Thermal Properties of Materials

Topics included:

- How do materials respond to the application of heat?
- How do we define and measure...
  -- heat capacity and specific heat?
  -- thermal expansion?
  -- thermal conductivity?
  -- thermal shock resistance?
- Mechanism of heat absorbtion in solids.
- Difference between the thermal properties of ceramics, metals, and polymers?

What is meant by thermal properties of materials

- Thermal property refers to the response of a material to the application of heat.
- When solid absorbs energy in the form of heat, its temperature rises and its dimensions increase.
- The energy may be transported to cooler regions of the specimen if temperature gradients exist, and ultimately, the specimen may melt.
- Heat capacity, thermal expansion, and thermal conductivity are properties that are often critical in the practical use of solids.

Heat Capacity

The ability of a material to absorb heat, i.e.

- the amount of energy required to produce a unit temperature rise

heat capacity (J/mol-K)

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

energy input (J/mol)

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

- Heat capacity has units of $\frac{\text{J}}{\text{mol} \cdot \text{K}} \left(\frac{\text{Btu}}{\text{lb - mol} \cdot {}^\circ\text{F}} \right)$

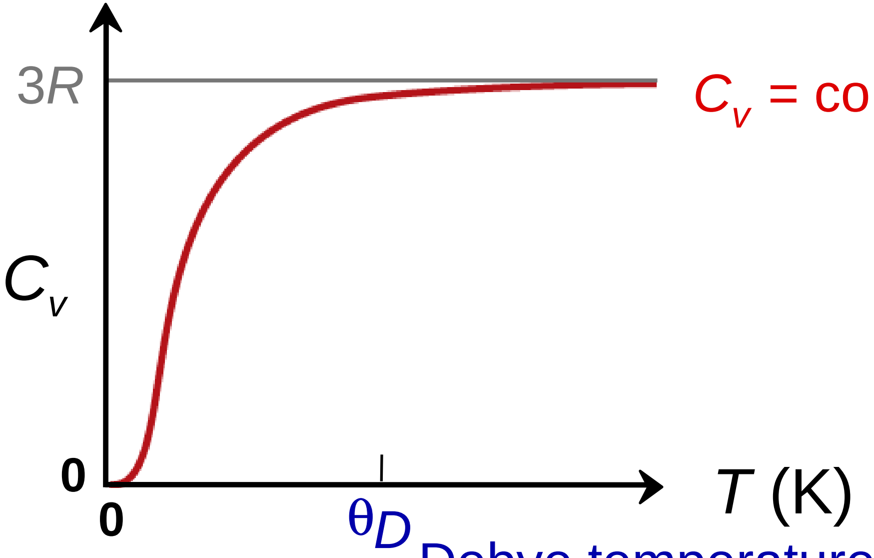
Specific Heat

- Often denoted by a lowercase c
- this represents the heat capacity per unit mass
- units (J/kg · K, cal/g · K)

Dependence of Heat Capacity on Temperature

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

R = gas constant
= 8.31 J/mol-K



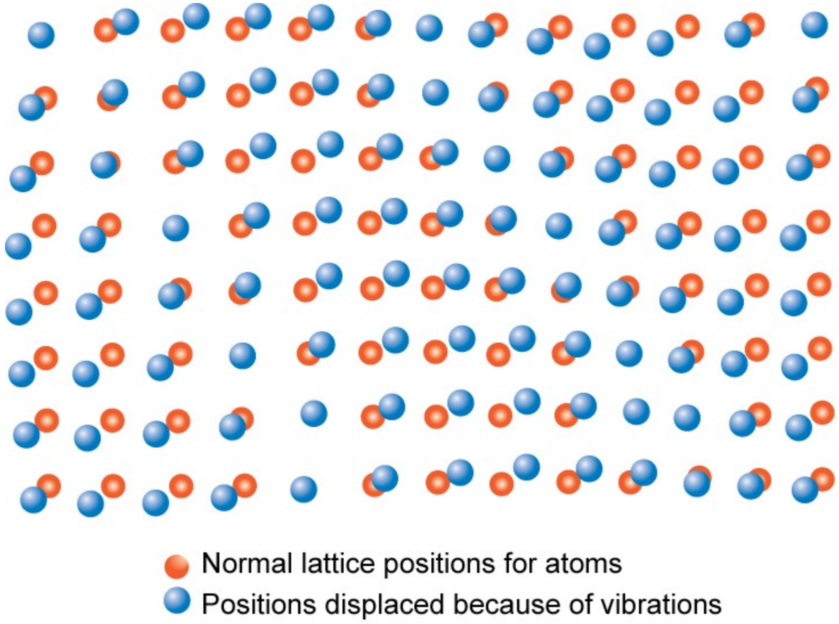
C_v = constant

θ_D Debye temperature (usually less than T_{room})

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

Atomic Vibrations

- Vibrational Heat Capacity
- Atoms in solid materials are constantly vibrating at very high frequencies and with relatively small amplitudes.
- Atomic vibrations are in the form of elastic waves
- Single quantum of vibrational energy is called a **phonon**



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)

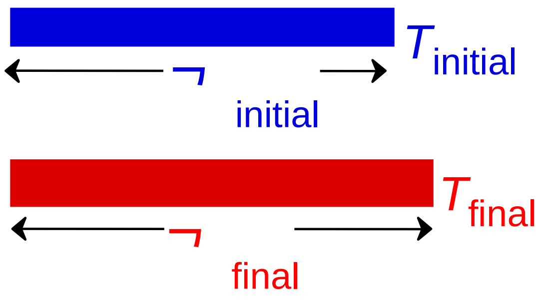
C_p (heat capacity): (J/mol-K)

- Why is c_p significantly larger for polymers?

Thermal Expansion

Materials change size when temperature is changed

✔ Most solid materials expand upon heating and contract when cooled.



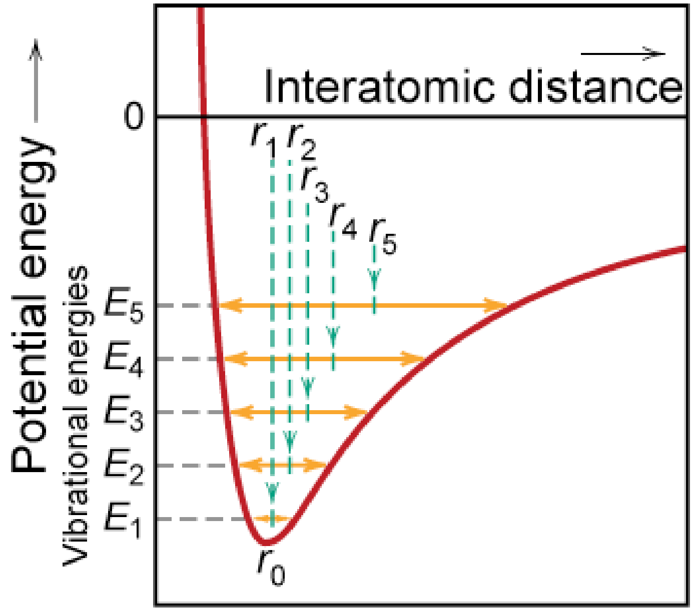
$T_{final} > T_{initial}$

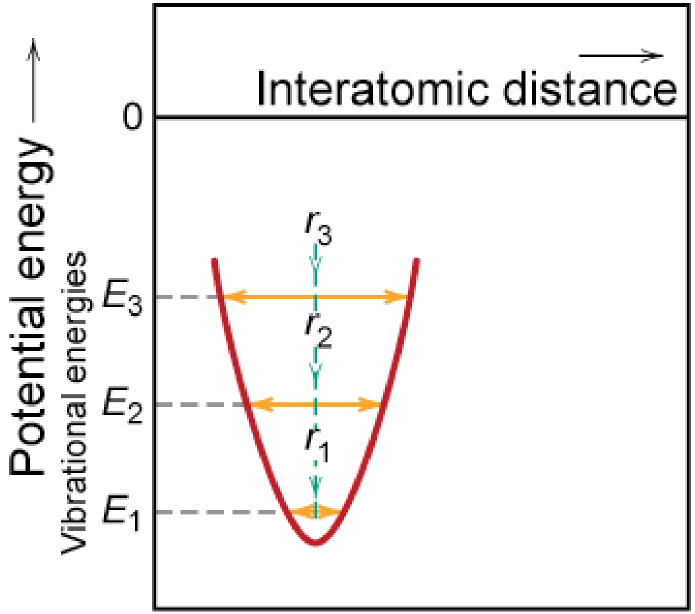
$$\frac{l_{final} - l_{initial}}{l_{initial}} = \alpha_l (T_{final} - T_{initial})$$

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

- α – a material property
- extent to which a material expands upon heating
- units of reciprocal temperature [(°C)$^{-1}$ or (°F)$^{-1}$]

Atomic Perspective: Thermal Expansion





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

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

Coefficient of Thermal Expansion: Comparison

increasing E_{bond}

Material	α $(10^{-6}\,(^{o}C)^{-1})$ 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

Polymers have larger α values because of weak secondary bonds

Q: Why does α generally decrease with increasing bond energy?

Thermal Expansion: Example

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

- For Cu $\alpha_\ell = 16.5 \times 10^{-6}\ (^\circ C)^{-1}$

Thermal Expansion: Example

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

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

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

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 (Unit?)

$T_2 > T_1$

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

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Mechanisms of Heat Conduction

In solid materials,

- heat is transported by both lattice vibration waves (phonons) and free electrons.
- Thermal conductivity is associated with each of these mechanisms,
- Total conductivity is the sum of the two contributions,

$$k = k_l + k_e$$

- Thermal energy associated with phonons or lattice waves is transported in the direction of their motion.

- 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.

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.
- Because free electrons are responsible for both electrical and thermal conduction in pure metals, the two conductivities should be related.
- According to the Wiedemann–Franz law:

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

where σ is the electrical conductivity,
T is the absolute temperature, and
L is a constant, known as Lorenz number with a theoretical value of
$2.44 \times 10^{-8}\ V^2/K^2$, should be independent of temperature
and the same for all metals if the heat energy is transported entirely by free electrons.

Ceramics

- they lack large numbers of free electrons
- the phonons are primarily responsible for thermal conduction:
- k_e is much smaller than k_l
- 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.
- phonon scattering is much dominant when the atomic structure is highly disordered and irregular.
- Porosity in ceramic materials may have a dramatic influence on thermal conductivity;
- Increasing the pore volume results in a reduction of the thermal conductivity.

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 has a greater conductivity than the equivalent amorphous material

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	

Thermal Stresses

- Occur due to:
  -- restrained thermal expansion/contraction
  -- temperature gradients that lead to differential dimensional changes
  – May result in fracture or undesirable plastic deformation.

Thermal stress

$$\sigma = E\alpha_l (T_0 - T_f) = E\alpha_l \Delta T$$

Upon heating ($T_f > T_0$), the stress is compressive ($\sigma < 0$) because rod expansion has been constrained.
If the rod specimen is cooled ($T_f < T_0$), a tensile stress is imposed ($\sigma > 0$).

Example:

-- A brass rod is stress-free at room temperature (20ºC).

-- It is heated up, but held rigidly to the clamps.

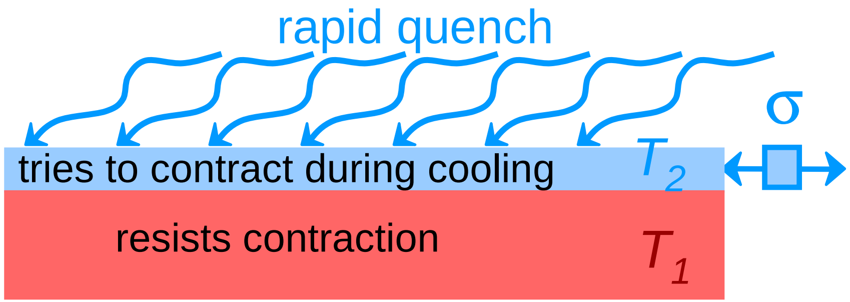
-- At what temperature does the *compressive* stress reach 172 Mpa?

– Assume a modulus of elasticity of 100 GPa for brass.

– linear coefficient of thermal expansion for brass: 20.0×10^{-6} $(°C)^{-1}$

Thermal Shock Resistance

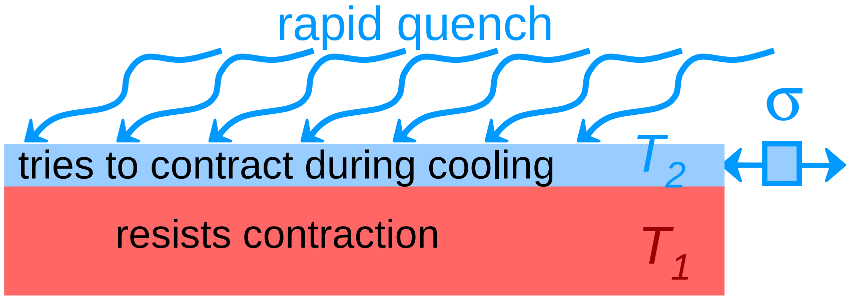
- Occurs due to: nonuniform heating/cooling
- Ex: Assume top thin layer is rapidly cooled from T_1 to T_2



Tension develops at surface

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

Thermal Shock Resistance



Tension develops at surface

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

Temperature difference that can be produced by cooling:

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

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

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

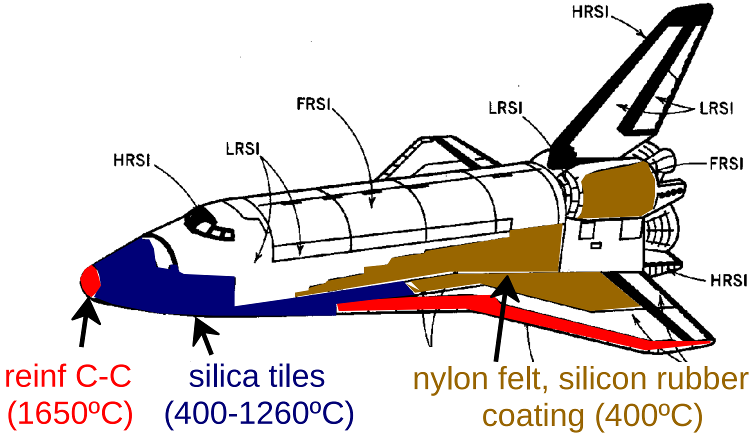
set equal

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

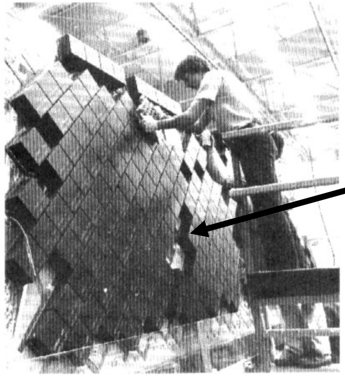
Thermal Protection Systems prevalent for different kind of materials

Thermal Protection System

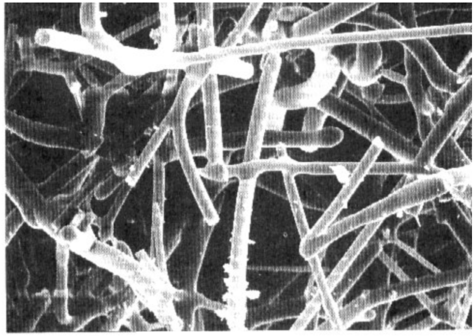
- Application:



- Silica tiles (400-1260ºC):
  -- large scale application



-- microstructure:



←100 μm→

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

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 $\dfrac{\sigma_f k}{E\alpha_\ell}$