Chapter 11: Thermal Properties

ISSUES TO ADDRESS...

- How do materials respond to the application of heat?
- How do we define and measure...
  -- heat capacity?
  -- thermal expansion?
  -- thermal conductivity?
  -- thermal shock resistance?
- How do the thermal properties of ceramics, metals, and polymers differ?

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Heat Capacity

The ability of a material to absorb heat

- **Quantitatively**: "The energy required to produce a unit rise in temperature for one mole of a material"

heat capacity (J/mol-K)

$$C = \frac{dQ}{dT}$$

dQ: energy required to produce a dT temperature change (J/mol)

dT: temperature change (K)

- Two ways to measure heat capacity:
  C_p : Heat capacity at constant pressure.
  C_v : Heat capacity at constant volume.

  C_p usually > C_v (*This difference is very slight for most solid materials at room temperature and below*)

- Heat capacity has units of $\frac{\mathrm{J}}{\mathrm{mol} \cdot \mathrm{K}}$

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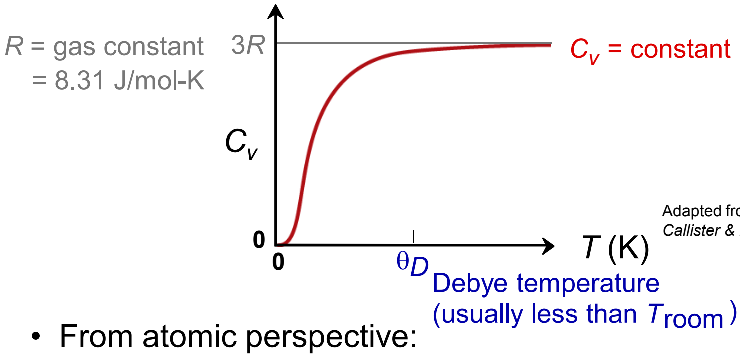
Dependence of Heat Capacity on Temperature

- Heat capacity...
  -- increases with temperature
  -- for solids it reaches a limiting value of $3R$



Adapted from Fig. 19.2, *Callister & Rethwisch 8e.*

- From atomic perspective:
  -- Energy is stored as atomic vibrations.
  -- As temperature increases, the average energy of atomic vibrations increases.

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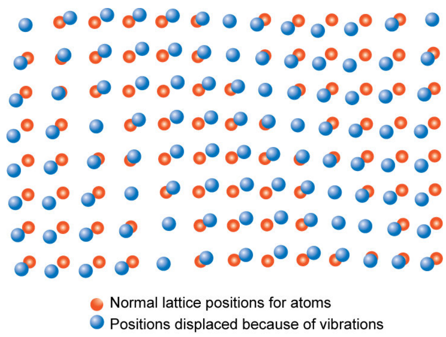
Atomic Vibrations

- Atomic vibrations are in the form of lattice waves or **phonons**

•Atoms in solid materials are constantly vibrating at very high frequencies and with relatively small amplitudes.

•Rather than being independent of one another, the vibrations of adjacent atoms are coupled by virtue of the atomic bonding.



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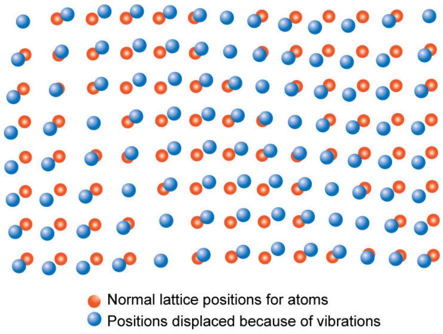
Atomic Vibrations

•These vibrations are coordinated in such a way that traveling lattice waves are produced.

•These may be thought of as **elastic waves** or simply **sound waves**, having short wavelengths and very high frequencies, which propagate through the crystal at the velocity of sound.

•The vibrational thermal energy for a material consists of a series of these elastic waves: A single quantum of vibrational energy is called a "**phonon**".



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Specific Heat: Comparison

increasing c_p

Material	c_p (J/kg-K) at room T
• Polymers	
Polypropylene	1925
Polyethylene	1850
Polystyrene	1170
Teflon	1050
• Ceramics	
Magnesia (MgO)	940
Alumina (Al_2O_3)	775
Glass	840
• Metals	
Aluminum	900
Steel	486
Tungsten	138
Gold	128

c_p (specific heat): (J/kg-K)
C_p (heat capacity): (J/mol-K)

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Mechanism of Heat Conduction:

•Heat is transported in solid materials by both "**lattice vibration waves (phonons)**" and "**free electrons**".
•A thermal conductivity is associated with each of these mechanisms, and the total conductivity is the sum of the two contributions.

$$k = k_l + k_e$$

•The k_l contribution results from a net movement of phonons from high to low temperature regions of a body across which a temperature gradient exists.

•Free or conducting electrons participate in electronic thermal conduction. They gain kinetic energy, and then migrate to colder areas, where some of this kinetic energy is transferred to the atoms themselves as a consequence of collisions with phonons or other imperfections in the crystal.

•The relative contribution of $\mathbf{k_e}$ *to the total thermal conductivity increases with increasing free electron concentrations, since more electrons are available to participate in this heat transference process.*

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Metals:

•In high-purity metals, the "**electron mechanism**" of heat transport is much more efficient than the "**phonon**" contribution because electrons are not as easily scattered as phonons and have higher velocities.

•Relatively large numbers of free electrons exist that participate in thermal conduction.

•Alloying metals with impurities results in a reduction in the thermal conductivity, for the same reason that the electrical conductivity is diminished:

- ➢ The impurity atoms, especially if in solid solution, act as scattering centers, lowering the efficiency of electron motion.

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Ceramics:

•Nonmetallic materials are thermal insulators: they lack large numbers of free electrons. Thus the "**phonons**" are primarily responsible for thermal conduction:

•The phonons are not as effective as free electrons in the transport of heat energy as a result of the very efficient phonon scattering by lattice imperfections.

•The scattering of lattice vibrations becomes more pronounced with rising temperature; hence, the thermal conductivity of most ceramic materials normally diminishes with increasing temperature.

•Porosity in ceramic materials may have a dramatic influence on thermal conductivity; increasing the pore volume will, under most circumstances, result in a reduction of the thermal conductivity.

(Many ceramics that are used for thermal insulation are porous. Heat transfer across pores is ordinarily slow and inefficient. Internal pores normally contain still air, which has an extremely low thermal conductivity. Furthermore, gaseous convection within the pores is also comparatively ineffective)

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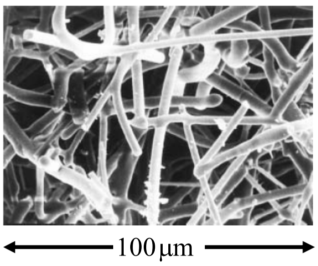

Silica fiber insulation
offers low heat conduction

•This photograph shows a white hot cube of a **silica fiber insulation material**, which, only seconds after having been removed from a hot furnace, can be held by its edges with the bare hands.

•Initially, the heat transfer from the surface is relatively rapid; however, the thermal conductivity of this material is so small that heat conduction from the interior [**maximum temperature approximately 1250 °C**] is extremely slow.

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Polymers:

•Energy transfer is accomplished by the vibration and rotation of the chain molecules.

•The magnitude of the thermal conductivity depends on the degree of crystallinity; a polymer with a highly crystalline and ordered structure will have a greater conductivity than the equivalent amorphous material.

•This is due to the more effective coordinated vibration of the molecular chains for the crystalline state.

•Polymers are often utilized as thermal insulators because of their low thermal conductivities.

•As with ceramics, their insulative properties may be further enhanced by the introduction of small pores (foamed polystyrene)

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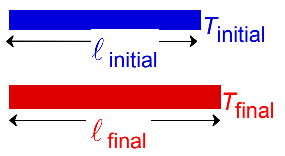
Thermal Expansion

Materials change size when temperature is changed.



$T_{\text{final}} > T_{\text{initial}}$

$$\frac{l_{\text{final}} - l_{\text{initial}}}{l_{\text{initial}}} = \alpha_l \left(T_{\text{final}} - T_{\text{initial}}\right)$$

linear coefficient of thermal expansion (1/K or 1/ºC)

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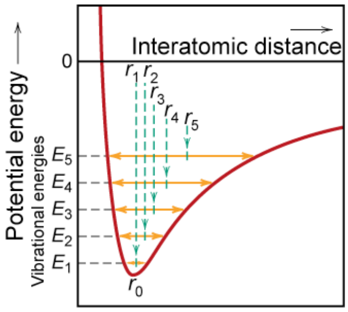
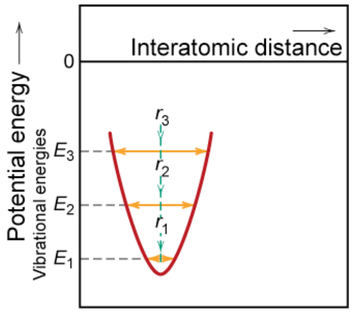
Atomic Perspective: Thermal Expansion





Asymmetric curve:
- -- increase temperature,
- -- increase in interatomic separation
- -- thermal expansion

Symmetric curve:
- -- increase temperature,
- -- no increase in interatomic separation
- -- no thermal expansion

Adapted from Fig. 19.3, *Callister & Rethwisch 8e*.

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Coefficient of Thermal Expansion: Comparison

Material	α_ℓ (10^{-6}/°C) at room *T*
• Polymers	
Polypropylene	145-180
Polyethylene	106-198
Polystyrene	90-150
Teflon	126-216
• Metals	
Aluminum	23.6
Steel	12
Tungsten	4.5
Gold	14.2
• Ceramics	
Magnesia (MgO)	13.5
Alumina (Al_2O_3)	7.6
Soda-lime glass	9
Silica (cryst. SiO_2)	0.4

increasing α_ℓ

Polymers have larger α_ℓ values because of weak secondary bonds

- **Q: Why does α_ℓ generally decrease with increasing bond energy?**

Selected values from Table 19.1, *Callister & Rethwisch 8e*.

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Thermal Expansion: Example

Ex: A copper wire 15 m long is cooled from 40 to -9ºC. How much change in length will it experience?

- Answer: For Cu $\alpha_\ell = 16.5 \text{ x } 10^{-6} \; (^\circ\text{C})^{-1}$

$$\Delta\ell = \alpha_\ell \ell_0 \Delta T = [16.5 \text{ x } 10^{-6}(1/^\circ\text{C})](15\text{ m})[40^\circ\text{C} - (-9^\circ\text{C})]$$

$$\boxed{\Delta\ell = 0.012\text{ m} = 12\text{ mm}}$$

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Thermal Conductivity

The ability of a material to transport heat.

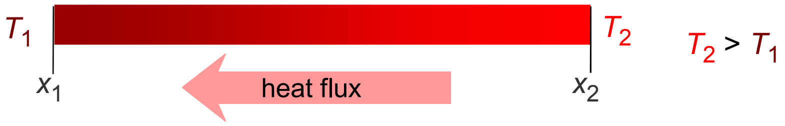
Fourier's Law

$$q = -k\frac{dT}{dx}$$

heat flux (J/m²-s)

temperature gradient

thermal conductivity (J/m-K-s)



- Atomic perspective: Atomic vibrations and free electrons in hotter regions transport energy to cooler regions.

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Thermal Conductivity: Comparison

increasing k

Material	k (W/m-K)	Energy Transfer Mechanism
• Metals		
Aluminum	247	atomic vibrations and motion of free electrons
Steel	52	
Tungsten	178	
Gold	315	
• Ceramics		
Magnesia (MgO)	38	atomic vibrations
Alumina (Al_2O_3)	39	
Soda-lime glass	1.7	
Silica (cryst. SiO_2)	1.4	
• Polymers		
Polypropylene	0.12	vibration/rotation of chain molecules
Polyethylene	0.46-0.50	
Polystyrene	0.13	
Teflon	0.25	

Selected values from Table 19.1, *Callister & Rethwisch 8e*.

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Thermal Stresses

•Thermal stresses are stresses induced in a body as a result of changes in temperature.

- Occur due to:
  -- restrained thermal expansion/contraction
  -- temperature gradients that lead to differential dimensional changes

$$\text{Thermal stress} = \sigma = E\alpha_\ell(T_0 - T_f) = E\alpha_\ell \Delta T$$

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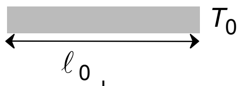
Example Problem

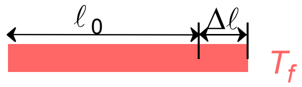
-- A brass rod is stress-free at room temperature (20ºC).
-- It is heated up, but prevented from lengthening.
-- At what temperature does the stress reach -172 MPa?

Solution:



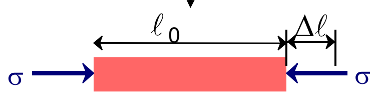
Original conditions

Step 1: Assume unconstrained thermal expansion



$$\frac{\Delta \ell}{\ell_{room}} = \varepsilon_{thermal} = \alpha_\ell (T_f - T_0)$$

Step 2: Compress specimen back to original length



$$\varepsilon_{compress} = \frac{-\Delta \ell}{\ell_{room}} = -\varepsilon_{thermal}$$

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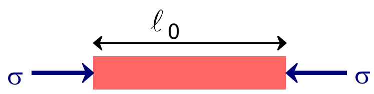
Example Problem (cont.)



The thermal stress can be directly calculated as

$$\sigma = E(\varepsilon_{compress})$$

Noting that $\varepsilon_{compress}$ = -$\varepsilon_{thermal}$ and substituting gives

$$\sigma = -E(\varepsilon_{thermal}) = -E\alpha_\ell (T_f - T_0) = E\alpha_\ell (T_0 - T_f)$$

Rearranging and solving for T_f gives

20ºC

-172 MPa (since in compression)

$$T_f = T_0 - \frac{\sigma}{E\alpha_\ell}$$

Answer: 106ºC

100 GPa

20 x 10^{-6}/ºC

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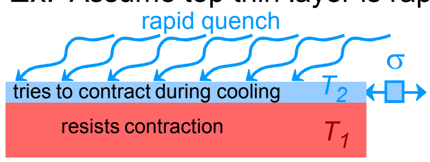
Thermal Shock Resistance

- Occurs due to: non-uniform heating/cooling
- Ex: Assume top thin layer is rapidly cooled from T_1 to T_2



Tension develops at surface

$$\sigma = -E\alpha_\ell (T_1 - T_2)$$

Temperature difference that can be produced by cooling:

$$(T_1 - T_2) = \frac{\text{quench rate}}{k}$$

Critical temperature difference for fracture (set $\sigma = \sigma_f$)

$$(T_1 - T_2)_{\text{fracture}} = \frac{\sigma_f}{E\alpha_\ell}$$

set equal

- $(\text{quench rate})_{\text{for fracture}} = \text{Thermal Shock Resistance } (TSR) \propto \dfrac{\sigma_f k}{E\alpha_\ell}$
- Large TSR when $\dfrac{\sigma_f k}{E\alpha_\ell}$ is large

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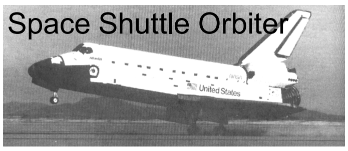
Thermal Protection System

- Application:



Chapter-opening photograph, Chapter 23, *Callister 5e* (courtesy of the National Aeronautics and Space Administration.)

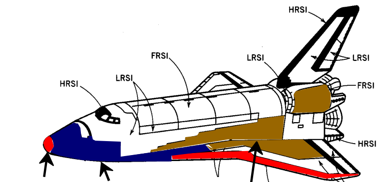
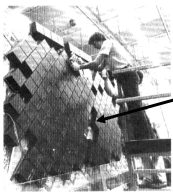
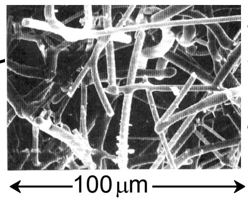


Fig. 19.2W, *Callister 6e*. (Fig. 19.2W adapted from L.J. Korb, C.A. Morant, R.M. Calland, and C.S. Thatcher, "The Shuttle Orbiter Thermal Protection System", *Ceramic Bulletin*, No. 11, Nov. 1981, p. 1189.)

- Silica tiles (400-1260°C):
  -- large scale application

-- microstructure:





~90% porosity!
Si fibers bonded to one another during heat treatment.

Fig. 19.3W, *Callister 5e*. (Fig. 19.3W courtesy the National Aeronautics and Space Administration.)

Fig. 19.4W, *Callister 5e*. (Fig. 219.4W courtesy Lockheed Aerospace Ceramics Systems, Sunnyvale, CA.)

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Summary

The thermal properties of materials include:

- **Heat capacity**:
  -- energy required to increase a mole of material by a unit *T*
  -- energy is stored as atomic vibrations
- **Coefficient of thermal expansion**:
  -- the size of a material changes with a change in temperature
  -- polymers have the largest values
- **Thermal conductivity**:
  -- the ability of a material to transport heat
  -- metals have the largest values
- **Thermal shock resistance**:
  -- the ability of a material to be rapidly cooled and not fracture
  -- is proportional to $\frac{\sigma_f k}{E\alpha_\ell}$