

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The **heat capacity**, C , of a system is the ratio of the heat added to the system, or withdrawn from the system, to the resultant change in the temperature:

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

- 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?

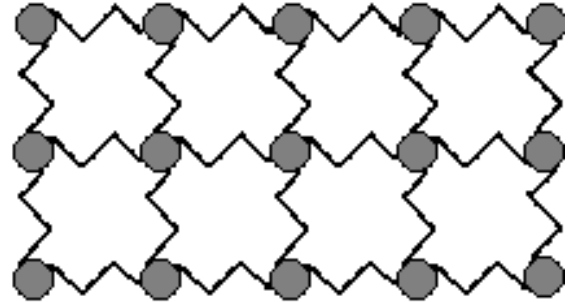
Hint: The difference between C_P and C_V is very small for solids and liquids, but large for gases.

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 larger is the mean atomic velocity and the amplitude of atomic vibrations \rightarrow larger thermal energy



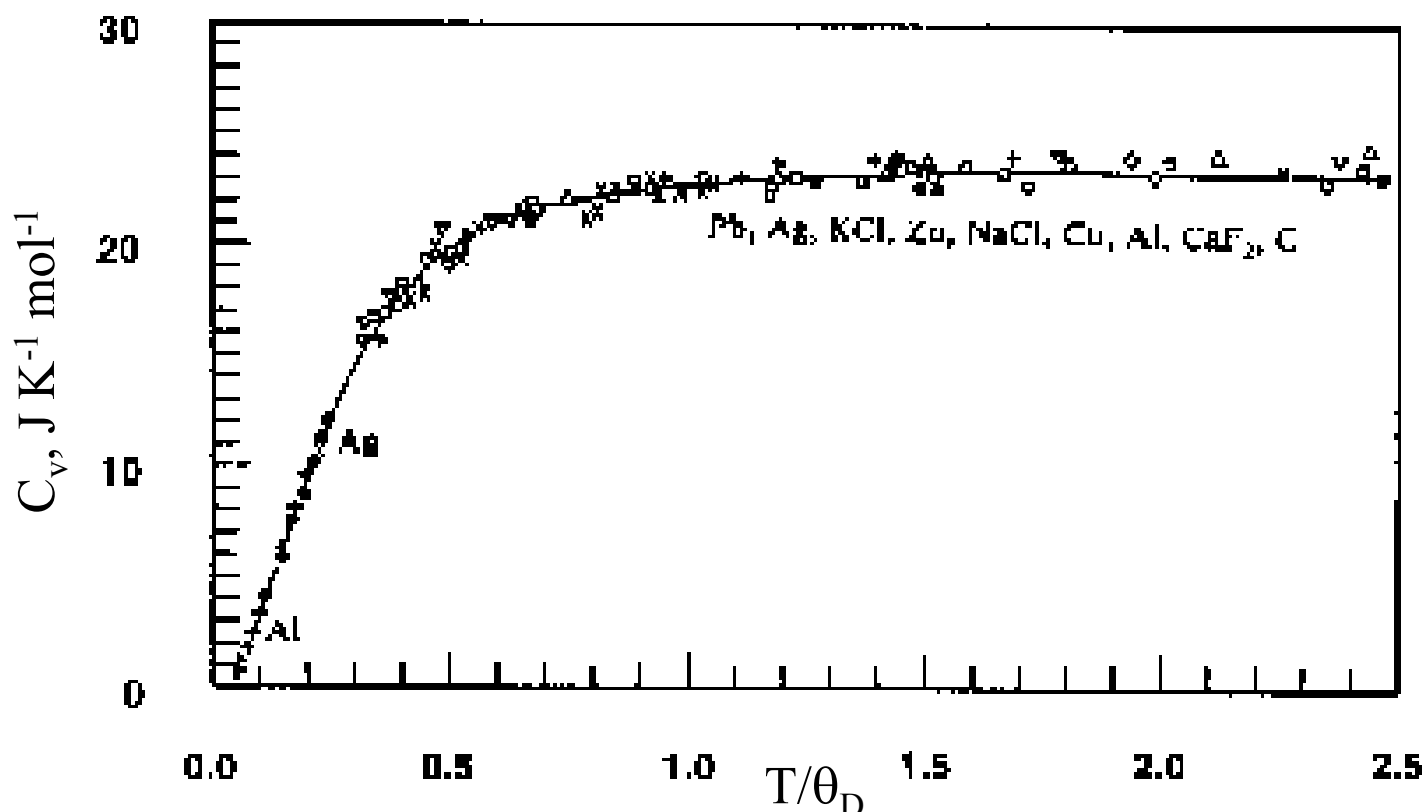
Vibrations of individual atoms in solids are not independent from each other. The coupling of atomic vibrations of adjacent atoms results in waves of atomic displacements. Each wave is characterized by its wavelength and frequency. For a wave of a given frequency ν , there is the smallest “quantum” of 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 θ_D) but decreases down to zero as T approaches 0K.

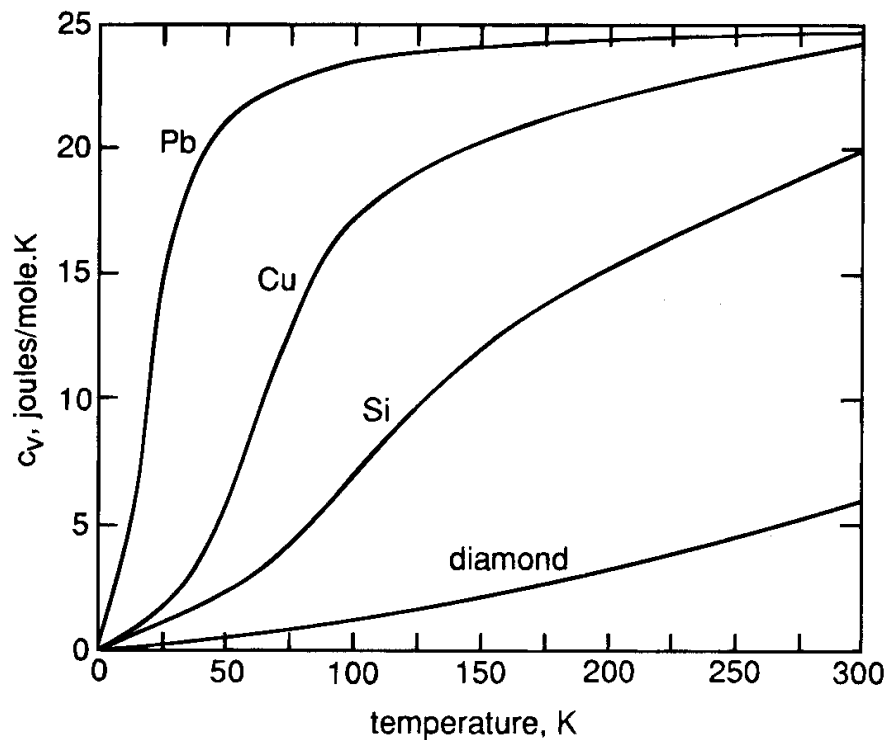


The constant value of the heat capacity of many simple solids is sometimes called *Dulong – Petit law*

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

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.

Temperature dependence of heat capacity



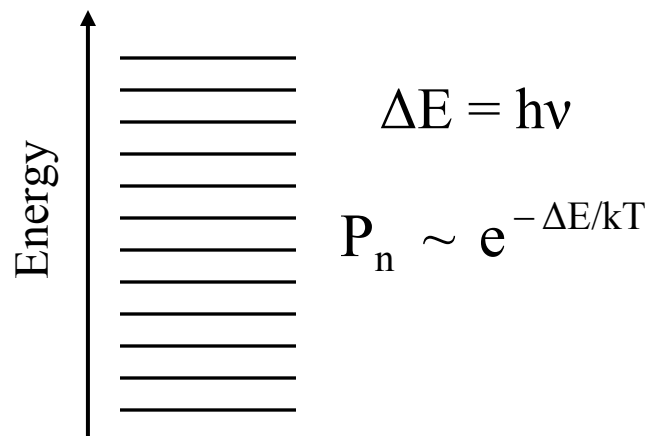
The **low-T behavior can be explained by quantum theory**. The first explanation was proposed by Einstein in 1906. He considered a solid as an ensemble of independent quantum harmonic oscillators vibrating at a frequency ν . Debye advanced the theory by treating the quantum oscillators as collective 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

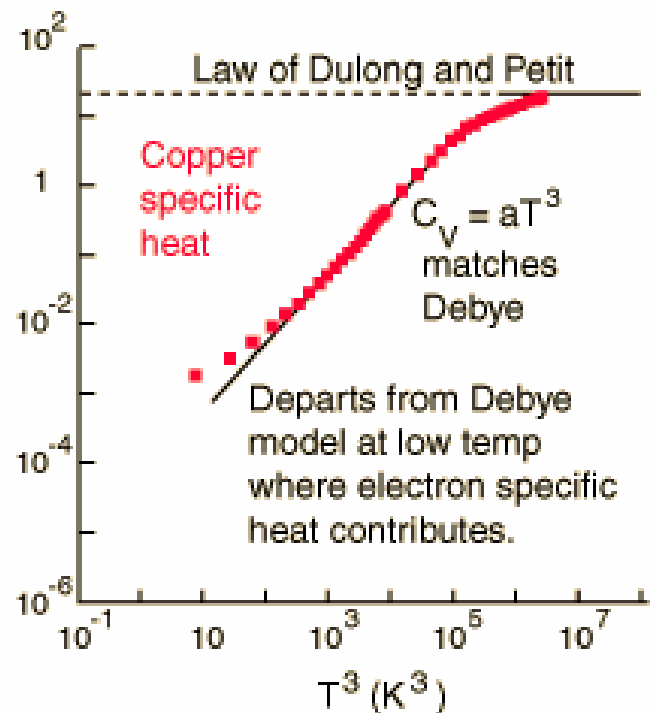
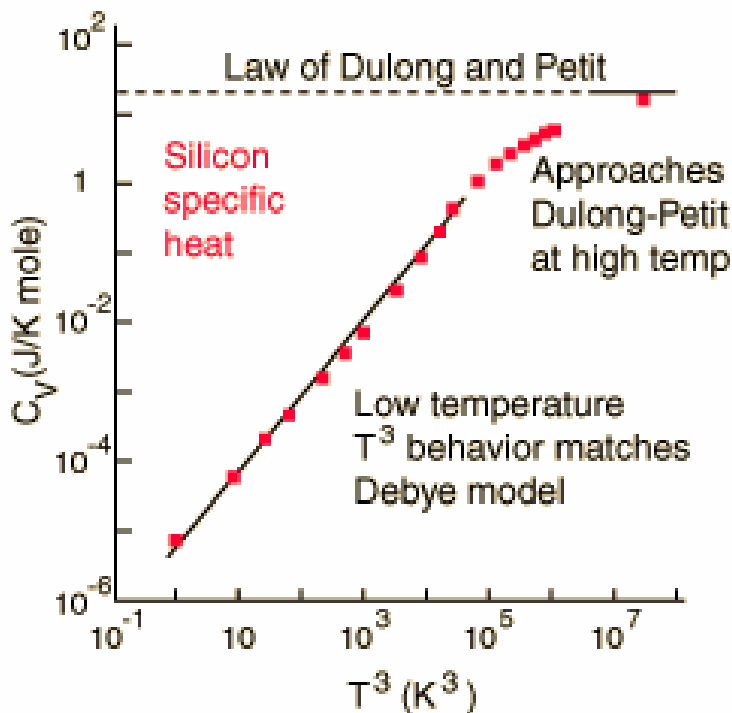


Heat capacity of metals – electronic contribution

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, $\sim kT$. 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 $T \rightarrow 0K$).



Heat capacity of various materials (at RT)

<i>Material</i>	c_p (J/kg·K) ^a
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

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

α_l is the linear coefficient of thermal expansion

Similarly, the volume change with T can be described as

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

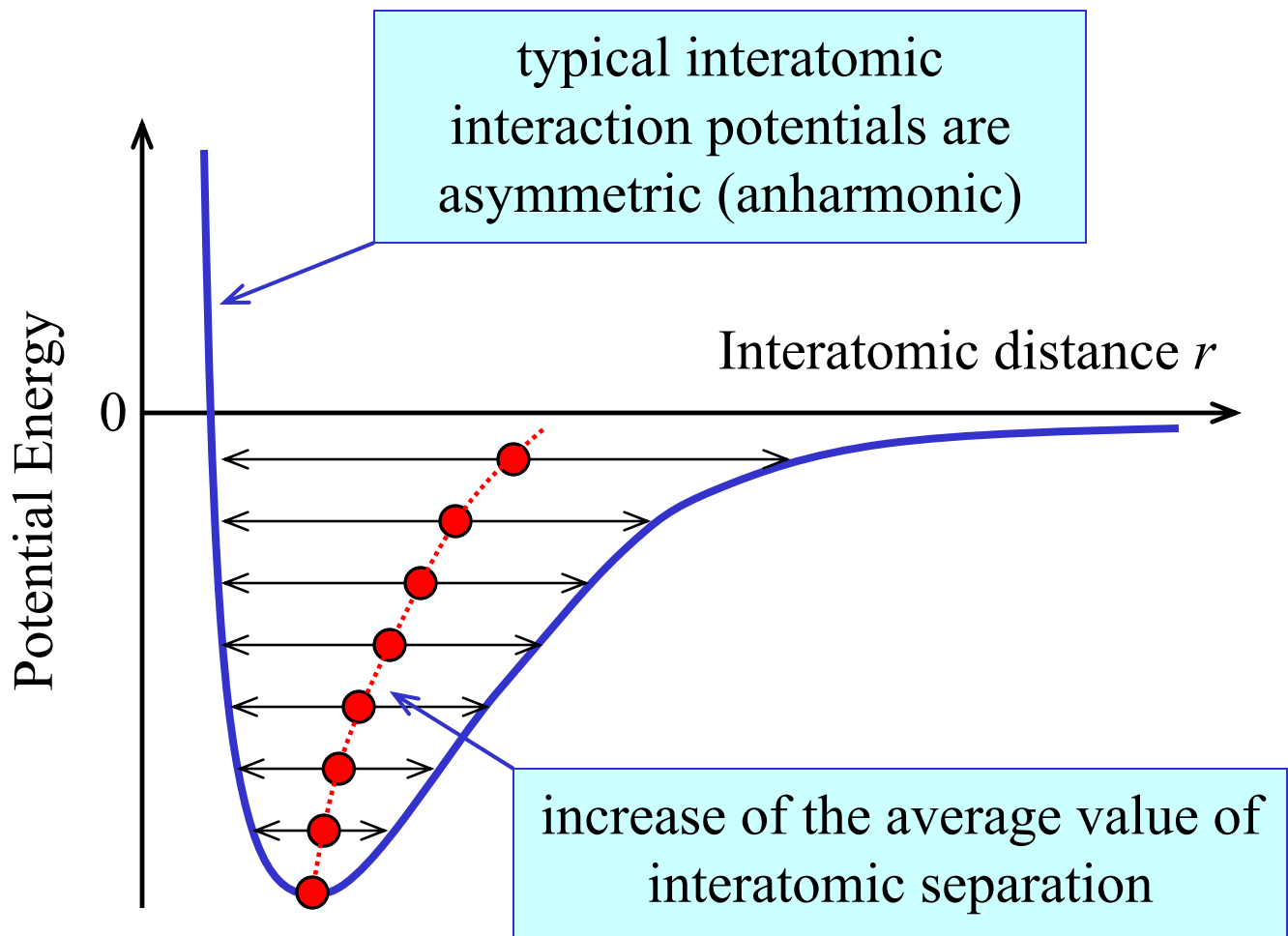
where **α_V is the volume coefficient of thermal expansion**

For isotropic materials and small expansions, **$\alpha_V \approx 3\alpha_l$**

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

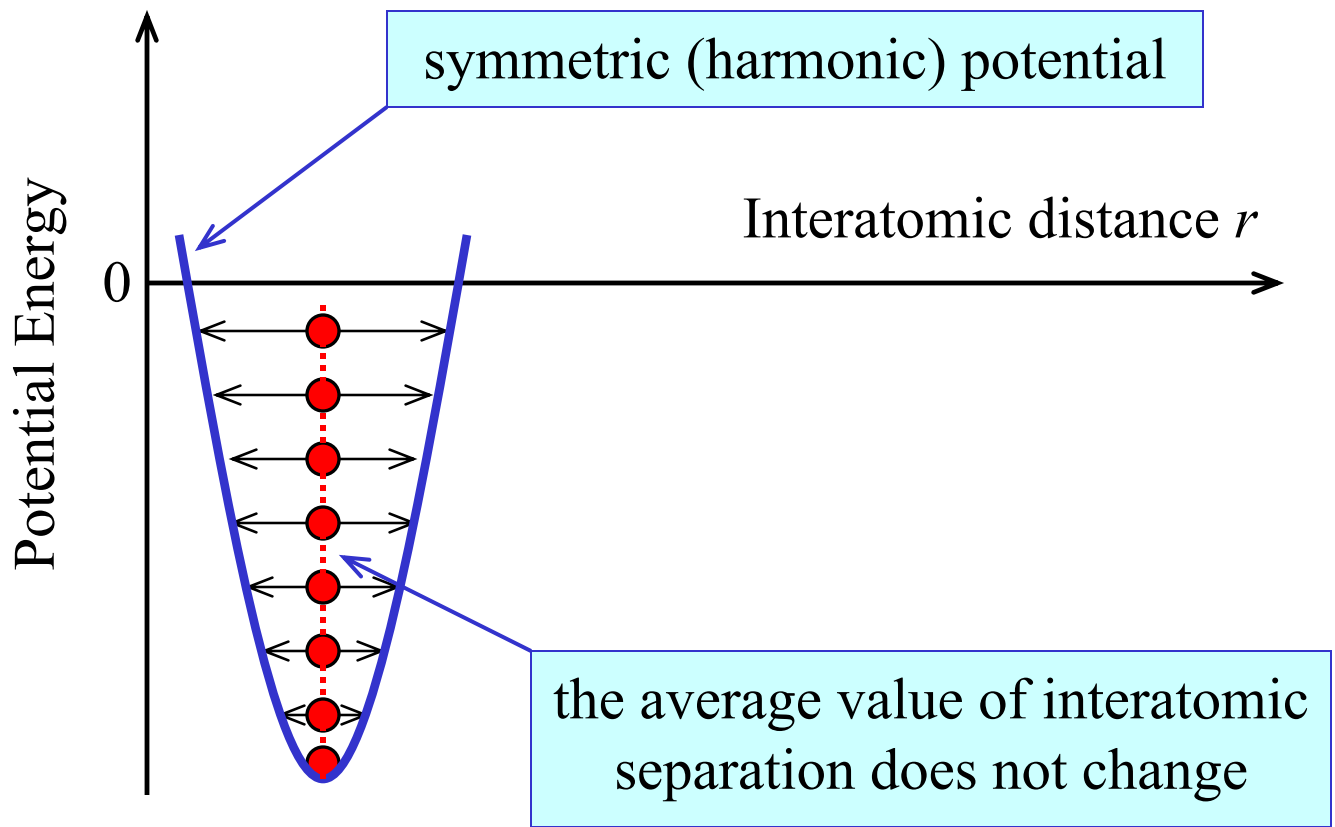
$$V_f \approx V_0 + 3V_0 \frac{\Delta l}{l_0} \quad \Rightarrow \quad \frac{V_f - V_0}{V_0} = \frac{\Delta V}{V_0} \approx 3 \frac{\Delta l}{l_0} \quad \Rightarrow \quad \alpha_V \Delta T \approx 3\alpha_l \Delta T$$

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

<i>Material</i>	$[\text{(^{\circ}\text{C})}^{-1} \times 10^{-6}]^b$
Metals	
Aluminum	23.6
Copper	17.0
Gold	14.2
Iron	11.8
Nickel	13.3
Silver	19.7
Tungsten	4.5
1025 Steel	12.0
316 Stainless steel	16.0
Brass (70Cu–30Zn)	20.0
Kovar (54Fe–29Ni–17Co)	5.1
Invar (64Fe–36Ni)	1.6
Super Invar (63Fe–32Ni–5Co)	0.72
Ceramics	
Alumina (Al_2O_3)	7.6
Magnesia (MgO)	13.5 ^d
Spinel (MgAl_2O_4)	7.6 ^d
Fused silica (SiO_2)	0.4
Soda–lime glass	9.0
Borosilicate (Pyrex) glass	3.3
Polymers	
Polyethylene (high density)	106–198
Polypropylene	145–180
Polystyrene	90–150
Polytetrafluoroethylene (Teflon)	126–216
Phenol-formaldehyde, phenolic	122
Nylon 6,6	144
Polyisoprene	220

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_2O_8 , quartz at very low T.

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

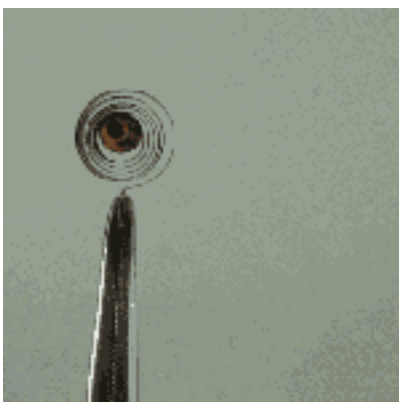
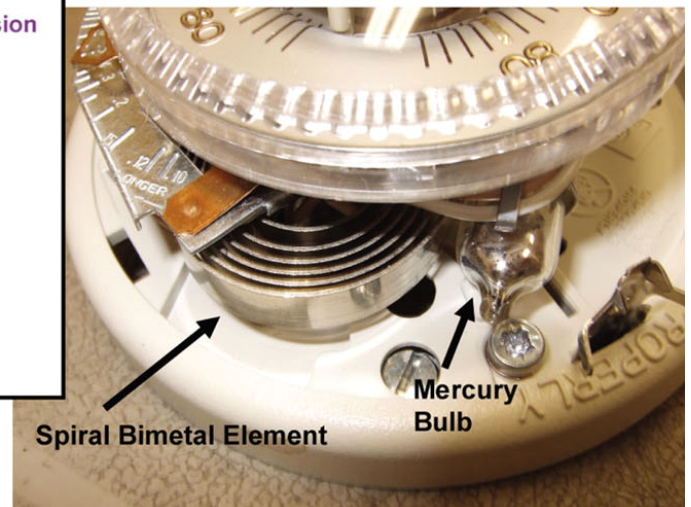
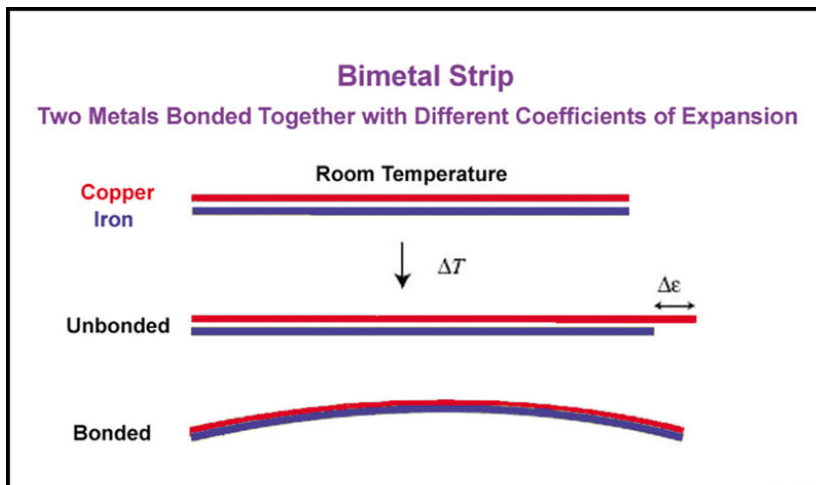
The values of α_l and α_v are increasing with rising T

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

Units: q [W/m²], 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:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad \frac{\partial T}{\partial t} = \frac{k}{c_p \rho} \frac{\partial^2 T}{\partial x^2}$$

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 σ is the electrical conductivity and L is a constant

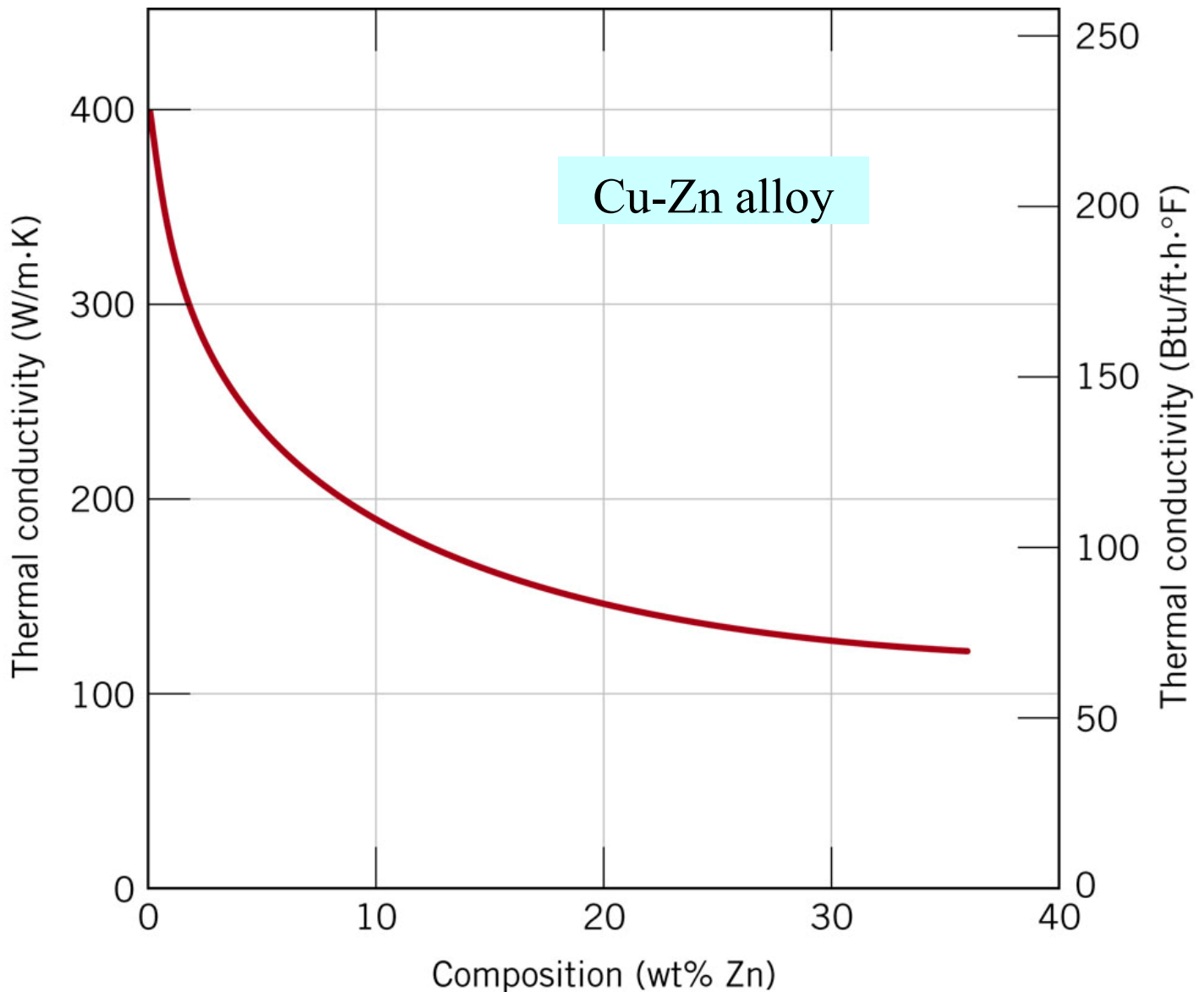
Wiedemann-Franz law

$$L = \frac{k}{\sigma T}$$

<i>Material</i>	$\frac{L}{[\Omega \cdot W / (K)^2 \times 10^{-8}]}$
Aluminum	2.20
Copper	2.25
Gold	2.50
Iron	2.71
Nickel	2.08
Silver	2.13
Tungsten	3.20
1025 Steel	—
316 Stainless steel	—
Brass (70Cu–30Zn)	—
Kovar (54Fe–29Ni–17Co)	2.80
Invar (64Fe–36Ni)	2.75
Super Invar (63Fe–32Ni–5Co)	2.68

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 .



Quest for good thermoelectric (TE) materials

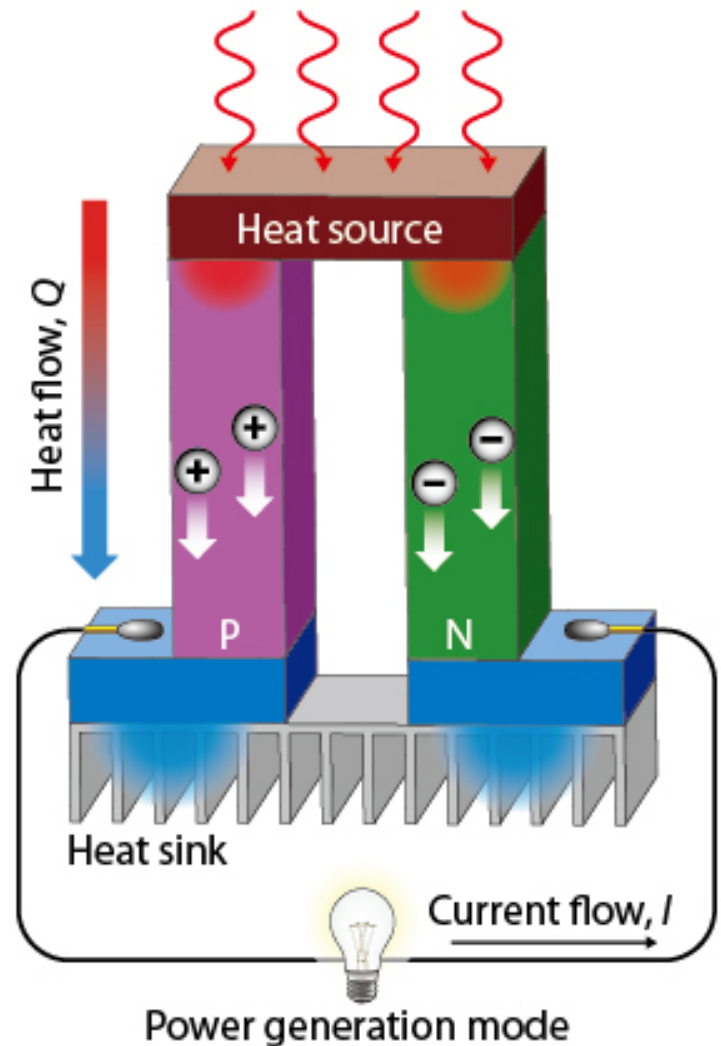
Thermoelectric conversion: conversion of thermal to electrical energy

An applied temperature difference ΔT 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 ΔV .

Figure of merit of TE material:

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

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



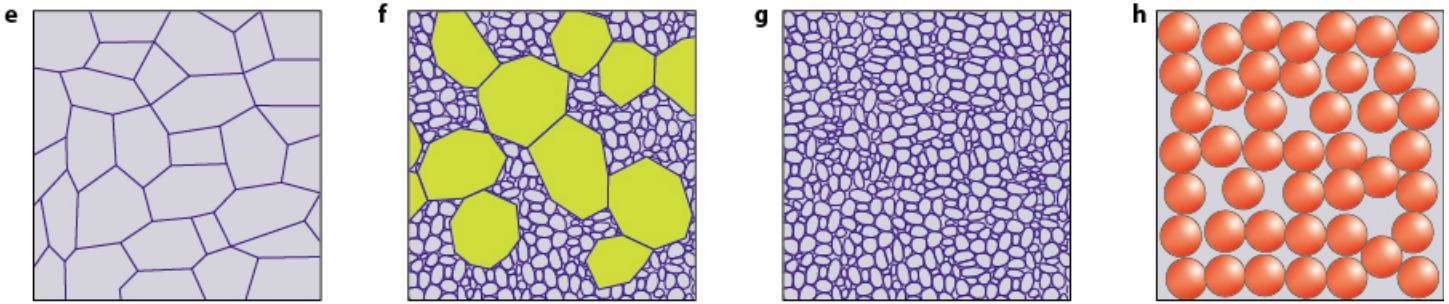
Li et al., *Nat. Asia Mater.*, 152, 2010

Good TE material: High σ (low Joule heating), large Seebeck coefficient (large ΔV), low κ (large ΔT) are necessary.

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

Quest for good thermoelectric (TE) materials

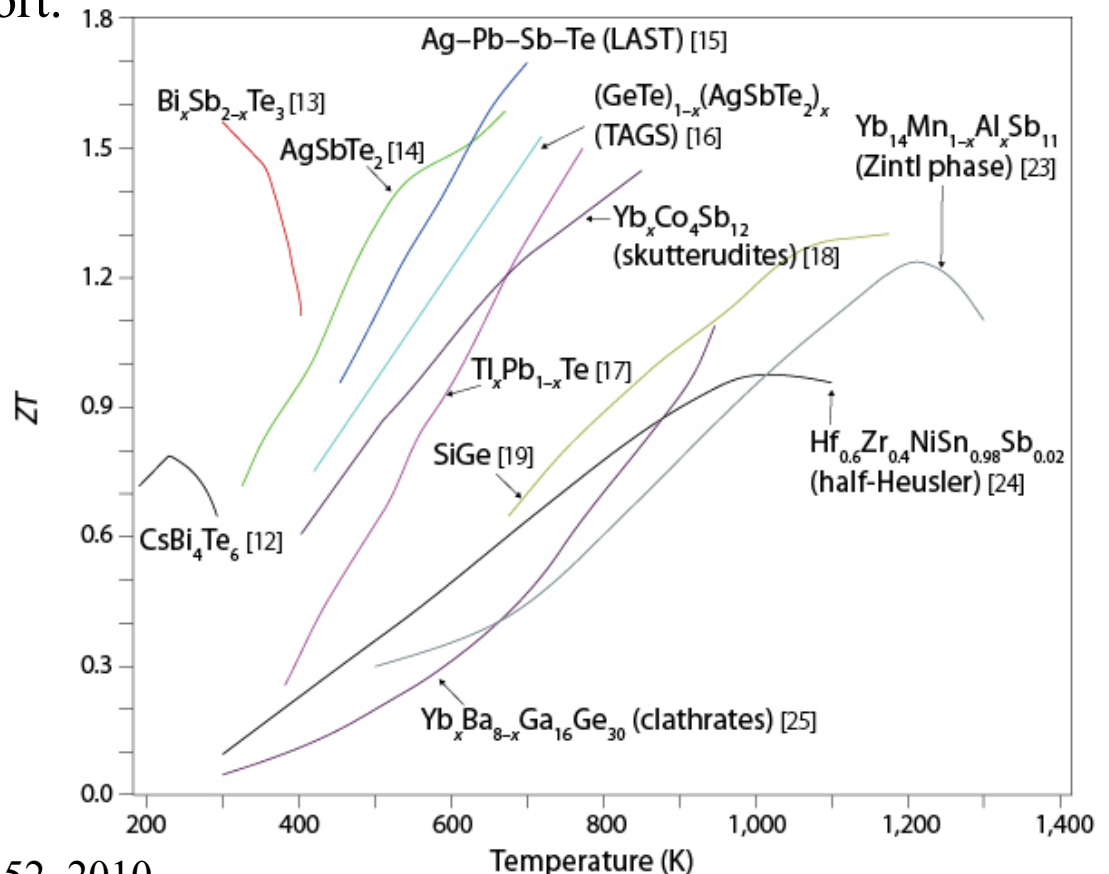
Nanostructured materials - a chance to disconnect the linkage between the thermal and electrical transport by controlling scattering mechanisms



grain boundaries, interfaces – reduction of k , but also the deterioration of carrier mobility (μ).

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



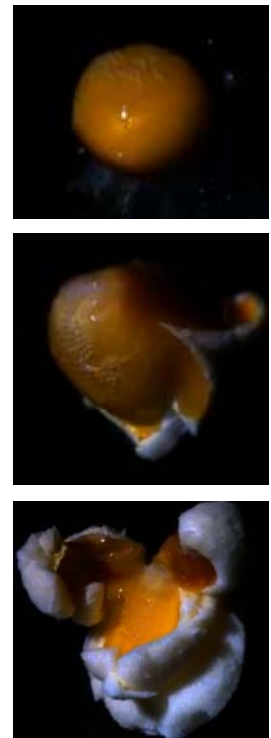
Li et al.,
Nat. Asia Mater., 152, 2010

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:

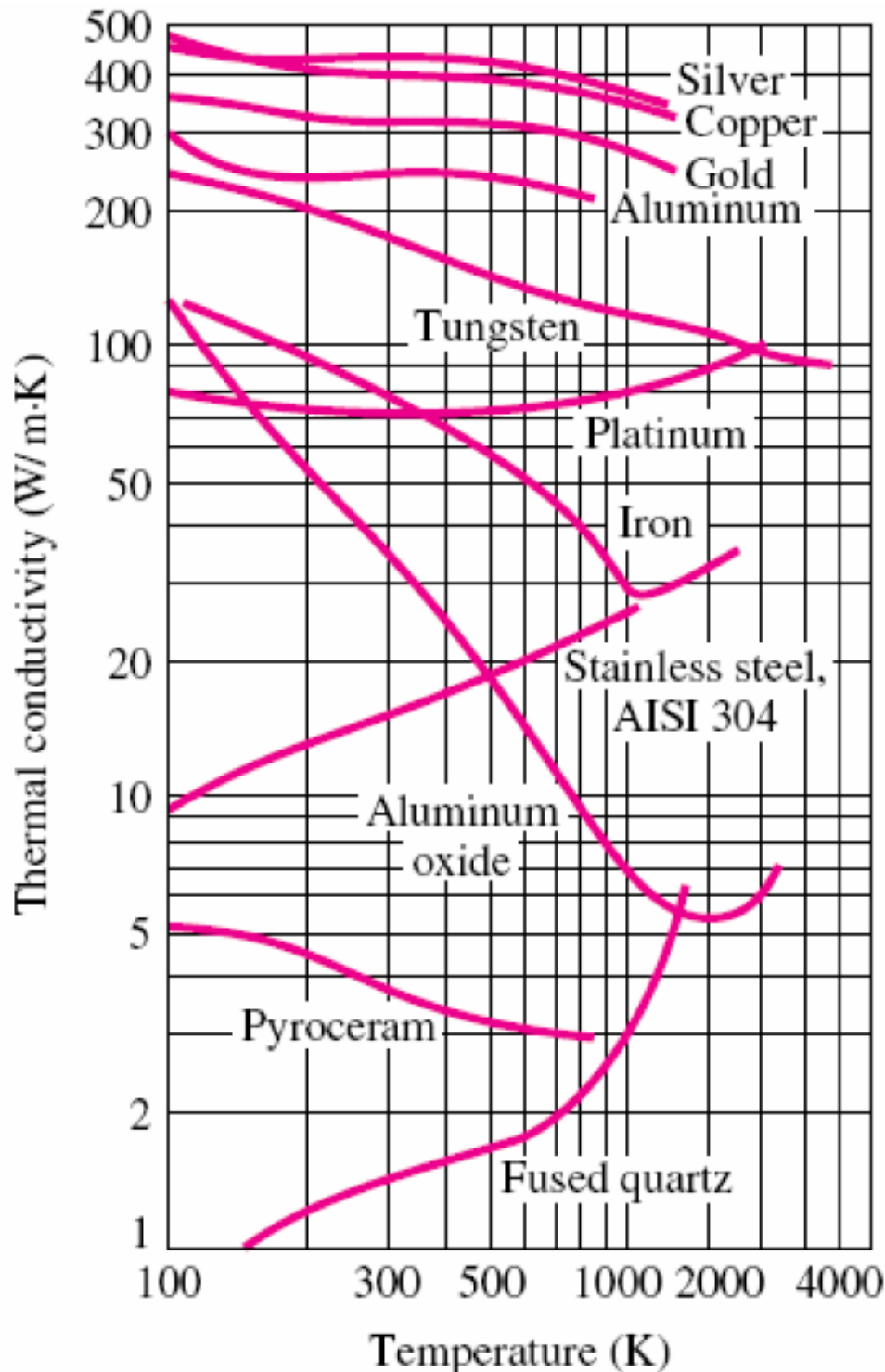
- glasses and amorphous ceramics have lower k compared to the crystalline ones (phonon scattering is more effective in irregular or disordered materials).
 - Thermal conductivity decreases with porosity (e.g. foamed polystyrene is used for drinking cups).
 - Thermal conductivity of polymers depends on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

<i>Material</i>	<i>k</i> (W/m·K) ^c
Aluminum	247
Copper	398
Gold	315
Iron	80
Nickel	90
Silver	428
Tungsten	178
1025 Steel	51.9
316 Stainless steel	15.9
Brass (70Cu–30Zn)	120
Kovar (54Fe–29Ni–17Co)	17
Invar (64Fe–36Ni)	10
Super Invar (63Fe–32Ni–5Co)	10
Alumina (Al ₂ O ₃)	39
Magnesia (MgO)	37.7
Spinel (MgAl ₂ O ₄)	15.0 ^e
Fused silica (SiO ₂)	1.4
Soda–lime glass	1.7
Borosilicate (Pyrex) glass	1.4
Polyethylene (high density)	0.46–0.50
Polypropylene	0.12
Polystyrene	0.13
Polytetrafluoroethylene (Teflon)	0.25
Phenol-formaldehyde, phenolic	0.15
Nylon 6,6	0.24
Polyisoprene	0.14

Diamond: 2310

Graphite:

along c-axis: 2000

along a-axis: 9.5

SiO₂

crystalline

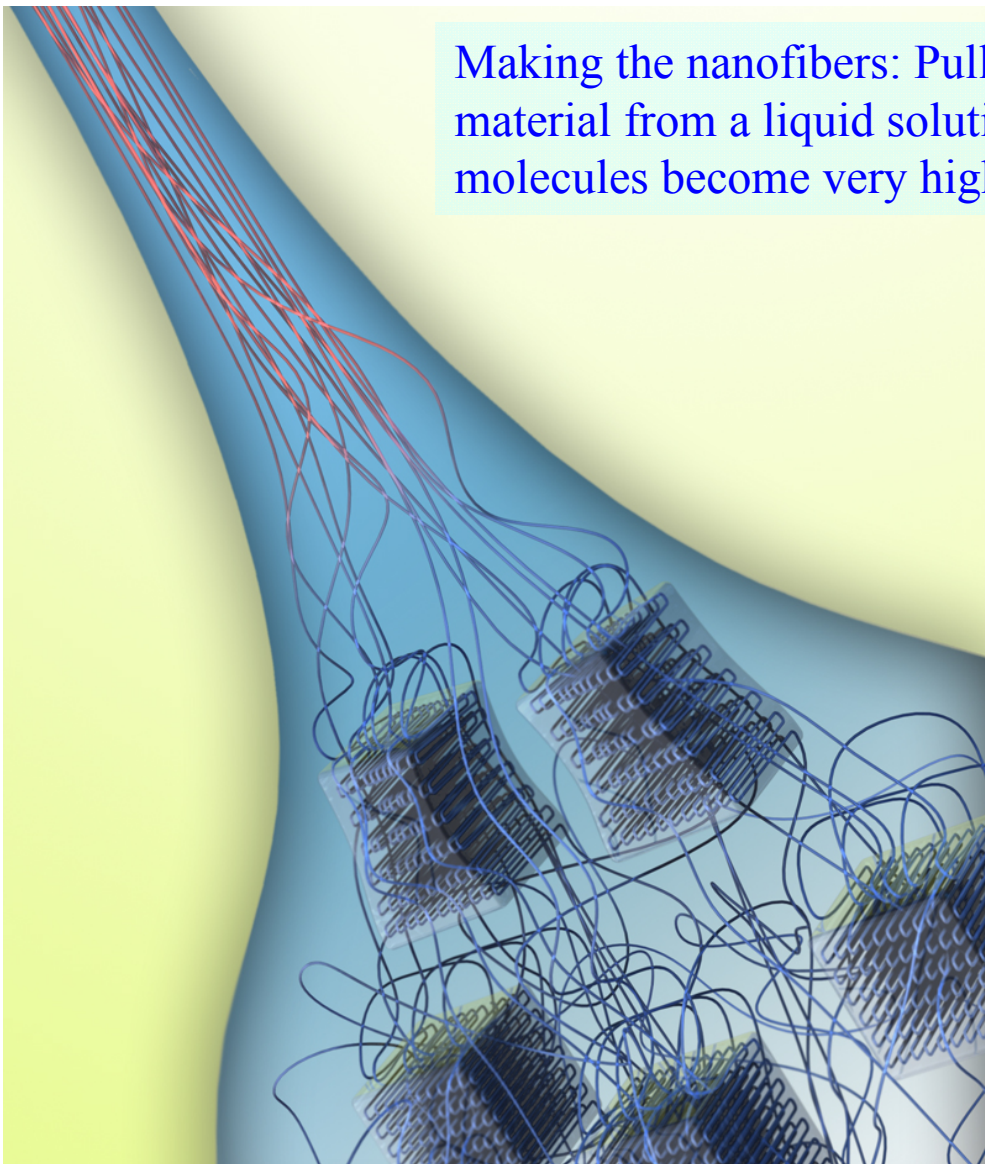
along c-axis: 10.4

along a-axis: 6.2

amorphous: 1.38

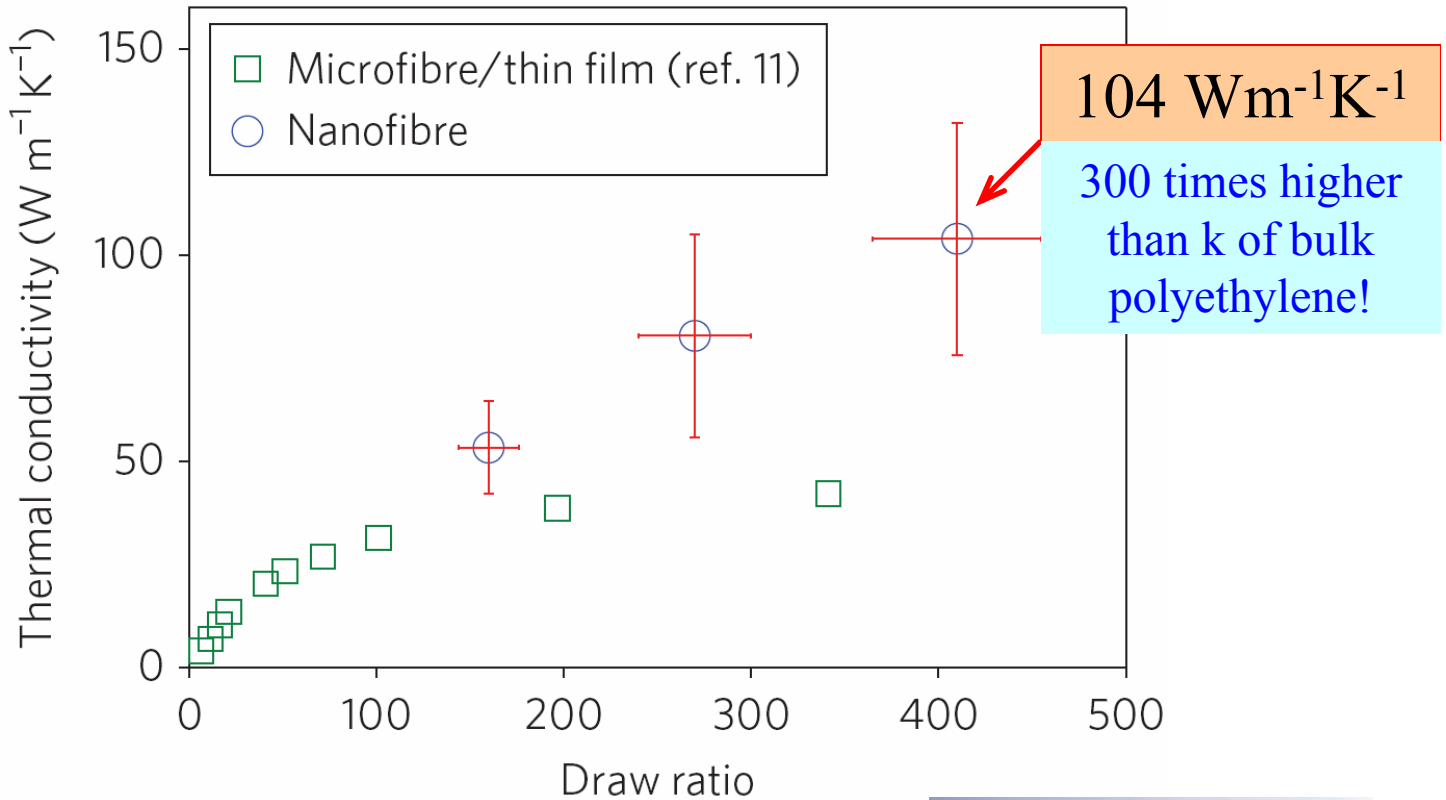
Thermal conductivity of polymer nanofibers

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.



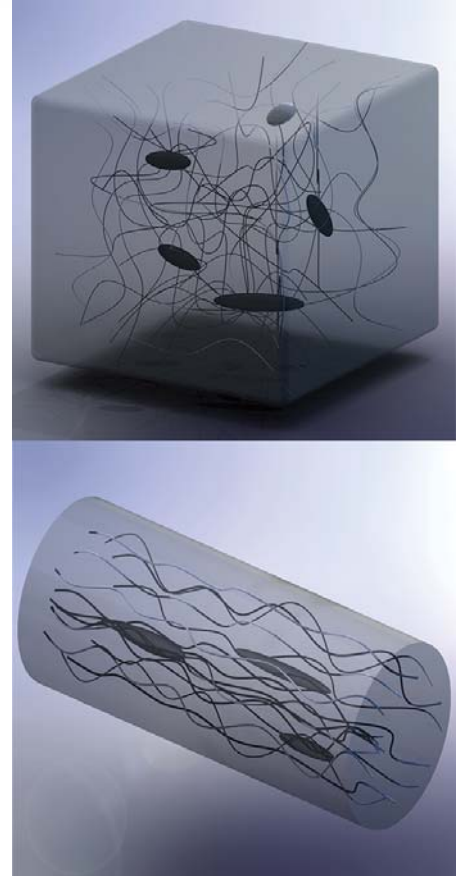
Making the nanofibers: Pulling a thin thread of material from a liquid solution - polymer molecules become very highly aligned.

Thermal conductivity of polymer nanofibers



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

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.



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, α_l is the linear coefficient of thermal expansion and ΔT is the temperature change.

Stresses from temperature gradient

Rapid heating can result in strong temperature gradients → 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):

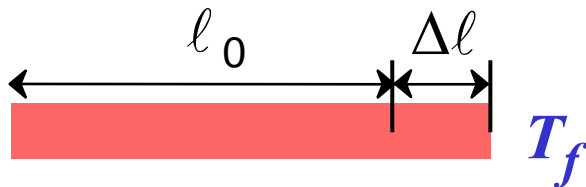
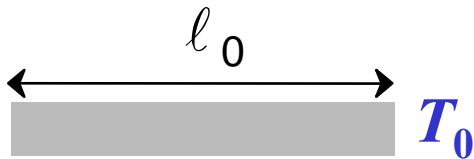
$$TSR \propto \frac{\sigma_f k}{E \alpha_\ell} \quad \text{where } \sigma_f \text{ is fracture strength of the material}$$

Restrained thermal expansion: Example problem

A brass rod is restrained but stress-free at RT (20°C).

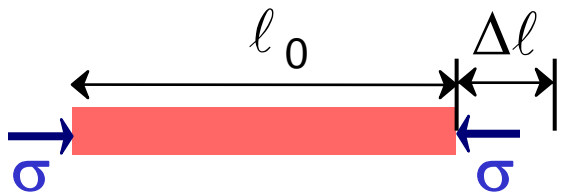
Young's modulus of brass is 100 GPa, $\alpha_\ell = 20 \times 10^{-6} \text{ } 1/^\circ\text{C}$

At what temperature does the stress reach -172 MPa?



$$\frac{\Delta \ell}{\ell_{\text{RT}}} = \epsilon_{\text{th}} = \alpha_\ell (T_f - T_0)$$

if thermal expansion is unconstrained



$$\epsilon_{\text{compress}} = -\epsilon_{\text{th}} = -\frac{\Delta \ell}{\ell_{\text{RT}}}$$

if expansion is constrained

$$\sigma = E \epsilon_{\text{compress}} = -E \alpha_\ell (T_f - T_0) = E \alpha_\ell (T_0 - T_f)$$

$$T_f = T_0 - \frac{\sigma}{E \alpha_\ell} = 20 - \frac{-172 \times 10^6 \text{ Pa}}{100 \times 10^9 \text{ Pa} \times 20 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}} = 106 \text{ } ^\circ\text{C}$$

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

