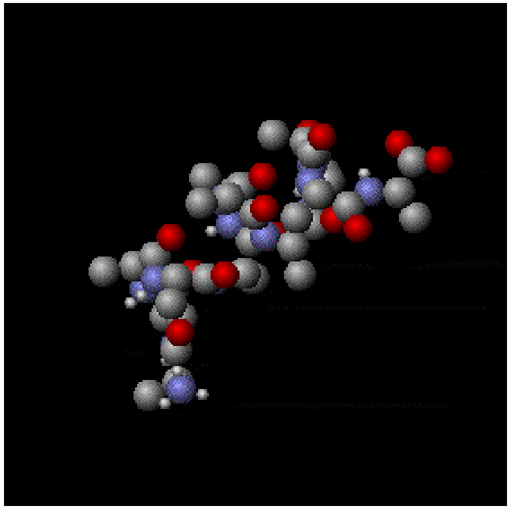
MS31007: Chapter 11

Thermal Properties

Dr. Prasana Sahoo, MSC, IIT Kharagpur
prasana@matsc.iitkgp.ac.in

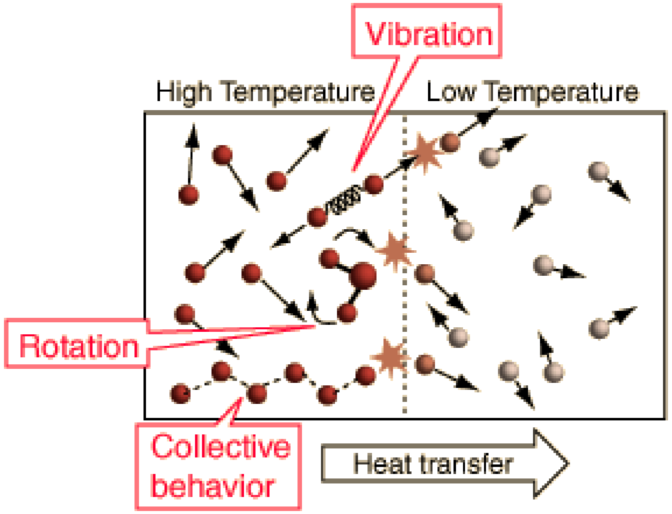
Thermal Properties

- Heat capacity
  - ✓ atomic vibrations, phonons
  - ✓ temperature dependence
  - ✓ contribution of electrons
- Specific Heat
- Thermal Energy Mechanism
  - ✓ connection to anharmonicity of interatomic potential
  - ✓ linear and volume coefficients of thermal expansion
- Thermal Expansion
- Thermal Conductivity heat transport by phonons and electrons
- Thermal Stresses
- Thermal Shock
- Applications where these parameters are significant

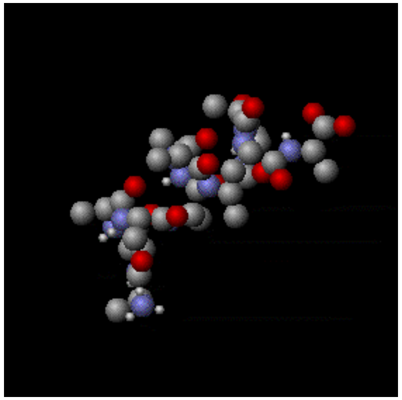


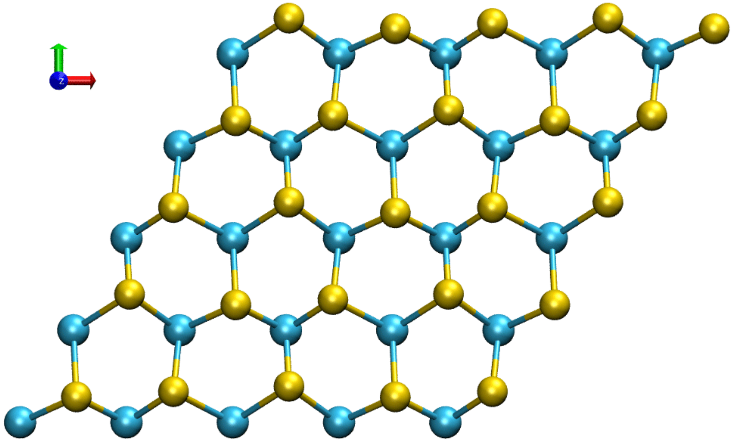
Thermal Energy

- The energy needed to raise the temperature of an object depends on the mass and composition of the object.
- An object's temperature is a measure of the random molecular motions. Individual atoms and molecules are never still.



Atomic Vibrations

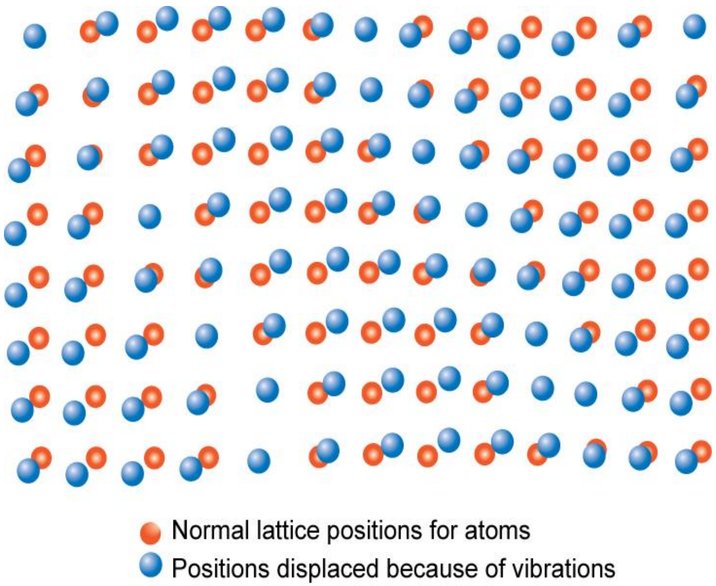




• Faster molecules striking slower ones at the boundary in elastic collisions will increase the velocity of the slower ones and decrease the velocity of the faster ones, transferring energy from the higher temperature to the lower temperature region.

• With time, the molecules in the two regions approach the same average kinetic energy (same temperature) and in this condition of thermal equilibrium there is no longer any net transfer of energy from one object to the other.

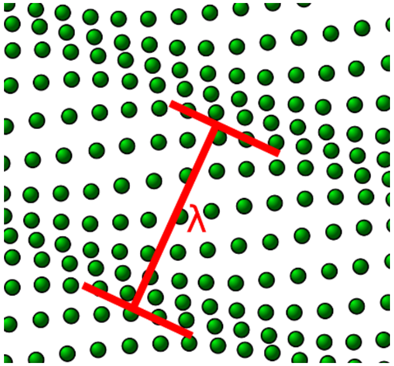
Atomic Vibrations

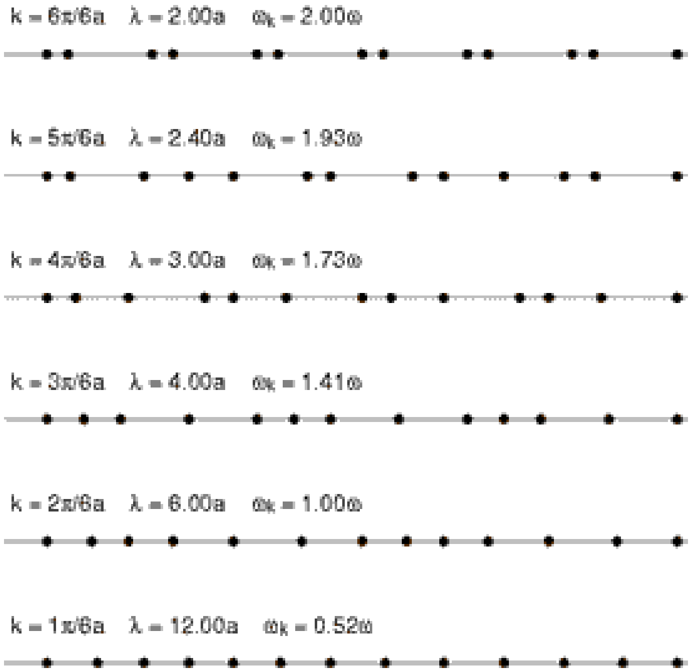


Longitudinal Acoustical Mode:

Transverse Acoustical Mode:

Atomic vibrations are in the form of lattice waves or phonons.





Animation showing the first 6 normal modes of a one-dimensional lattice: a linear chain of particles. The shortest wavelength is at top, with progressively longer wavelengths below.

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 v, there is the smallest "quantum" of **vibrational energy**, *hv*, called **phonon**.

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

Heat Capacity

Heat Capacity (C) - a material's ability to absorb heat from the external surroundings

- Quantitatively: The energy required to produce a unit rise in temperature for one mole of a material.
  - an extensive property dependent on the amount of material.
  - measures the combined effect of mass and composition.

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

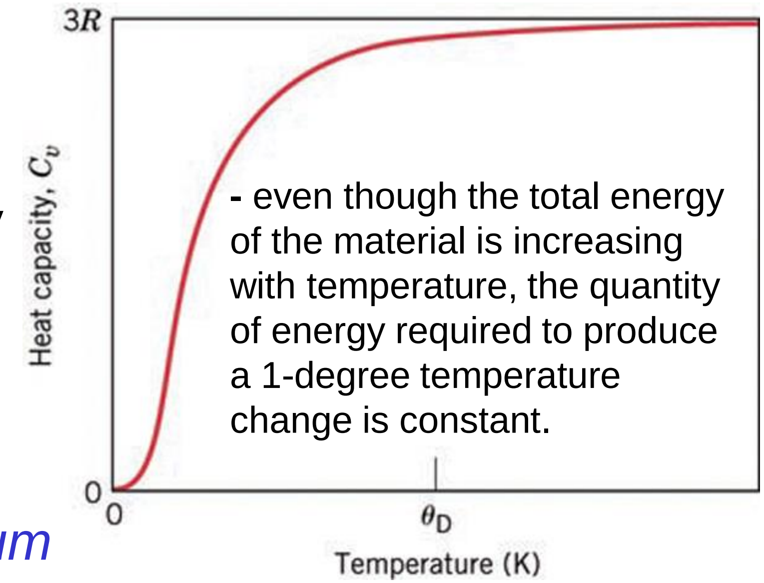
- Heat capacity has units of $\frac{\mathrm{J}}{\mathrm{mol \cdot K}}$

Specific heat, c, is sometimes used; this represents the heat capacity per unit mass and has various units (J/kg · K, cal/g · K, Btu/lb_m · °F)

- is a property of the composition only
- It measures the energy required to increase the temperature of a unit quantity of a specific substance by a specific temperature interval.

Temperature Dependence of the Heat Capacity

Heat capacity has a weak temperature dependence **at high temperatures** (> Debye temperature θ_D) but decreases down to zero as T approaches 0K.



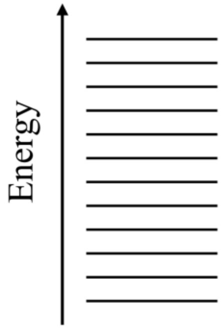
The constant value of the heat capacity of many simple solids is sometimes called *Dulong – Petit law*

For many solids at room temperature,

$$C_v \approx 3R = 25\ JK^{-1}mol^{-1}$$

The low-T behavior can be explained by *quantum theory* -Debye advanced the theory by treating the quantum oscillators as collective modes in the solid (phonons) and showed that

$$C_v \sim AT^3 \text{ at } T \rightarrow 0K$$



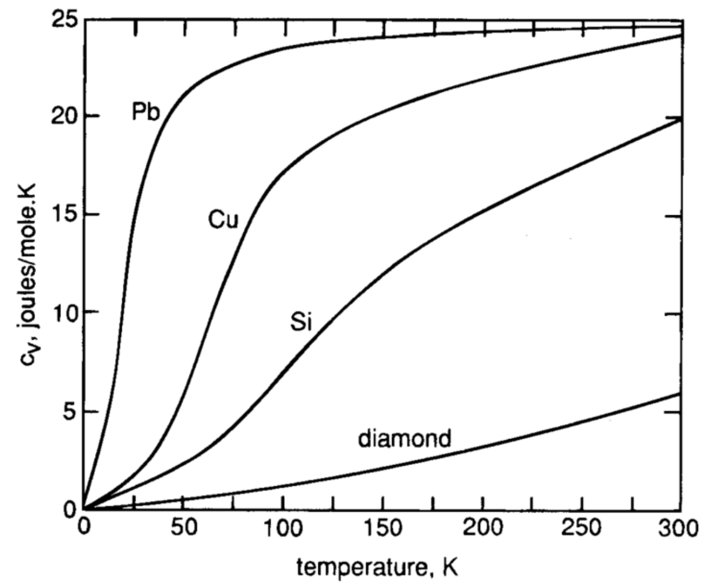
$\Delta E = h\nu$

$P_n \sim e^{-\Delta E/kT}$

Quantized energy levels

$\Delta E << kT$ - classical behavior

$\Delta E \geq kT$ - quantum behavior



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)

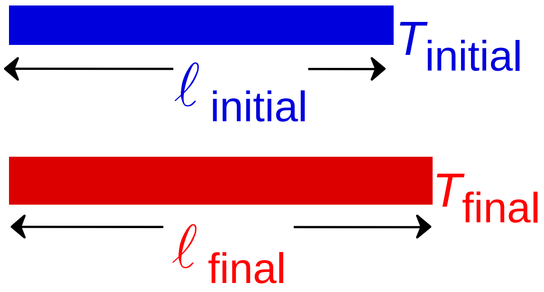
C_p (heat capacity): (J/mol-K)

- More heat energy is required to increase the temperature of a substance with high specific heat capacity than one with low specific heat capacity.
- For instance, compare the specific heat energy required to increase the temperature of glass (c_p = 840 J/kg-K) with that required for gold of the same mass (c_p = 128 J/kg-K) .

Thermal Expansion

- Almost all materials (solids, liquids and gases) expand when they are heated and contract when they are cooled.
- Increased temperature increases the frequency and magnitude of the molecular motion of the atoms and produces more energetic collisions.
- Increasing the energy of the collisions forces the molecules further apart and causes the material to expand.

Length increases when temperature increases.



$$\frac{\ell_{final} - \ell_{initial}}{\ell_{initial}} = \boxed{\alpha_\ell} (T_{final} - T_{initial})$$

linear coefficient of thermal expansion (1/K or 1/°C)

$T_{final} > T_{initial}$

When temperature varies 1° C, for a 10 km long

- Steel rod would vary 11 cm,
- Brass rod, 19 cm
- Al rod would increase in length by 25.5 cm.

Volume coefficient of thermal expansion

Similarly, the volume change with T can be described as

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

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

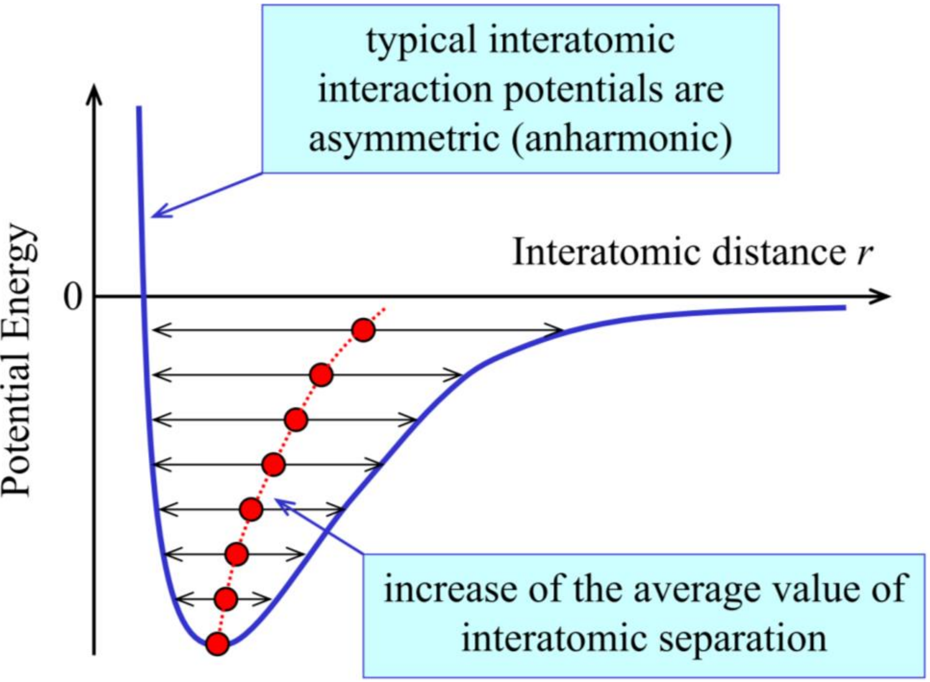
For isotropic materials

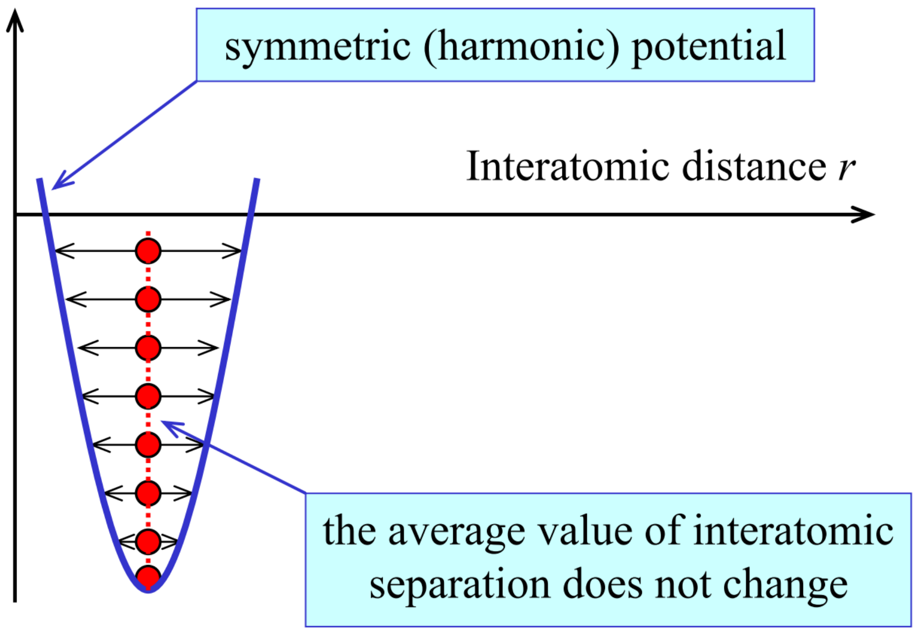
$$V_f = l_f^3 = \left(l_0 + \Delta l\right)^3 = l_0^3 + 3l_0^2 \Delta l + 3l_0 \Delta l^2 + \Delta l^3 \approx l_0^3 + 3l_0^2 \Delta l = V_0 + 3V_0 \frac{\Delta l}{l_0}$$

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

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

Physical origin of thermal expansion





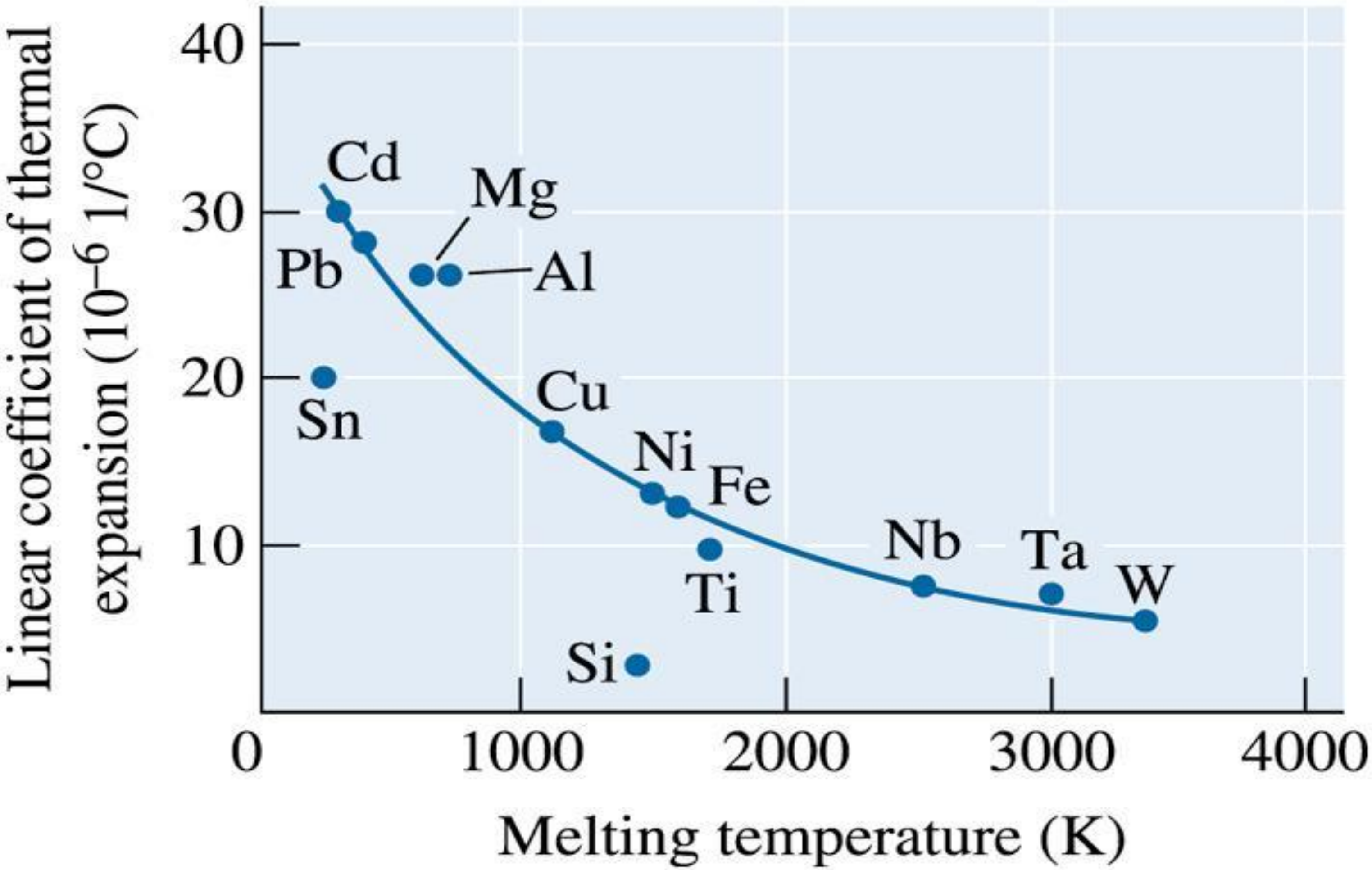
Rising temperature results in the increase of the average amplitude of atomic vibrations.

- For an anharmonic potential, this corresponds to the increase in the average value of interatomic separation, i.e. thermal expansion.

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.

The relationship between the linear coefficient of thermal expansion and the melting temperature in metals. Higher melting point metals tend to expand to a lesser degree.



Thermal Conductivity

The ability of a material to transport heat.

Thermal conductivity: heat is transferred from high to low temperature regions of the material

Fourier's Law

heat flux (J/m^2-s)

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

temperature gradient

thermal conductivity (J/m-K-s)

(amount of thermal energy flowing through a unit area per unit time)

$T_2 > T_1$

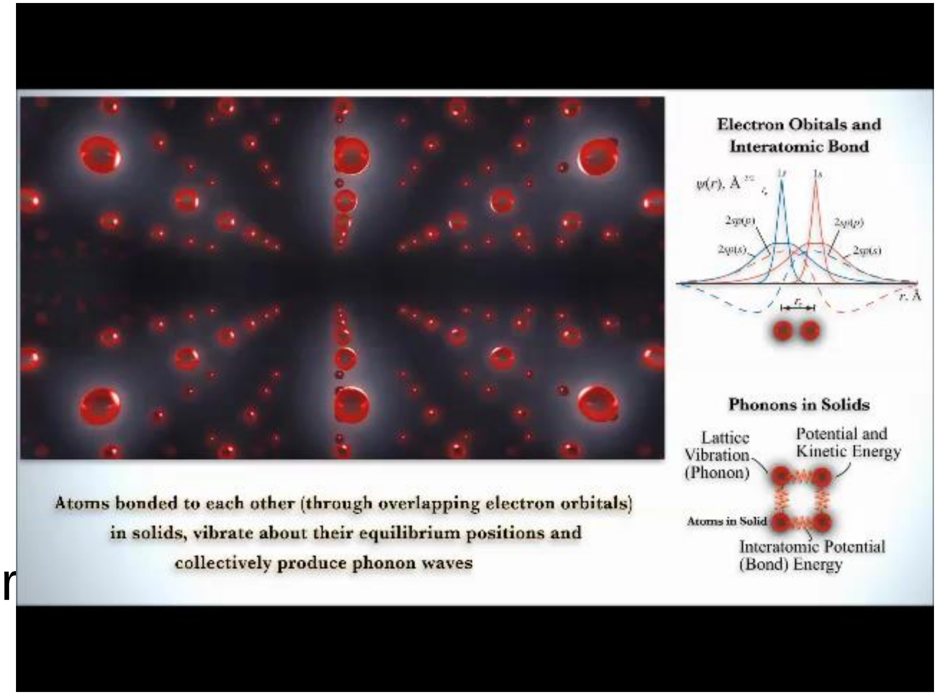
- Atomic perspective: Atomic vibrations and free electrons in hotter regions transport energy to cooler regions.

https://htp.engin.umich.edu/insights/epanimations/

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: $k = k_l + k_e$



https://htp.engin.umich.edu/insights/epanimations/

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.

Wiedemann-Franz law $$L = \frac{k}{\sigma T}$$

—for metals, the ratio of thermal conductivity and the product of the electrical conductivity and temperature should be a constant

where σ is the electrical conductivity, T is the absolute temperature, and L is a constant. The theoretical value of L, $2.44 \times 10^{-8}\ \Omega \cdot \mathrm{W/(K)^2}$, should be independent of temperature and the same for all metals if the heat energy is transported entirely by free electrons.

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.

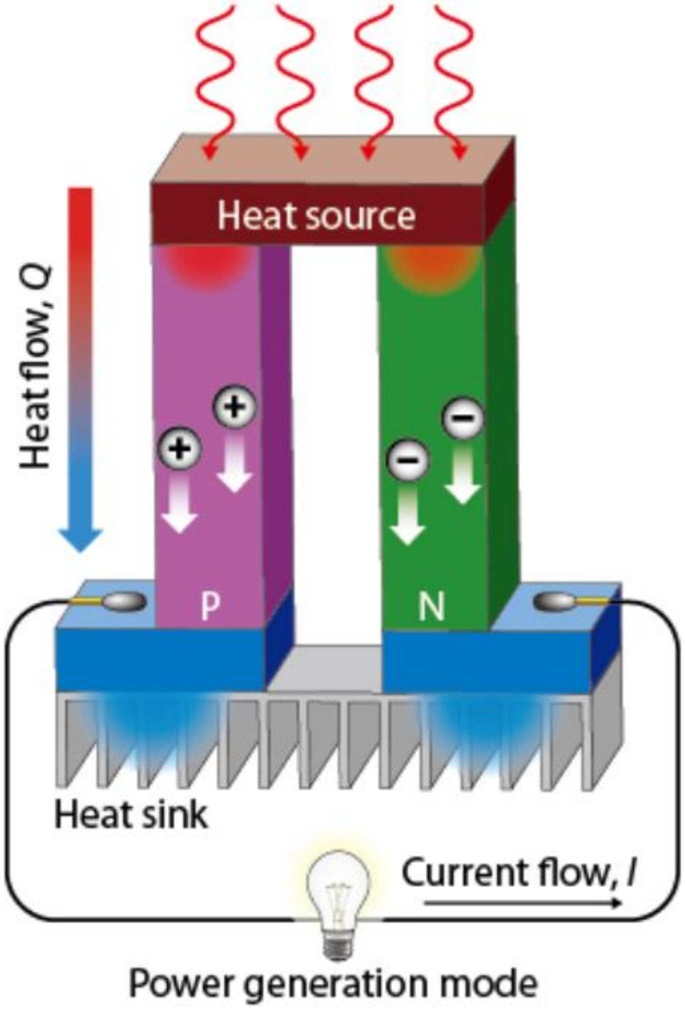
Figure of merit of TE material:

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

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

Good TE material: High $\boldsymbol{\sigma}$ (low Joule heating), large Seebeck coefficient (large ΔV), low $\boldsymbol{k}$ (large ΔT) are necessary.

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



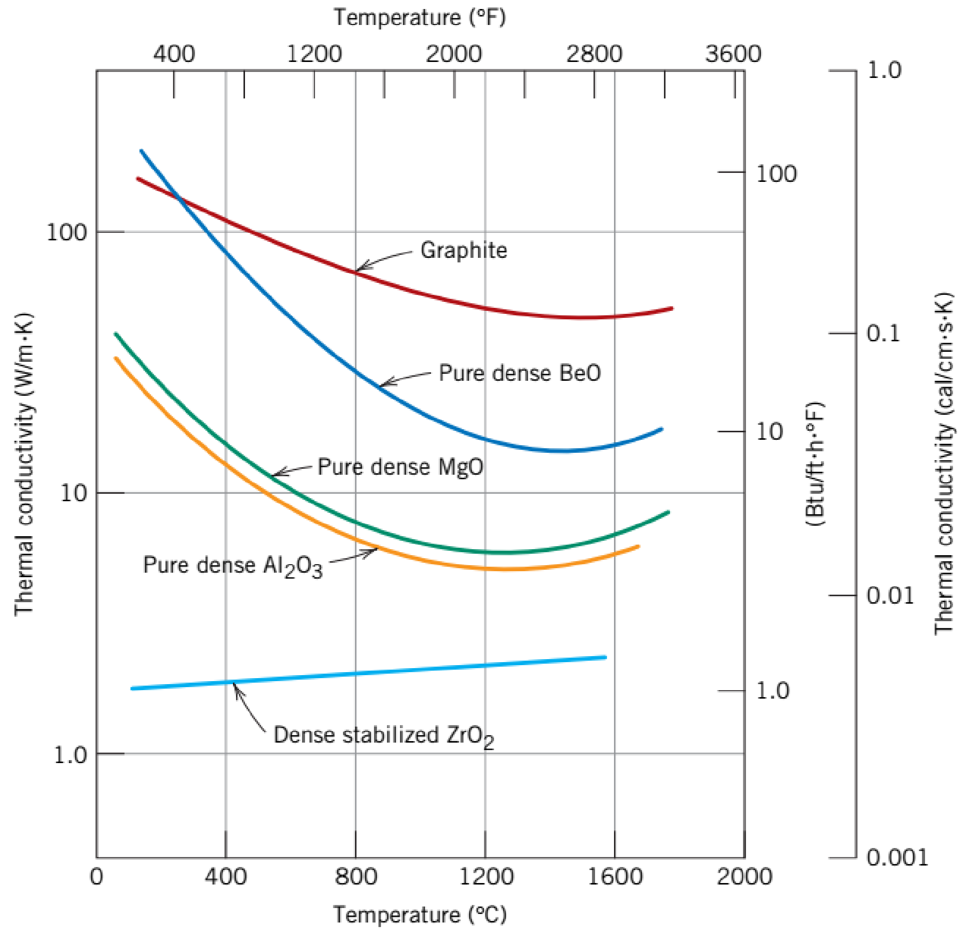
Li et al., *Nat. Asia Mater.*, 152, 2010

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*

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



Thermal Stresses

- Thermal stresses occur due to:

  -- restrained thermal expansion/contraction

  -- temperature gradients that lead to differential dimensional changes

can result in plastic deformation or fracture.

In a rod with restrained axial deformation:

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

where *E* is the elastic modulus, α_l is the linear coefficient of thermal expansion and ΔT is the temperature change.

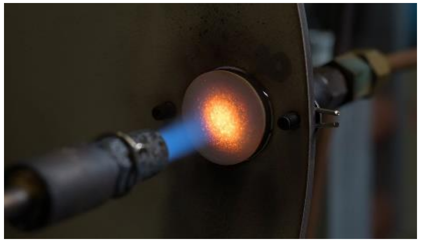
Stresses from temperature gradient

Compressive stress : 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 shock

- Change in temperature can cause stress
- If these are large enough can have plastic deformation (for metals)
- But brittle materials can't deform plastically!
- Brittle materials, ceramics, can fracture due to large temperature changes (thermal shock)
  - because are very good insulators

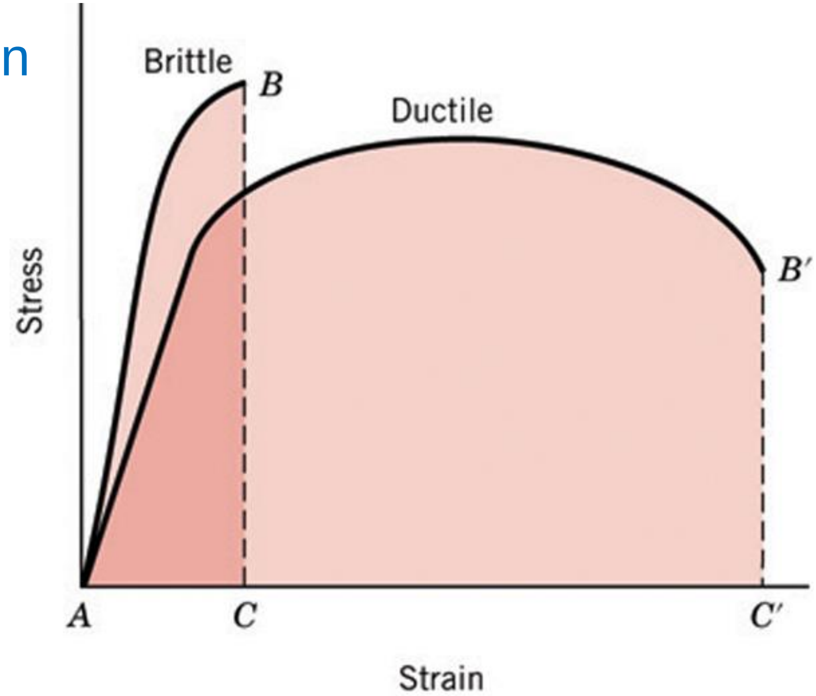


Thermal stresses can cause plastic deformation (in ductile materials) or fracture (in brittle materials).

How to know when thermal shock can happen – thermal shock resistance parameter

The ability of material to withstand thermal stresses due to the rapid cooling/heating is called ***thermal shock resistance***

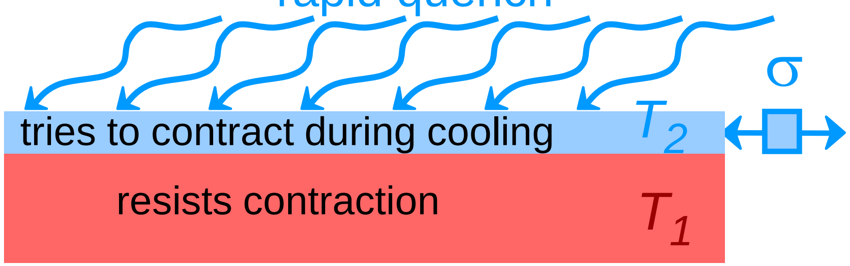
$$TSR \cong \frac{\sigma_f k}{E\alpha_l}$$



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

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

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

$$(\text{quench rate})_{\text{for fracture}} = \text{Thermal Shock Resistance } (TSR) \propto \frac{\sigma_f k}{E\alpha_\ell}$$

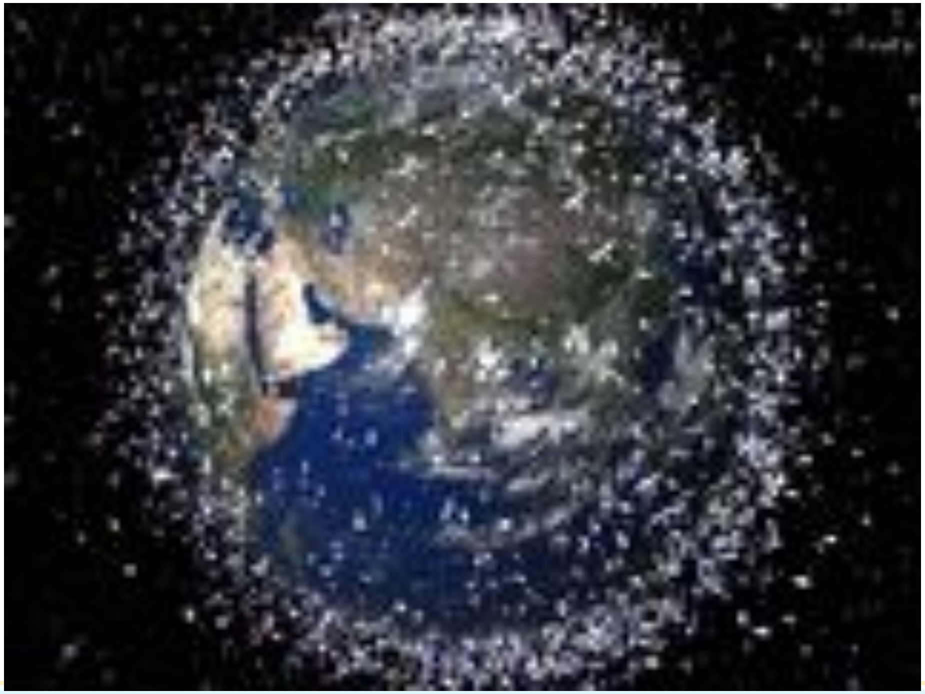
- Large *TSR* when $\dfrac{\sigma_f k}{E\alpha_\ell}$ is large

High fracture strengths
High thermal conductivities
Low elasticity modulus
Low coeff. thermal expansion

Thermal Cycling

- Satellites, spacecraft and all components must be able to withstand the rigors of a space environment while maintaining structural integrity throughout a mission that might last 10 years in low Earth orbit.

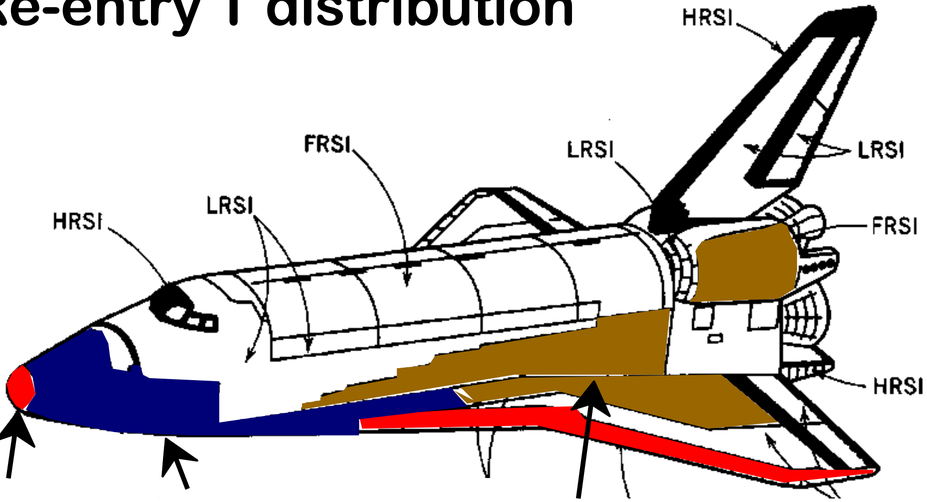


Thermal Protection System

Space Shuttle Atlantis

Re-entry T distribution



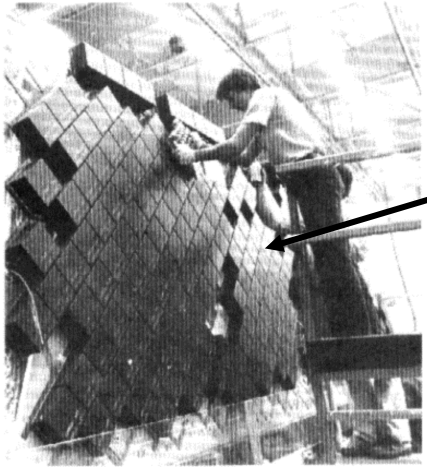
reinf C-C (1650°C)

silica tiles (400-1260°C)

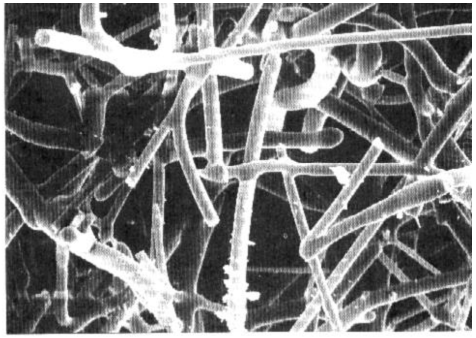
nylon felt, silicon rubber coating (400°C)

- Silica tiles (400-1260°C):

  -- large scale application



-- microstructure:

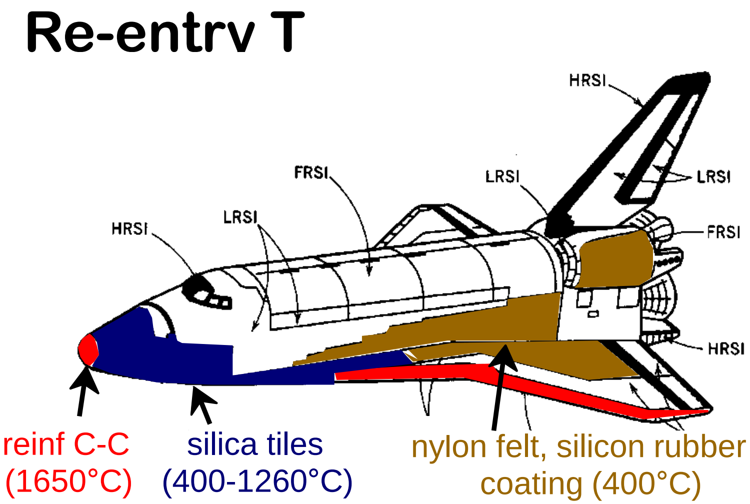


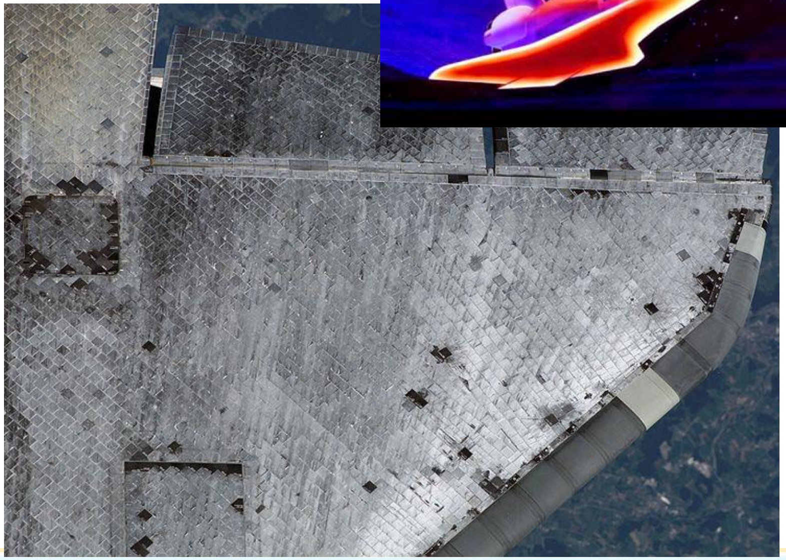
100 μm

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

Thermal Protection System (TPS)

- The thermal protection system consists of various materials applied externally to the outer structural skin of the orbiter to maintain the skin within acceptable temperatures, primarily during the entry phase of the mission.
- The orbiter's outer structural skin is constructed of aluminum and graphite epoxy.
- The materials are reusable for 100 missions with maintenance and perform in temperature ranges from -156 ^{o}C (space) to entry temperatures that reach nearly 1650 ^{o}C .
- Reinforced carbon-carbon (RCC), used in the nose cap and wing leading edges. Used where reentry temperature exceeds 1260 °C (2300 °F).
- High-temperature reusable surface insulation (HRSI) tiles, used on the orbiter underside. Made of coated LI-900 Silica ceramics. Used where reentry temperature is below 1260 °C.
- Fibrous refractory composite insulation (FRCI) tiles, used to provide improved strength, durability, resistance to coating cracking and weight reduction.





View of the Space Shuttle Discovery's underside starboard wing and Thermal Protection System tiles

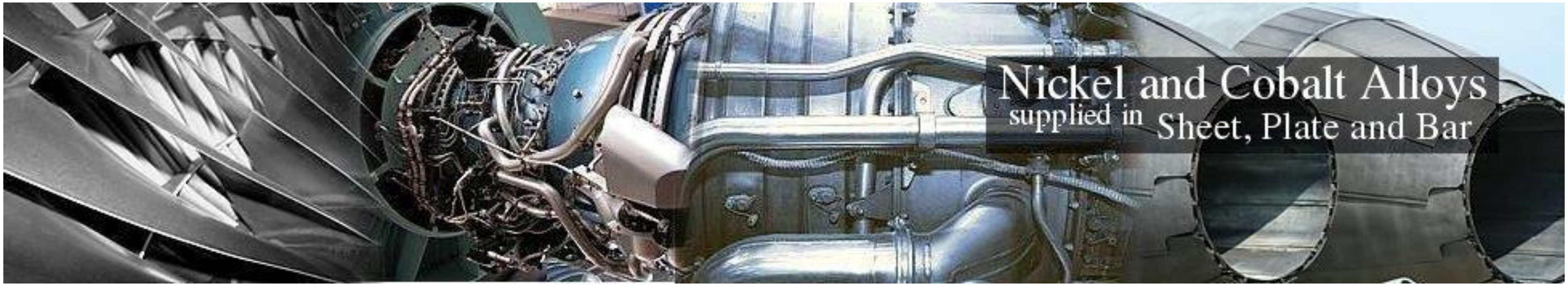
Invar

Invar (64 wt% Fe, 36 wt% Ni) is a nickel steel alloy notable for its uniquely low coefficient of thermal expansion (CTE).

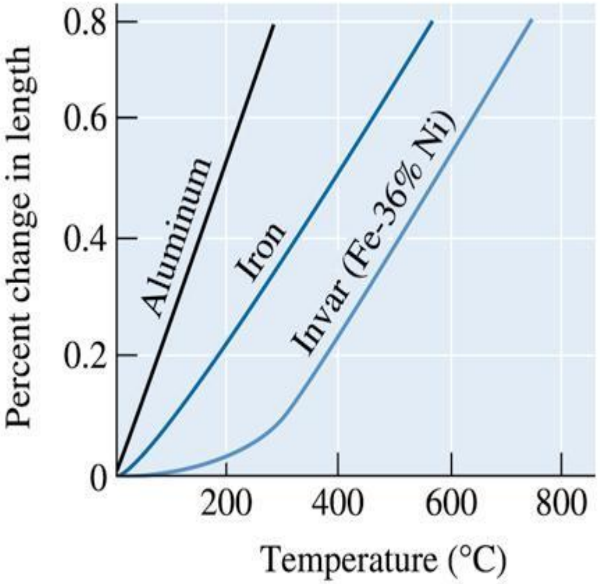
- When temperature varies 1° C, an Invar rod 10 km long expands in length by 0.8 - 2 cm depending on how it has been worked.
- A steel rod in the same conditions would vary 11 cm, a brass rod, 19 cm and an aluminum rod would increase in length by 25.5 cm.

Process: Pure iron and nickel powders were weighed, mixed, pressed into a mold and sintered in controlled atmosphere. Half of the resulting product was extruded and half was hot hammered.

The exceptional properties were attributed to the high purity of the alloy, especially to the very low carbon content (under 0.01%).



Invar Elements	Composition (% by Weight)
Carbon	0.1 Max.
Manganese	0.3 to 0.6
Phosphorus	0.025 Max.
Sulphur	0.025 Max.
Silicon	0.35 Max.
Nickel	35 to 37
Cobalt	0.5 Max.
Chromium	0.5
Molybdenum	0.5
Iron	Remainder



Aerogel Properties

Aerogel is a synthetic porous ultralight material derived from a gel, in which the liquid component for the gel has been replaced with a gas. The result is a solid with extremely low density and extremely low thermal conductivity.

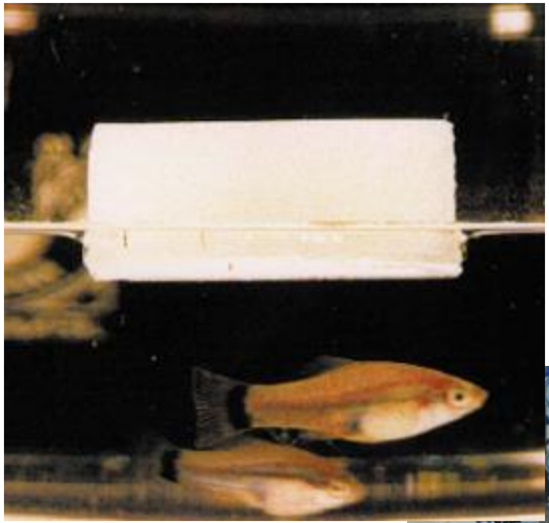
- Aerogel types: Carbon, Silica, Alumina
- Other typical "extreme" properties of silica aerogel materials are:
- Aerogels have the lowest thermal conductivity values of any solid
- Aerogels are exceptional reflectors of audible sound, making excellent barrier materials; aerogels have very low sound velocity through structure (~100 m/s)
- Aerogels can be exotic energy absorbers, showing capability to capture high velocity dust particles in space that would penetrate thick steel
- High internal surface areas (up to 1500 m^2/g)
- Ultra-low refractive index values for a solid (1.025), approaching that for air
- Ultra-low dielectric constants for a solid (can be < 1.1)

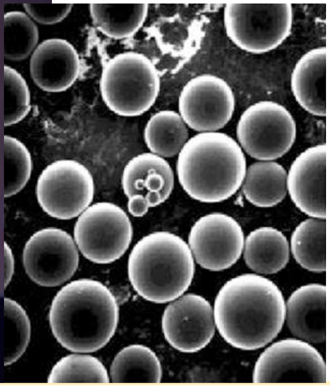
http://www.aspenaerogels.com/features/morphology.html
http://en.wikipedia.org/wiki/Aerogel

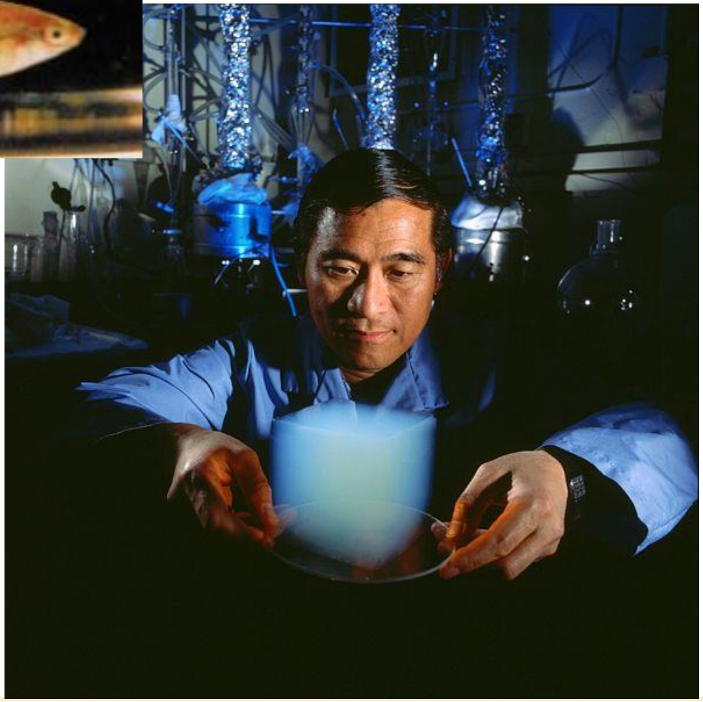
Silica Aerogels

- One of the extraordinary properties that was discovered about first silica aerogels was their very low thermal conductivity.
- In the1980s it was apparent that silica aerogels were an attractive alternative to traditional insulation due to their high insulating value and environment-friendly production methods.
- Aerogel materials are open cell, nanoporous materials that have a very high proportion of free void volume (typically >90%) compared to conventional solid materials.
- Excellent thermal insulation properties have also been reported in organic and carbon based aerogels as well as other inorganic metal oxides produced using sol-gel processing.
- The passage of thermal energy through an insulating material occurs through three mechanisms; solid conductivity, gaseous conductivity and radiative (infrared) transmission. The sum of these three components gives the total thermal conductivity of the material. For dense silica, solid conductivity is relatively high (a single-pane window transmits a large amount of thermal energy). However, silica aerogels possess a very small (~1-10%) fraction of solid silica.

A 2.5 kg brick is supported on top of a piece of aerogel weighing only 2 grams

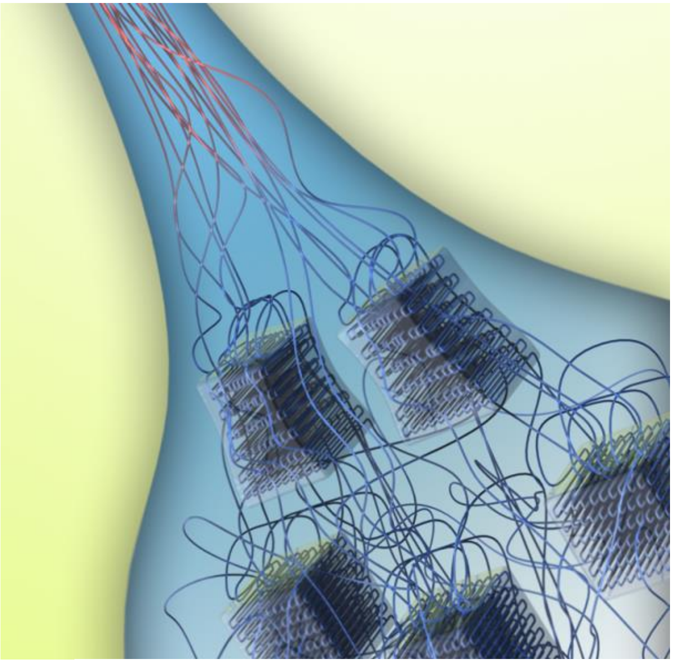




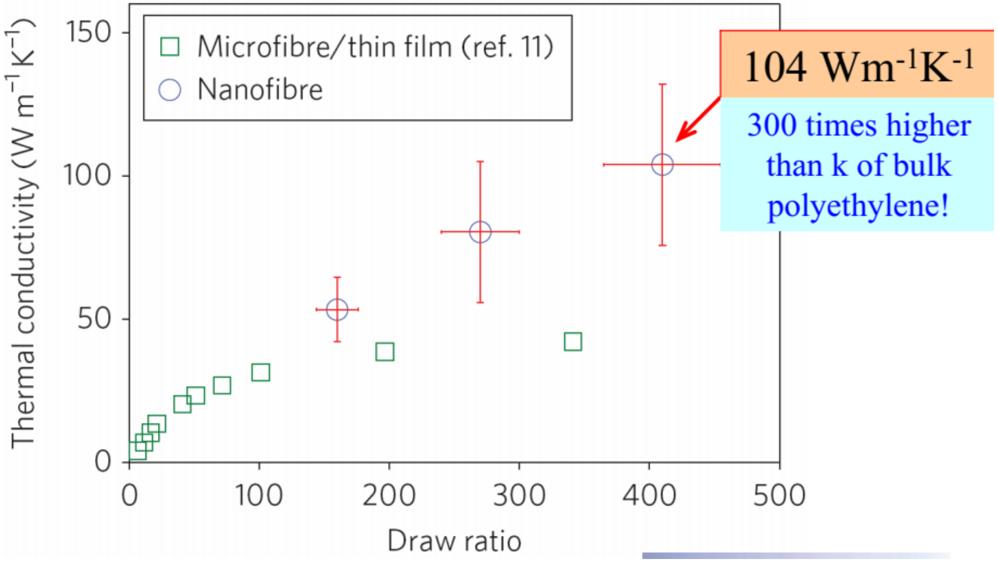


Thermal conductivity of polymer nanofibers

Although, normally, polymers are thermal insulators ($k \sim 0.1\ Wm^{-1}K^{-1}$), it has been demonstrated in atomistic simulations [Henry & Chen, Phys. Rev. Lett.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**.



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.



Home assignment

1. (a) Explain why a brass lid ring on a glass canning jar loosens when heated.
   (b) Suppose the ring is made of tungsten instead of brass. What will be the effect of heating the lid and jar? Why
2. Which of a linear polyethylene (Mn = 450,000 gmol) and a lightly branched polyethylene (Mn = 650,000 gmol) has the higher thermal conductivity? Why?
3. Explain why, on a cold day, the metal door handle of an automobile feels colder to the touch than a plastic steering wheel, even though both are at the same temperature.
4. Railroad tracks made of 1025 steel are to be laid during the time of year when the temperature averages 4°C (40°F). If a joint space of 5.4 mm (0.210 in.) is allowed between standard rails of length 11.9 m (39 ft), what is the highest possible temperature that can be tolerated without the introduction of thermal stresses?

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

We welcome


Highly motivated students
to do part of their undergraduate project in the field of
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prasana@matsc.iitkgp.ac.in

Effect of impurities on thermal conductivity

The factors that affect the electrical conductivity also affect thermal conductivity in metals.

E.g., adding impurities introduces scattering centers for conduction band electrons and reduce *k*.