of distortion of interatomic bonds.

The higher is T, the large is the mean atomic velocity and the amplitude of atomic vibrations → larger thermal energy

Vibrations of individual atoms in solids are not independent from each other. The coupling of atomic vibrations of adjacent atoms results in waves of atomic displacements. Each wave is characterized by its wavelength and frequency. For a wave of a given frequency $\nu$, there is the smallest “quantum” of vibrational energy, $h\nu$, called **phonon**.

Thus, the thermal energy is the energy of all phonons (or all vibrational waves) present in the crystal at a given temperature.

Scattering of electrons on phonons is one of the mechanisms responsible for electrical resistivity (Chapter 18)
Temperature dependence of heat capacity

Heat capacity has a weak temperature dependence at high temperatures (above Debye temperature $\theta_D$) but decreases down to zero as $T$ approaches 0K.

The constant value of the heat capacity of many simple solids is sometimes called *Dulong–Petit law*

In 1819 Dulong and Petit found experimentally that for many solids at room temperature, $c_v \approx 3R = 25\text{ JK}^{-1}\text{mol}^{-1}$

This is consistent with equipartition theorem of *classical mechanics*: energy added to solids takes the form of atomic vibrations and both kinetic and potential energy is associated with the three degrees of freedom of each atom.
The low-T behavior can be explained by quantum theory. The first explanation was proposed by Einstein in 1906. He considered a solid as an ensemble of independent quantum harmonic oscillators vibrating at a frequency \( \nu \). Debye advanced the theory by treating the quantum oscillators as collective modes in the solid (phonons) and showed that

\[ c_v \sim AT^3 \text{ at } T \rightarrow 0K \]

Quantized energy levels

\( \Delta E \ll kT \) - classical behavior

\( \Delta E \geq kT \) - quantum behavior
Heat capacity of metals – electronic contribution

In addition to atomic vibrations (phonons), thermal excitation of electrons can also make contribution to heat capacity.

To contribute to bulk specific heat, the valence electrons would have to receive energy from the thermal energy, ~kT. Thus, only a small fraction of electrons which are within kT of the Fermi level makes a contribution to the heat capacity. This contribution is very small and insignificant at room temperature.

The electron contribution to \( c_v \) is proportional to temperature, \( c_v^{el} = \gamma T \) and becomes significant (for metals only) at very low temperatures (remember that contribution of phonons \( c_v \sim AT^3 \) at \( T \to 0K \)).
### Heat capacity of various materials (at RT)

| Material                                | \( c_p \)  
|-----------------------------------------|------------
| Aluminum                                | 900        
| Copper                                  | 386        
| Gold                                    | 128        
| Iron                                    | 448        
| Nickel                                  | 443        
| Silver                                  | 235        
| Tungsten                                | 138        
| 1025 Steel                              | 486        
| 316 Stainless steel                     | 502        
| Brass (70Cu–30Zn)                       | 375        
| Kovar (54Fe–29Ni–17Co)                  | 460        
| Invar (64Fe–36Ni)                       | 500        
| Super Invar (63Fe–32Ni–5Co)             | 500        
| Alumina (Al\(_2\)O\(_3\))             | 775        
| Magnesia (MgO)                          | 940        
| Spinel (MgAl\(_2\)O\(_4\))             | 790        
| Fused silica (SiO\(_2\))               | 740        
| Soda–lime glass                         | 840        
| Borosilicate (Pyrex) glass              | 850        
| Polyethylene (high density)             | 1850       
| Polypropylene                           | 1925       
| Polystyrene                             | 1170       
| Polytetrafluoroethylene (Teflon)        | 1050       
| Phenol-formaldehyde, phenolic           | 1590–1760  
| Nylon 6,6                               | 1670       

\( a \) Unit: \( J/kg \cdot K \)
Thermal expansion

Materials expand when heated and contract when cooled

\[
\frac{l_f - l_0}{l_0} = \frac{\Delta l}{l_0} = \alpha_l (T_f - T_0) = \alpha_l \Delta T
\]

where \( l_0 \) is the initial length at \( T_0 \), \( l_f \) is the final length at \( T_f \)

\( \alpha_l \) is the linear coefficient of thermal expansion

Similarly, the volume change with \( T \) can be described as

\[
\frac{V_f - V_0}{V_0} = \frac{\Delta V}{V_0} = \alpha_V (T_f - T_0) = \alpha_V \Delta T
\]

where \( \alpha_V \) is the volume coefficient of thermal expansion

For isotropic materials and small expansions, \( \alpha_V \approx 3 \alpha_l \)

\[
V_f = l_f^3 = (l_0 + \Delta l)^3 = l_0^3 + 3l_0^2 \Delta l + 3l_0 \Delta l^2 + \Delta l^3 \approx l_0^3 + 3l_0^2 \Delta l = V_0 + 3V_0 \frac{\Delta l}{l_0}
\]

\[
V_f \approx V_0 + 3V_0 \frac{\Delta l}{l_0} \quad \Rightarrow \quad \frac{V_f - V_0}{V_0} = \frac{\Delta V}{V_0} \approx 3 \frac{\Delta l}{l_0} \quad \Rightarrow \quad \alpha_V \Delta T \approx 3 \alpha_l \Delta T
\]
Physical origin of thermal expansion

Rising temperature results in the increase of the average amplitude of atomic vibrations. For an anharmonic potential, this corresponds to the increase in the average value of interatomic separation, i.e. thermal expansion.
Physical origin of thermal expansion

Thermal expansion is related to the asymmetric (anharmonic) shape of interatomic potential. If the interatomic potential is symmetric (harmonic), the average value of interatomic separation does not change, i.e. no thermal expansion.
Thermal expansion of various materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha_{l}$ $\times$ 10$^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>23.6</td>
</tr>
<tr>
<td>Copper</td>
<td>17.0</td>
</tr>
<tr>
<td>Gold</td>
<td>14.2</td>
</tr>
<tr>
<td>Iron</td>
<td>11.8</td>
</tr>
<tr>
<td>Nickel</td>
<td>13.3</td>
</tr>
<tr>
<td>Silver</td>
<td>19.7</td>
</tr>
<tr>
<td>Tungsten</td>
<td>4.5</td>
</tr>
<tr>
<td>1025 Steel</td>
<td>12.0</td>
</tr>
<tr>
<td>316 Stainless steel</td>
<td>16.0</td>
</tr>
<tr>
<td>Brass (70Cu–30Zn)</td>
<td>20.0</td>
</tr>
<tr>
<td>Kovar (54Fe–29Ni–17Co)</td>
<td>5.1</td>
</tr>
<tr>
<td>Invar (64Fe–36Ni)</td>
<td>1.6</td>
</tr>
<tr>
<td>Super Invar (63Fe–32Ni–5Co)</td>
<td>0.72</td>
</tr>
<tr>
<td>Ceramics</td>
<td></td>
</tr>
<tr>
<td>Alumina (Al$_2$O$_3$)</td>
<td>7.6</td>
</tr>
<tr>
<td>Magnesia (MgO)</td>
<td>13.5$^d$</td>
</tr>
<tr>
<td>Spinel (MgAl$_2$O$_4$)</td>
<td>7.6$^d$</td>
</tr>
<tr>
<td>Fused silica (SiO$_2$)</td>
<td>0.4</td>
</tr>
<tr>
<td>Soda–lime glass</td>
<td>9.0</td>
</tr>
<tr>
<td>Borosilicate (Pyrex) glass</td>
<td>3.3</td>
</tr>
<tr>
<td>Polymers</td>
<td></td>
</tr>
<tr>
<td>Polyethylene (high density)</td>
<td>106–198</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>145–180</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>90–150</td>
</tr>
<tr>
<td>Polytetrafluoroethylene (Teflon)</td>
<td>126–216</td>
</tr>
<tr>
<td>Phenol-formaldehyde, phenolic</td>
<td>122</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>144</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>220</td>
</tr>
</tbody>
</table>

Tendency to expand upon heating is counteracted by contraction related to ferromagnetic properties of this alloy (magnetostriction).

Negative thermal expansion: liquid water contracts when heated from 0 to 4°C. ZrVPO$_7$, ZrW$_2$O$_8$, quartz at very low T.

The stronger the interatomic bonding (deeper the potential energy curve), the smaller is the thermal expansion.

The values of $\alpha_l$ and $\alpha_v$ are increasing with rising T.
Implications and applications of thermal expansion

Railway tracks are built from steel rails laid with a gap between the ends.

Thermostats based on bimetal strips made of two metals with different coefficient of thermal expansion:

A bimetal coil from a thermometer reacts to the heat from a lighter, by Hustvedt, Wikipedia.
Thermal conductivity
Thermal conductivity: heat is transferred from high to low temperature regions of the material.

\[ q = -k \frac{dT}{dx} \quad - \text{Fourier's law} \]

where \( q \) is the \textit{heat flux} (amount of thermal energy flowing through a unit area per unit time) and \( dT/dx \) is the \textit{temperature gradient}, and \( k \) is the \textit{coefficient of thermal conductivity}, often called simply thermal conductivity.

Units: \( q \) [W/m\(^2\)], \( k \) [W/(m K)]

Note the similarity to the Fick’s first law for atomic diffusion (Chapter 5): the diffusion flux is proportional to the concentration gradient:

\[ J = -D \frac{dC}{dx} \]

Non-steady state heat flow and atomic diffusion are described by the same equation:

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \frac{\partial T}{\partial t} = \frac{k}{c_\rho \rho} \frac{\partial^2 T}{\partial x^2} \]
Mechanisms of heat conduction

Heat is transferred by phonons (lattice vibration waves) and electrons. The thermal conductivity of a material is defined by combined contribution of these two mechanisms:

\[ k = k_l + k_e \]

where \( k_l \) and \( k_e \) are the lattice and electronic thermal conductivities.

**Lattice conductivity**: Transfer of thermal energy phonons

**Electron conductivity**: Free (conduction band) electrons equilibrate with lattice vibrations in hot regions, migrate to colder regions and transfer a part of their thermal energy back to the lattice by scattering on phonons.

The electron contribution is dominant in metals and absent in insulators.

Since free electrons are responsible for both electrical and thermal conduction in metals, the two conductivities are related to each other by the Wiedemann-Franz law:

\[ L = \frac{k}{\sigma T} \]

where \( \sigma \) is the electrical conductivity and \( L \) is a constant
Wiedemann-Franz law

\[ L = \frac{k}{\sigma T} \]

<table>
<thead>
<tr>
<th>Material</th>
<th>[ L \left[ \Omega \cdot W/(K)^2 \times 10^{-8} \right] ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>2.20</td>
</tr>
<tr>
<td>Copper</td>
<td>2.25</td>
</tr>
<tr>
<td>Gold</td>
<td>2.50</td>
</tr>
<tr>
<td>Iron</td>
<td>2.71</td>
</tr>
<tr>
<td>Nickel</td>
<td>2.08</td>
</tr>
<tr>
<td>Silver</td>
<td>2.13</td>
</tr>
<tr>
<td>Tungsten</td>
<td>3.20</td>
</tr>
<tr>
<td>1025 Steel</td>
<td>-</td>
</tr>
<tr>
<td>316 Stainless steel</td>
<td>-</td>
</tr>
<tr>
<td>Brass (70Cu–30Zn)</td>
<td>-</td>
</tr>
<tr>
<td>Kovar (54Fe–29Ni–17Co)</td>
<td>2.80</td>
</tr>
<tr>
<td>Invar (64Fe–36Ni)</td>
<td>2.75</td>
</tr>
<tr>
<td>Super Invar (63Fe–32Ni–5Co)</td>
<td>2.68</td>
</tr>
</tbody>
</table>
Effect of alloying on heat conduction in metals

The same factors that affect the electrical conductivity (discussed in Chapter 18) also affect thermal conductivity in metals. E.g., adding impurities introduces scattering centers for conduction band electrons and reduce $k$. 

![Thermal conductivity graph](image)
**Quest for good thermoelectric (TE) materials**

**Thermoelectric conversion:** conversion of thermal to electrical energy

An applied temperature difference $\Delta T$ causes charge carriers in the material (electrons or holes) to diffuse from the hot side to the cold side, resulting in current flow through the circuit and producing an electrostatic potential $\Delta V$.

Figure of merit of TE material:

$$ZT = (\alpha^2\sigma/k)T$$

where $\sigma$, $\kappa$ and $\alpha$ are the electrical conductivity, thermal conductivity, and Seebeck coefficient defined as $\alpha = \Delta V/\Delta T$.

**Good TE material:** High $\sigma$ (low Joule heating), large Seebeck coefficient (large $\Delta V$), low $k$ (large $\Delta T$) are necessary.

$ZT \approx 3$ is needed for TE energy converters to compete with mechanical power generation and active refrigeration.

Li et al., *Nat. Asia Mater.*, 152, 2010
**Quest for good thermoelectric (TE) materials**

**Nanostructured materials** - a chance to disconnect the linkage between the thermal and electrical transport by controlling scattering mechanisms.

-grain boundaries, interfaces – reduction of k, but also the deterioration of carrier mobility ($\mu$).

-nano/microcomposite (f): nanoparticles scatter phonon, while microparticles can form a connected (percolating) network for electron transport.

The high performance of these materials is related to nanostructure engineering.

Li et al., *Nat. Asia Mater.*, 152, 2010

**MSE 2090: Introduction to Materials Science** Chapter 19, Thermal Properties 18
Heat conduction in nonmetallic materials

In insulators and semiconductors the heat transfer is by phonons and, generally, is lower than in metals. It is sensitive to structure:

- glasses and amorphous ceramics have lower $k$ compared to the crystalline ones (phonon scattering is more effective in irregular or disordered materials).
- Thermal conductivity decreases with porosity (e.g. foamed polystyrene is used for drinking cups).
- Thermal conductivity of polymers depends on the degree of crystallinity – highly crystalline polymer has higher $k$.

Corn kernels have a hard moisture-sealed hull and a softer core with a high moisture content. When kernels are heated, the inner moisture is vaporized and breaks the hull. The corn that “pops” and is used to make popcorn have hulls that are made from cellulose that is more crystalline than “non-popping” corn kernels. As a result, the hulls are good thermal conductors (2-3 times better than corns that do not pop) and are mechanically stronger (higher pressure can build up before popping).
Temperature dependence of thermal conductivity

Thermal conductivity tends to decrease with increasing temperature (more efficient scattering of heat carriers on lattice vibrations), but can exhibit complex non-monotonous behavior.
## Thermal conductivity of various materials at RT

<table>
<thead>
<tr>
<th>Material</th>
<th>$k$ (W/m·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>247</td>
</tr>
<tr>
<td>Copper</td>
<td>398</td>
</tr>
<tr>
<td>Gold</td>
<td>315</td>
</tr>
<tr>
<td>Iron</td>
<td>80</td>
</tr>
<tr>
<td>Nickel</td>
<td>90</td>
</tr>
<tr>
<td>Silver</td>
<td>428</td>
</tr>
<tr>
<td>Tungsten</td>
<td>178</td>
</tr>
<tr>
<td>1025 Steel</td>
<td>51.9</td>
</tr>
<tr>
<td>316 Stainless steel</td>
<td>15.9</td>
</tr>
<tr>
<td>Brass (70Cu–30Zn)</td>
<td>120</td>
</tr>
<tr>
<td>Kovar (54Fe–29Ni–17Co)</td>
<td>17</td>
</tr>
<tr>
<td>Invar (64Fe–36Ni)</td>
<td>10</td>
</tr>
<tr>
<td>Super Invar (63Fe–32Ni–5Co)</td>
<td>10</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>39</td>
</tr>
<tr>
<td>Magnesia (MgO)</td>
<td>37.7</td>
</tr>
<tr>
<td>Spinel (MgAl₂O₄)</td>
<td>15.0⁺</td>
</tr>
<tr>
<td>Fused silica (SiO₂)</td>
<td>1.4</td>
</tr>
<tr>
<td>Soda–lime glass</td>
<td>1.7</td>
</tr>
<tr>
<td>Borosilicate (Pyrex) glass</td>
<td>1.4</td>
</tr>
<tr>
<td>Polyethylene (high density)</td>
<td>0.46–0.50</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>0.12</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.13</td>
</tr>
<tr>
<td>Polytetrafluoroethylene (Teflon)</td>
<td>0.25</td>
</tr>
<tr>
<td>Phenol-formaldehyde, phenolic</td>
<td>0.15</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>0.24</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>0.14</td>
</tr>
</tbody>
</table>

**Diamond:** 2310  
along c-axis: 2000  
along a-axis: 9.5  

**Graphite:**  
along c-axis: 10.4  
along a-axis: 6.2  

**SiO₂**  
crystalline  
along c-axis: 10.4  
along a-axis: 6.2  
amorphous: 1.38
Thermal conductivity of polymer nanofibers

Although, normally, polymers are thermal insulators ($k \sim 0.1 \text{ Wm}^{-1}\text{K}^{-1}$), it has been demonstrated in atomistic simulations [Henry & Chen, PRL 101, 235502, 2008] that thermal conductivity of individual polymer chains can be very high. This finding has been supported by recent experimental study of high-quality ultra-drawn polyethylene nanofibers with diameters of 50-500 nm and lengths up to tens of millimeters [Shen et al., Nat. Nanotechnol. 5, 251, 2010] → it has been demonstrated that the nanofibers conducts heat just as well as most metals, yet remain electrical insulators.

Making the nanofibers: Pulling a thin thread of material from a liquid solution - polymer molecules become very highly aligned.
Thermal conductivity of polymer nanofibers

Highly anisotropic unidirectional thermal conductivity: may be useful for applications where it is important to draw heat away from an object, such as a computer processor chip.

Shen et al., Nat. Nanotechnol. 5, 251, 2010

104 Wm\(^{-1}\)K\(^{-1}\)

300 times higher than k of bulk polyethylene!

104 Wm\(^{-1}\)K\(^{-1}\)
Thermal stresses

- can be generated due to *restrained thermal expansion/contraction* or *temperature gradients* that lead to differential dimensional changes in different part of the solid body.

- can result in plastic deformation or fracture.

In a rod with restrained axial deformation: \( \sigma = E \alpha l \Delta T \)

where \( E \) is the elastic modulus, \( \alpha l \) is the linear coefficient of thermal expansion and \( \Delta T \) is the temperature change.

Stresses from temperature gradient

Rapid heating can result in strong temperature gradients \( \rightarrow \) confinement of expansion by colder parts of the sample. The same for cooling – tensile stresses can be introduced in a surface region of rapidly cooled piece of material.

Thermal stresses can cause plastic deformation (in ductile materials) or fracture (in brittle materials). The ability of material to withstand thermal stresses due to the rapid cooling/heating is called *thermal shock resistance*.

Shock resistance parameter for brittle materials (ceramics):

\[
TSR \propto \frac{\sigma_f k}{E\alpha l}
\]

where \( \sigma_f \) is fracture strength of the material.
Restrained thermal expansion: Example problem

A brass rod is restrained but stress-free at RT (20°C). Young’s modulus of brass is 100 GPa, \( \alpha_l = 20 \times 10^{-6} \text{ 1/°C} \). At what temperature does the stress reach -172 MPa?

If thermal expansion is unconstrained

\[
\frac{\Delta l}{l_{RT}} = \varepsilon_{th} = \alpha_l (T_f - T_0)
\]

If expansion is constrained

\[
\varepsilon_{compress} = -\varepsilon_{th} = -\frac{\Delta l}{l_{RT}}
\]

\[
\sigma = E\varepsilon_{compress} = -EA_l (T_f - T_0) = EA_l (T_0 - T_f)
\]

\[
T_f = T_0 - \frac{\sigma}{EA_l} = 20 - \frac{-172 \times 10^6 \text{ Pa}}{100 \times 10^9 \text{ Pa} \times 20 \times 10^{-6} \text{ °C}^{-1}} = 106 \text{ °C}
\]
Summary

Make sure you understand language and concepts:

- anharmonic potential
- atomic vibrations, phonons
- electron heat conductivity
- electronic contribution to heat capacity
- heat capacity, $C_p$ vs. $C_V$
- lattice heat conductivity
- linear coefficient of thermal expansion
- specific heat capacity
- thermal conductivity
- thermal expansion
- thermal stresses
- thermal shock resistance
- volume coefficients of thermal expansion

\[ C_v, \text{J K}^{-1} \text{mol}^{-1} \]

- Low $T$, $C_v \to 0$
- High $T$, $C_v \to 3R$

classical Dulong – Petit law

quantum Debye model