Cryogenic Engineering

Chapter 2.

LOW TEMPERATURE PROPERTIES OF ENGINEEING MATERIALS

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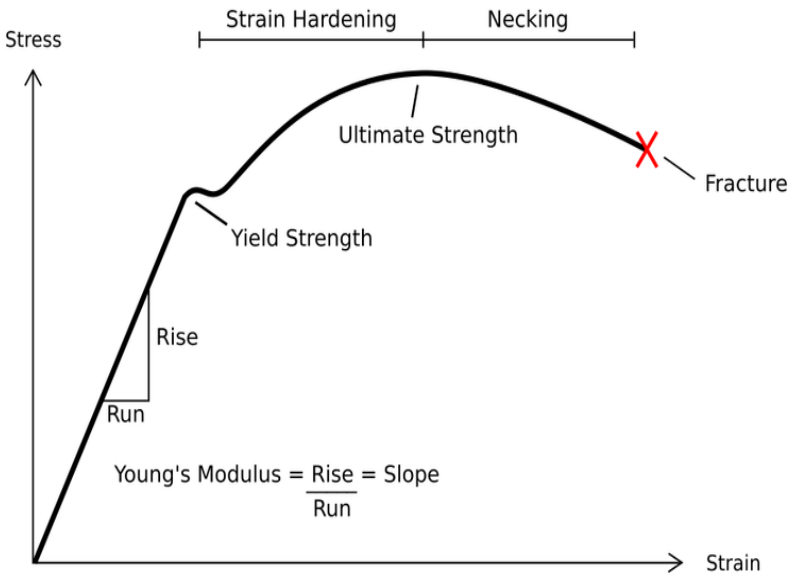
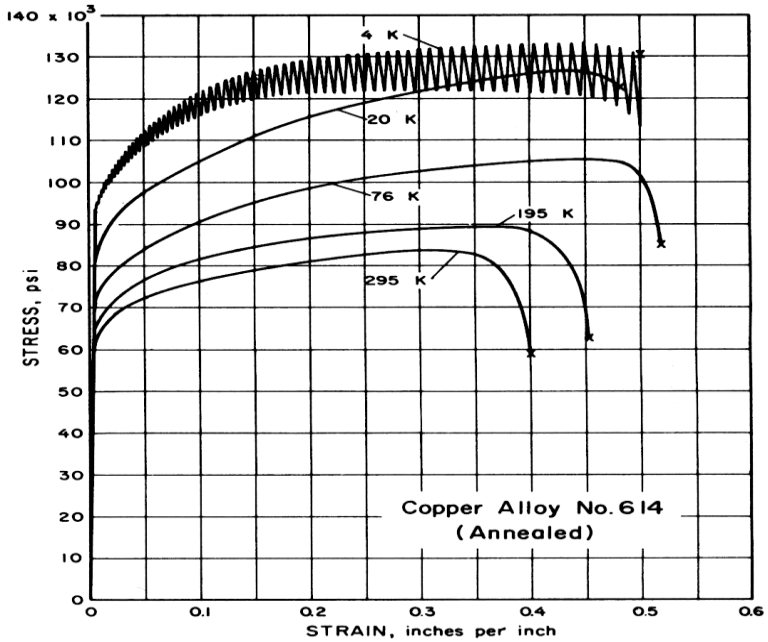
2.1 Introduction



Stress-strain curve at room temperature

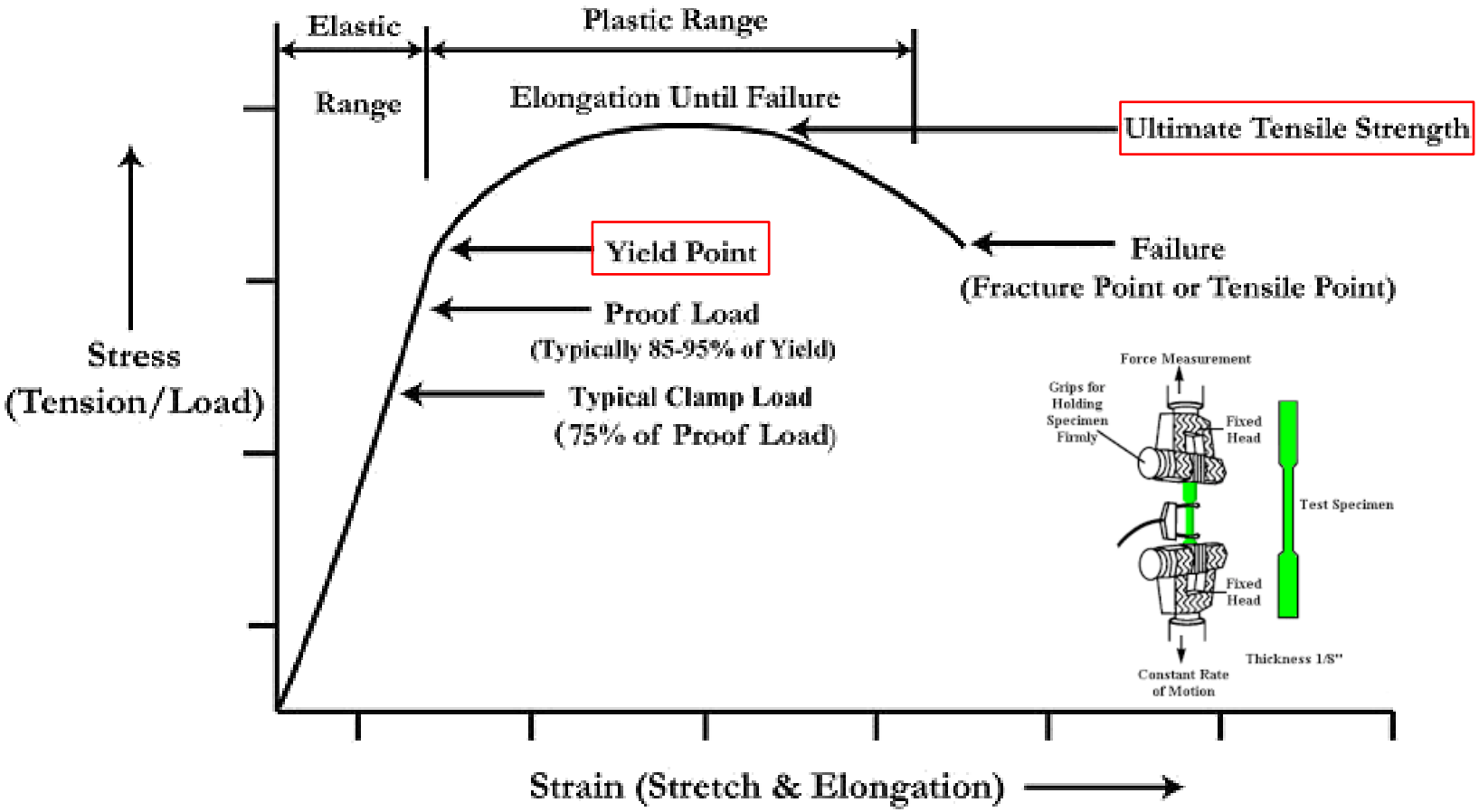


Stress-strain curve for cooper alloy at low temperature

Extrapolation for material properties at very low temperature is not exact !!

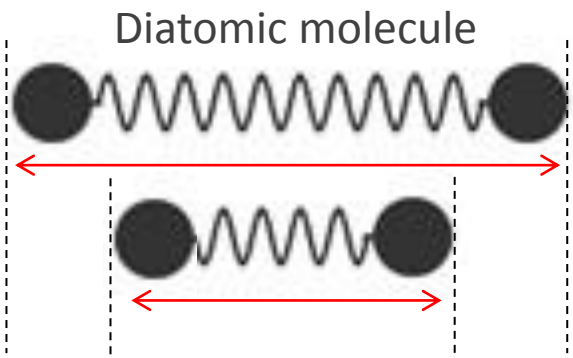
- Vanishing of specific heat
- Superconductivity phenomenon
- Ductile-brittle transition in carbon steel

2.2 Ultimate and yield strength

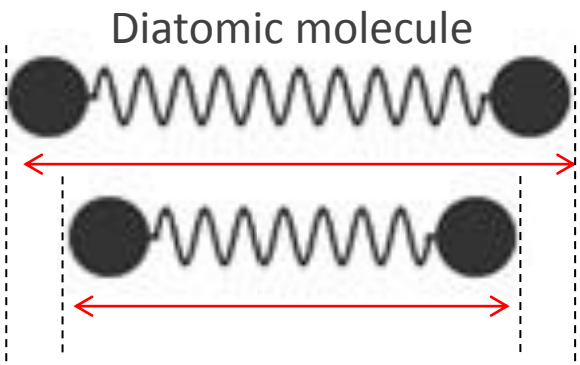


Tensile Stress-Strain Diagram

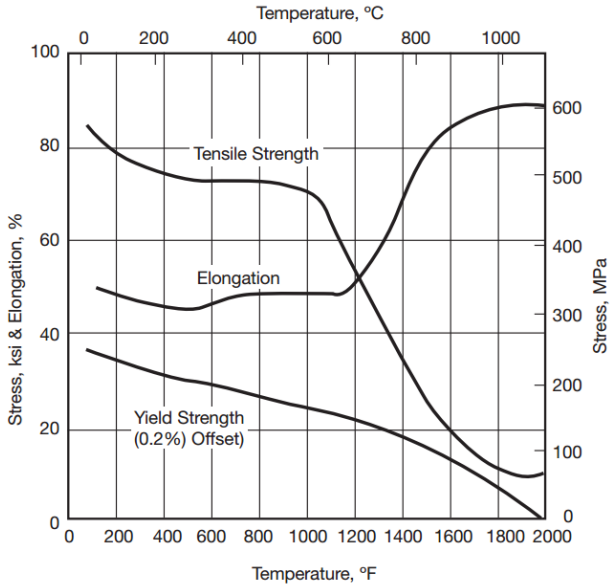
2.2 Ultimate and yield strength



Vigorous vibration at room temperature



Torpid vibration at low temperature



Nickel-Iron-Chromium Alloy

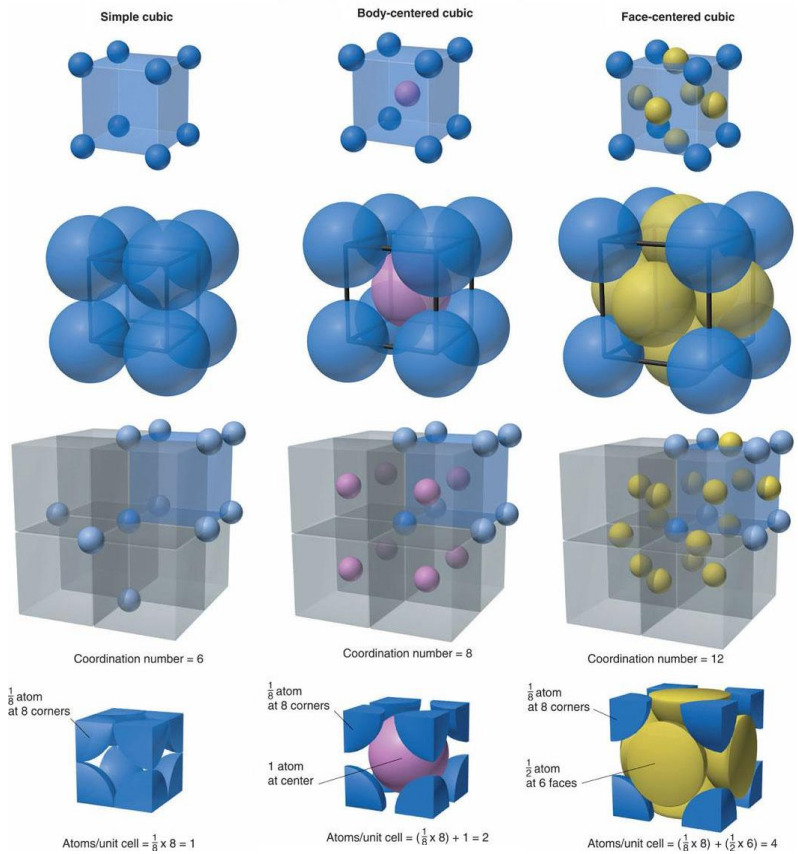
As temperature is lowered, atoms of the material vibrate less rigorously,
a larger applied stress is required to tear dislocations from their atmosphere of alloying atoms.

2.3 Impact Strength

The Charpy and the Izod impact tests

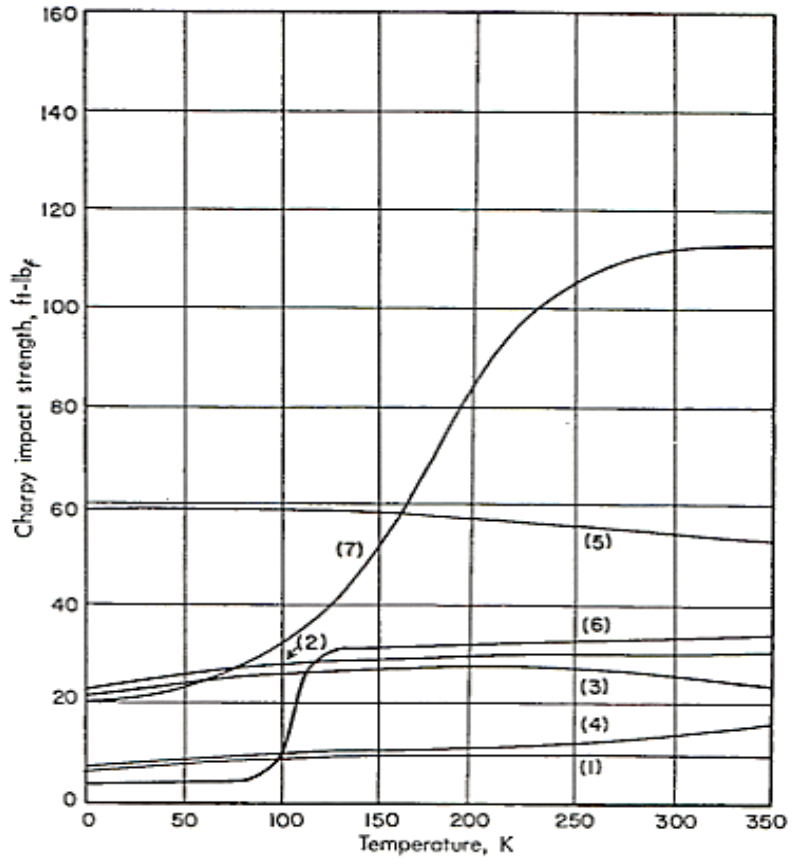
MaterialsScience2000 - Charpy Impact Test
https://www.youtube.com/watch?v=tpGhqQvftAo

2.3.1 Lattice Structure



<Lattice structures>

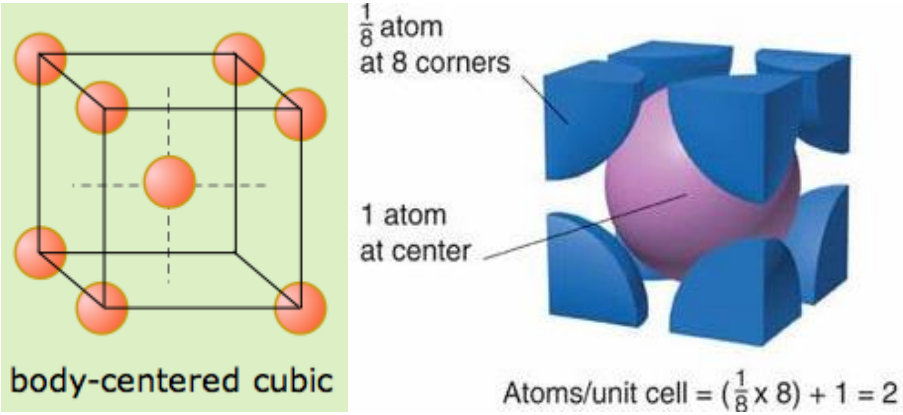
(1) 2024-T4 aluminum; (2) beryllium copper; (3) K Monel; (4) titanium;
(5) 304 stainless steel; (6) C1020 carbon steel; (7) 9 percent Ni steel (Durham et al. 1962)

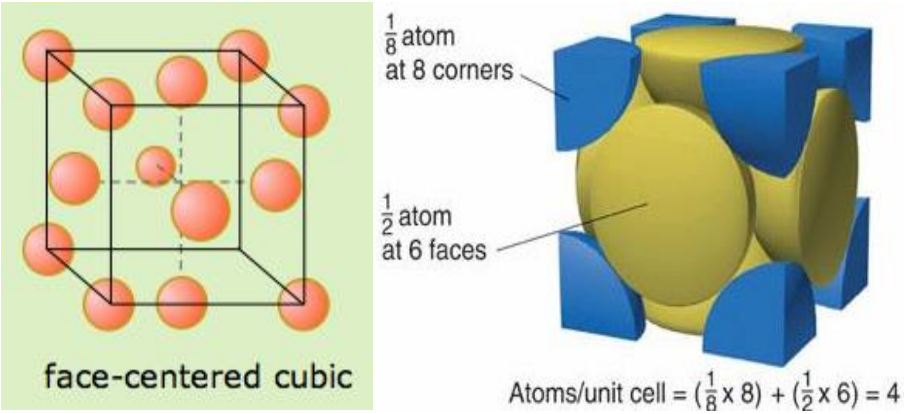


<Charpy impact strength at low temperature>
*Ductile-brittle transition

2.3.1 Lattice Structure

BCC (Body-Centered Cubic) vs FCC (Face-Centered Cubic)



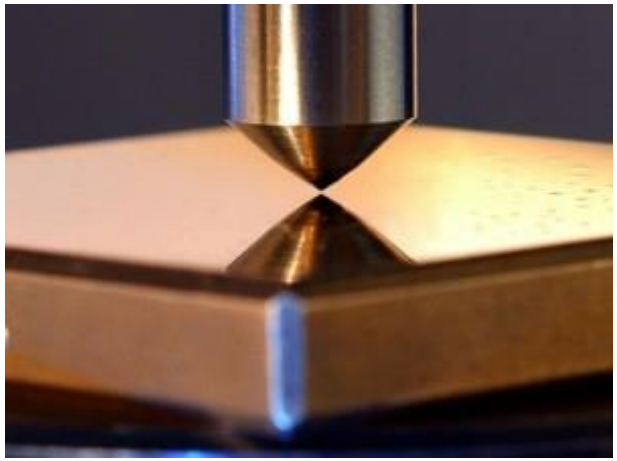


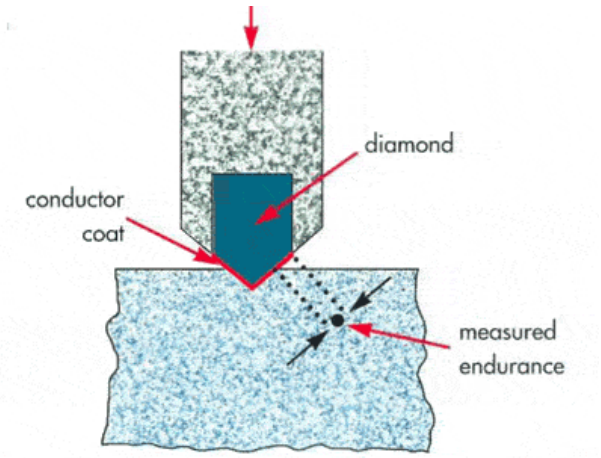
Copper-Nickel alloy
Aluminum alloy
Stainless steel
Zirconium
Titanium
} Ductile

Iron
Carbon alloy
Molybdenum
Zinc
Most plastics
} Brittle

2.4 Hardness and ductility

Hardness is a measure of how resistant solid matter is to various kinds of permanent shape change when a compressive force is applied. Some materials, such as metal, are harder than others. Macroscopic hardness is generally characterized by strong intermolecular bonds, but the behavior of solid materials under force is complex; therefore, there are different measurements of hardness: **scratch hardness, indentation hardness, and rebound hardness.**



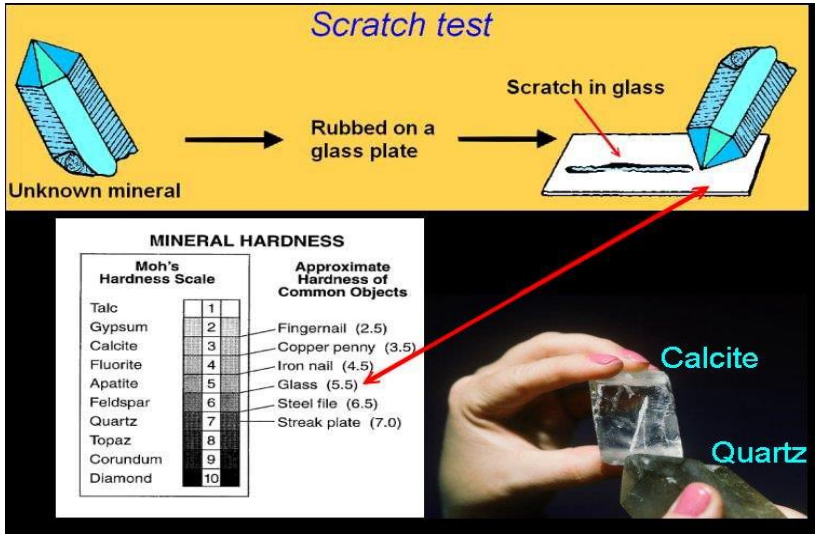


2.4 Hardness and ductility

- **Scratch hardness**

Scratch hardness tests are used to determine the hardness of a material to scratches and abrasion.

Pencil scratch hardness tester



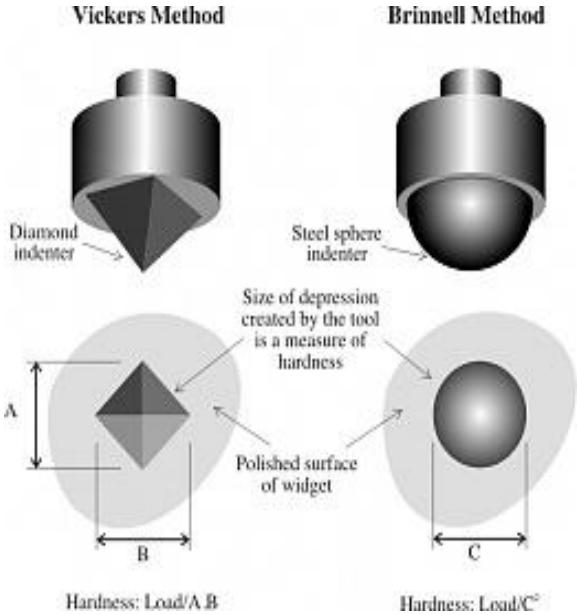
Scratch test

2.4 Hardness and ductility

- **Indentation hardness**

Indentation hardness tests are used in mechanical engineering to determine the hardness of a material to deformation.

Indentation hardness tester

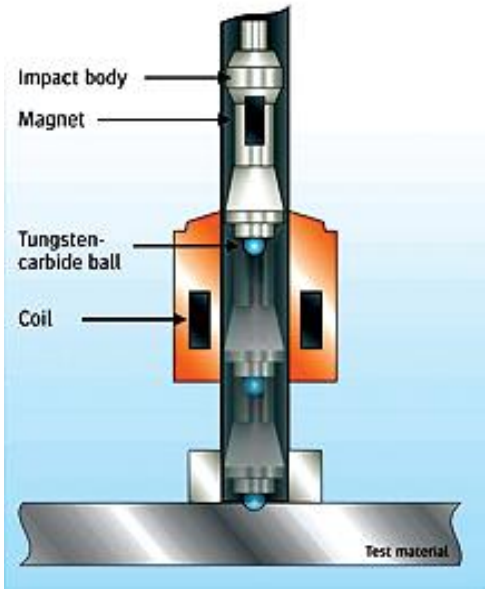


Two types of indentation

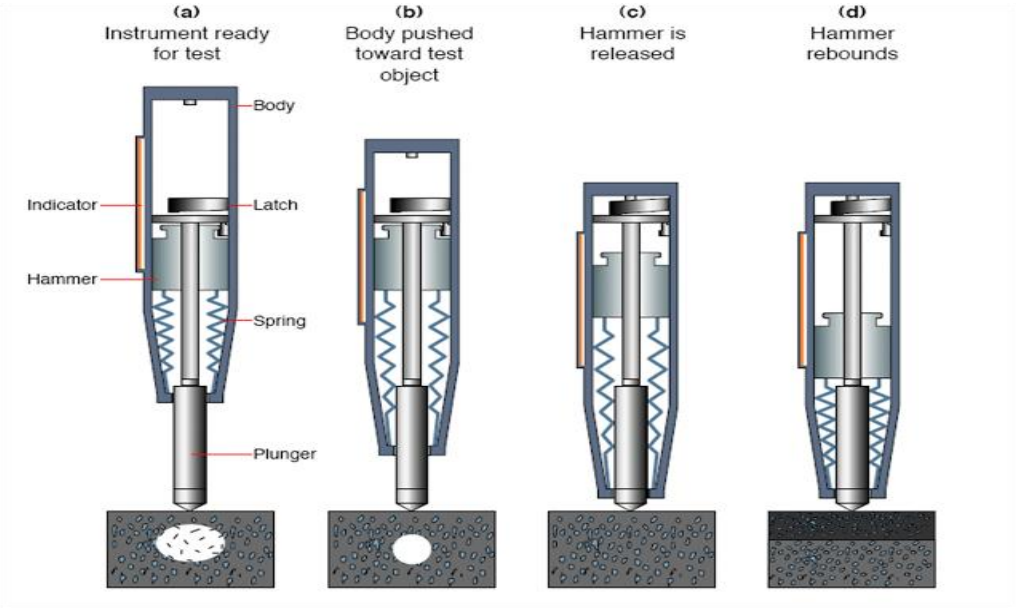
2.4 Hardness and ductility

- **Rebound hardness**

The **Leeb rebound hardness** test is one of the four most used methods for testing metal hardness.



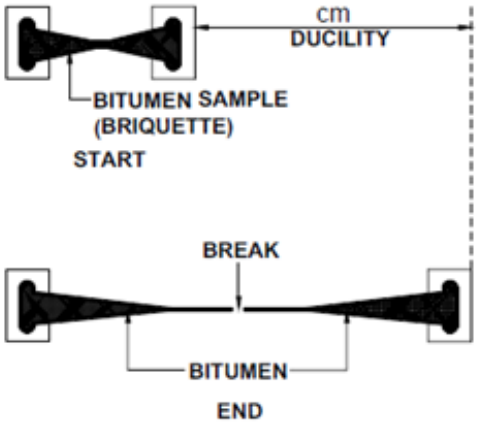
Portable rebound hardness testing machine.



Procedure of rebound hardness test

2.4 Hardness and ductility

In materials science, **ductility** is a solid material's ability to deform under tensile stress; this is often characterized by the material's ability to be stretched into a wire. **Malleability**, a similar property, is a material's ability to deform under compressive stress; this is often characterized by the material's ability to form a thin sheet by hammering or rolling.



Ductility test and measurement

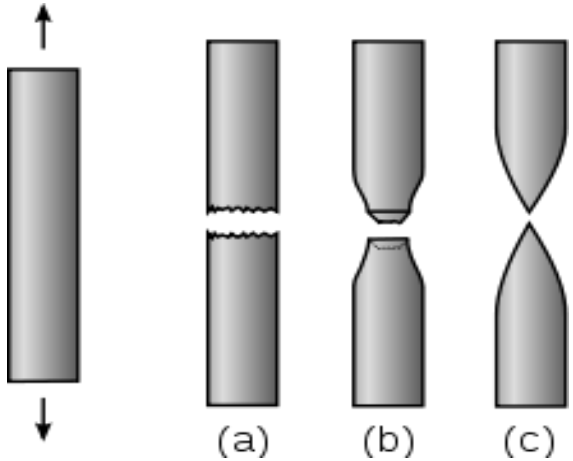
2.4 Hardness and ductility

Tensile test of an AlMgSi alloy. The local necking and the cup and cone fracture surfaces are typical for ductile metals.

This tensile test of a nodular cast iron demonstrates low ductility.

2.4 Hardness and ductility

Gold leaf can be produced owing to gold's malleability.



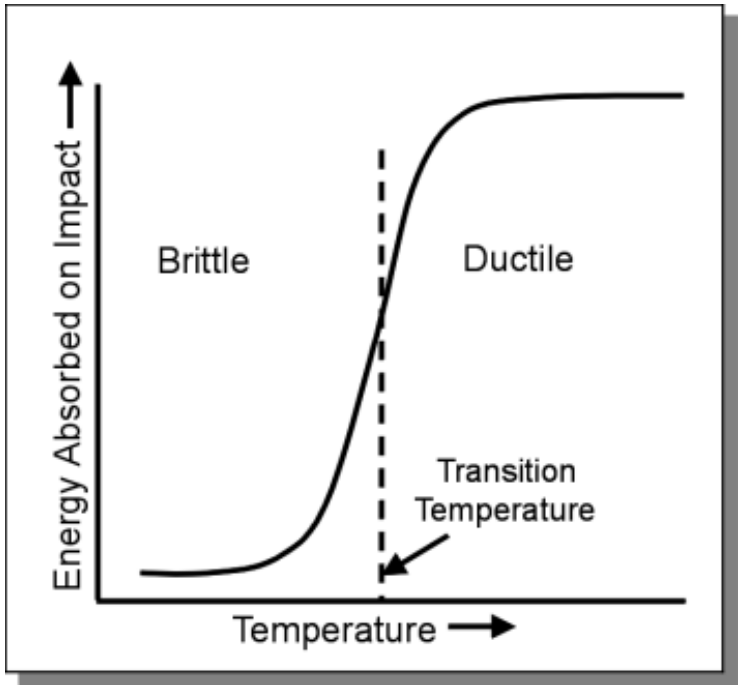
Schematic appearance of round metal bars after tensile testing.

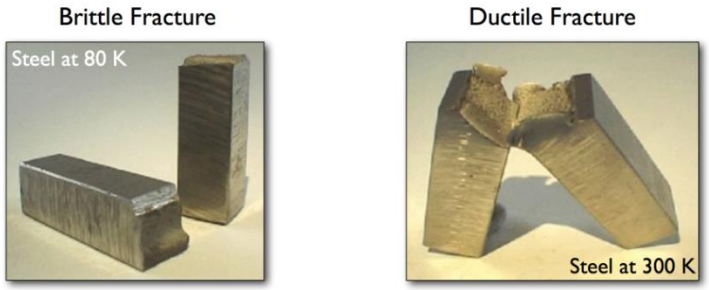
(a) Brittle fracture
(b) Ductile fracture
(c) Completely ductile fracture

2.4 Hardness and ductility

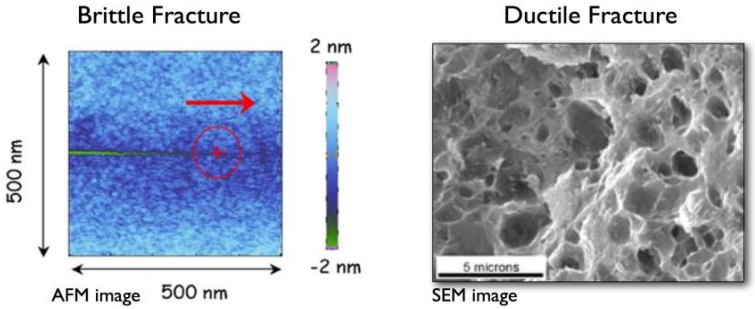
- **Ductile–brittle transition temperature**

At low temperatures some metals that would be ductile at room temperature become brittle. This is known as a ductile to brittle transition.





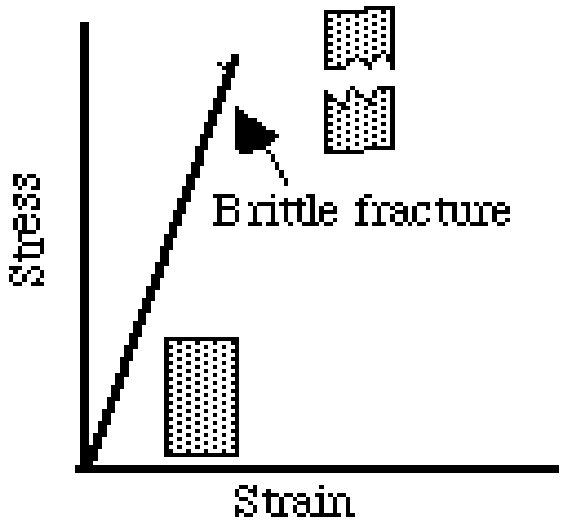
Brittle and ductile failure of steel, at low and high temperature respectively.



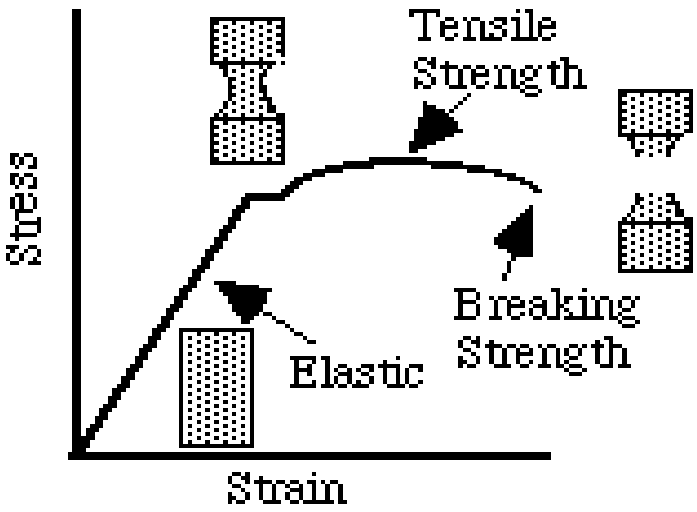
Brittle and ductile failure mechanisms, for silica and aluminium respectively. Image credits

2.4 Hardness and ductility

- **Stress-strain diagrams for typical brittle and ductile materials**



(a) Brittle materials

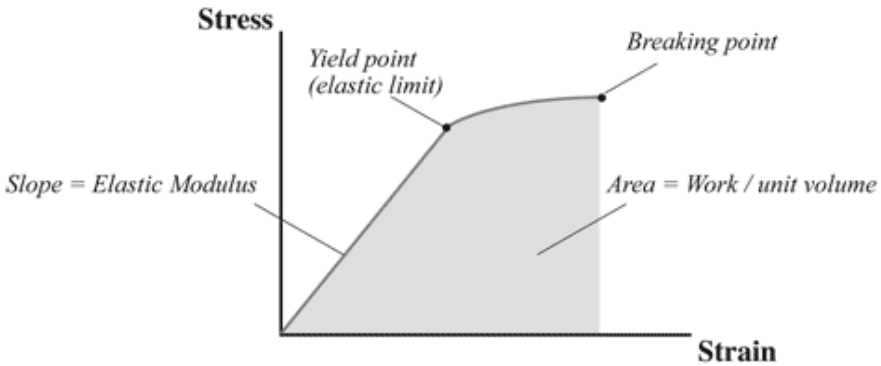


(b) Ductile materials

2.5 Elastic modulus

"Young's modulus" or **modulus of elasticity**, is a number that measures an object or substance's resistance to being deformed elastically (i.e., non-permanently) when a force is applied to it.

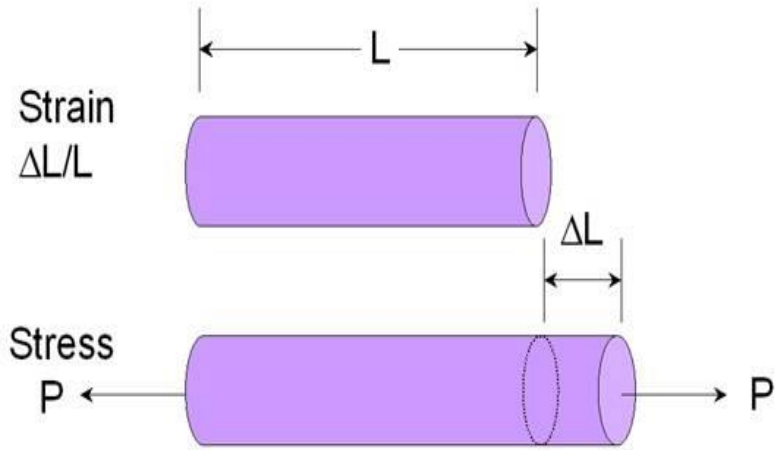
$$\text{elastic modulus} = \frac{\text{stress}}{\text{strain}}$$



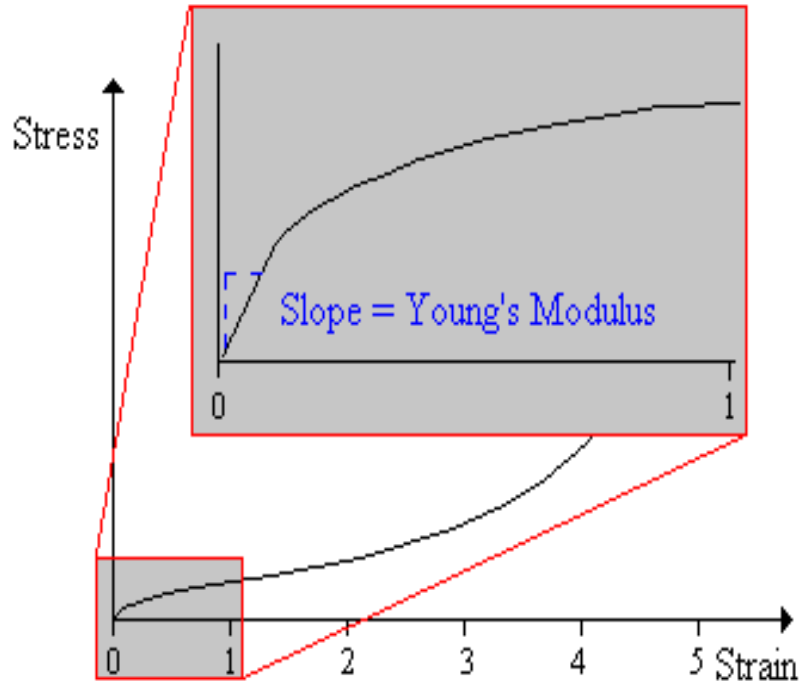
Curve of **Stress vs. Strain** *which describes the mechanical deformation of a solid body.*

2.5 Elastic modulus

- **Young's modulus, E**



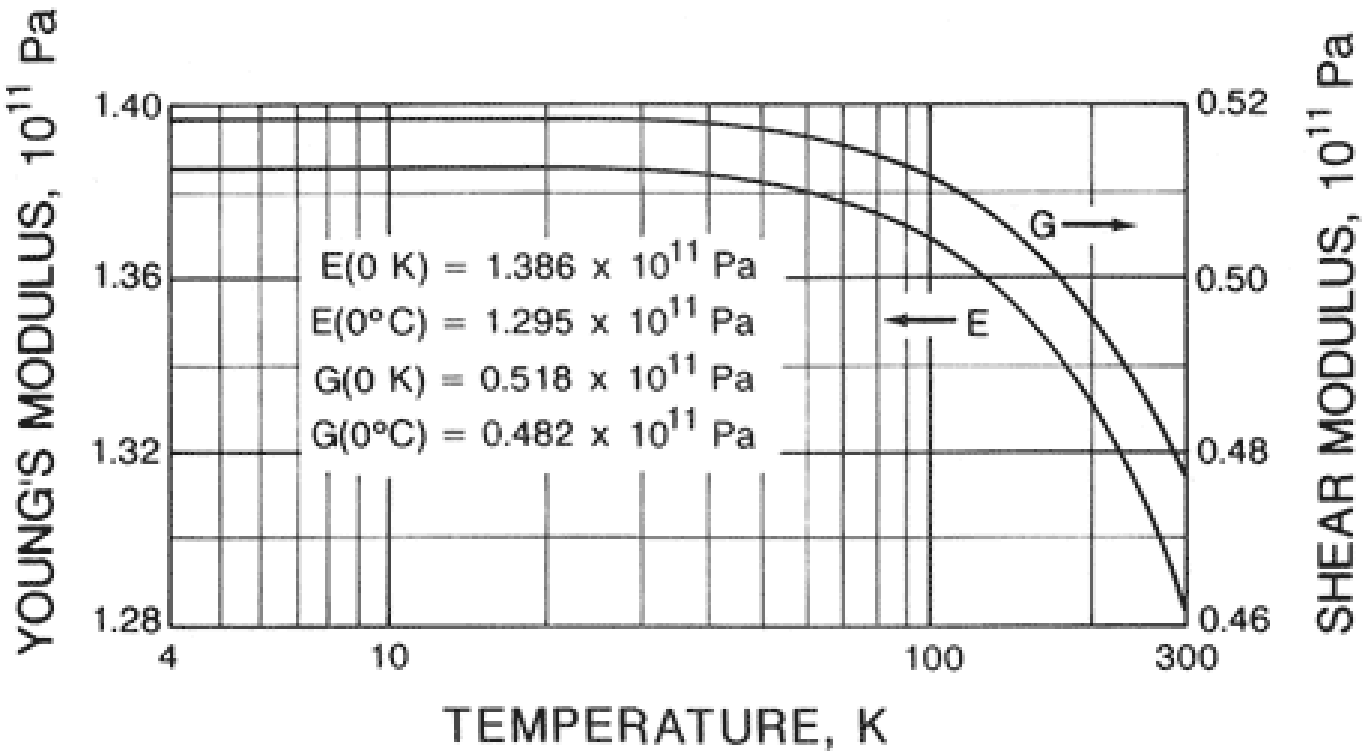
$$\text{Young's Modulus} = \frac{\text{Stress}}{\text{Strain}} = \frac{P}{\Delta L/L}$$



Young's modulus
(slope of a stress-strain curve)

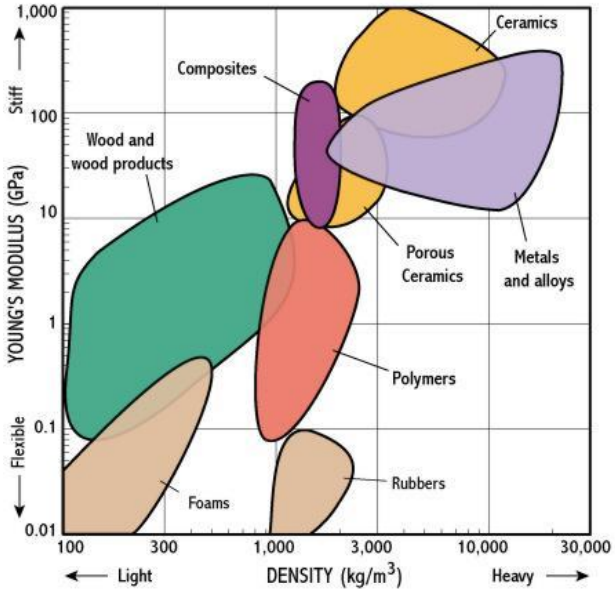
2.5 Elastic modulus

- Young's modulus, E



2.5 Elastic modulus

- **Young's modulus, E**



Young's Modulus - Density Materials Selection Chart, showing the classes of materials

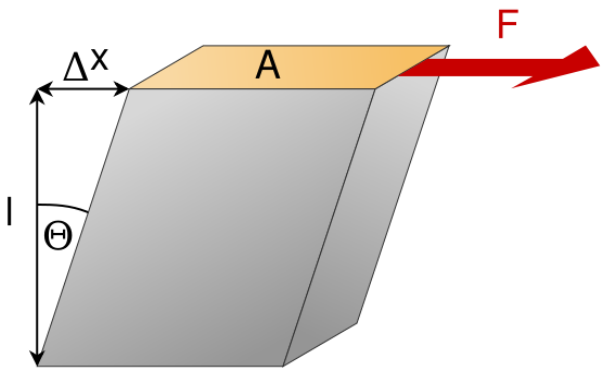
Material	Youngs Modulus /GPa
Mild Steel	210
Copper	120
Bone	18
Plastic	2
Rubber	0.02

2.5 Elastic modulus

- **Shear modulus, G**

In materials science, shear modulus or modulus of rigidity, denoted by G, or sometimes S or μ, is defined as the ratio of shear stress to the shear strain.

$$G \stackrel{\text{def}}{=} \frac{\tau_{xy}}{\gamma_{xy}} = \frac{F/A}{\Delta x/l} = \frac{Fl}{A\Delta x}$$



where

$\tau_{xy} = F/A$ = shear stress;

F is the force which acts

A is the area on which the force acts

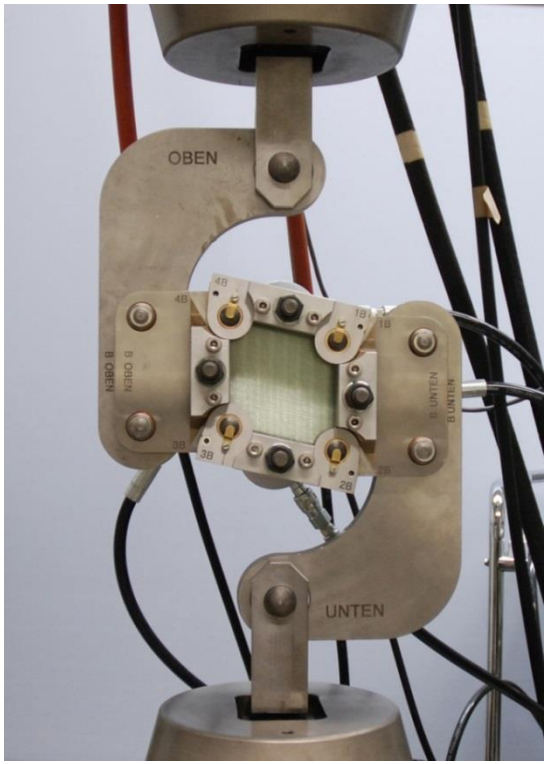
in engineering, $\gamma_{xy} = \Delta x/l = \tan\theta$ = shear strain. Elsewhere, $\gamma_{xy} = \theta$

Δx is the transverse displacement

l is the initial length

2.5 Elastic modulus

- **Shear modulus, G**



Shear frame for evaluation of the in-plane shear modulus and strength of FRP

2.5 Elastic modulus

- **Bulk modulus, B**

The bulk modulus (K or B) of a substance measures the substance's resistance to uniform compression. It is defined as the ratio of the infinitesimal pressure increase to the resulting relative decrease of the volume.

The bulk modulus $K > 0$ can be formally defined by the equation

$$K = -V\frac{\mathrm{d}P}{\mathrm{d}V}$$

where P is pressure, V is volume, and dP/dV denotes the derivative of pressure with respect to volume. Equivalently

$$K = \rho\frac{\mathrm{d}P}{\mathrm{d}\rho}$$

where ρ is density and dP/dρ denotes the derivative of pressure with respect to density. The inverse of the bulk modulus gives a substance's compressibility.

2.5 Elastic modulus

- **Bulk modulus, B**

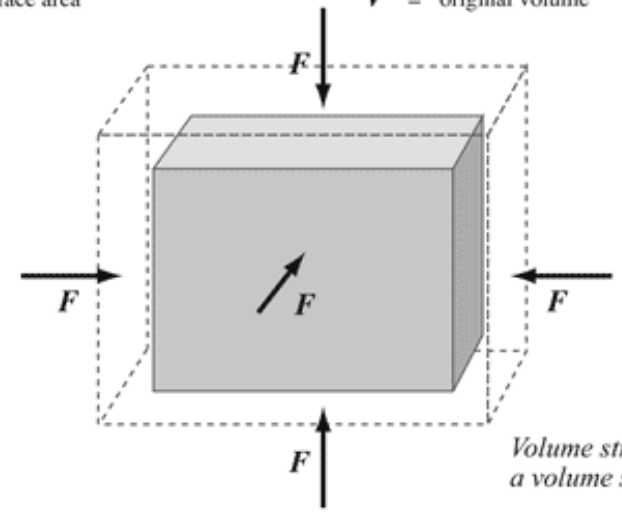
$$\text{bulk modulus} = -\frac{F/A}{\Delta V/V}$$

$$\text{volume stress} = \frac{F}{A}$$

F = normal force
A = surface area

$$\text{volume strain} = \frac{\Delta V}{V}$$

ΔV = change in volume
V = original volume



Volume strain produced by a volume stress

2.5 Elastic modulus

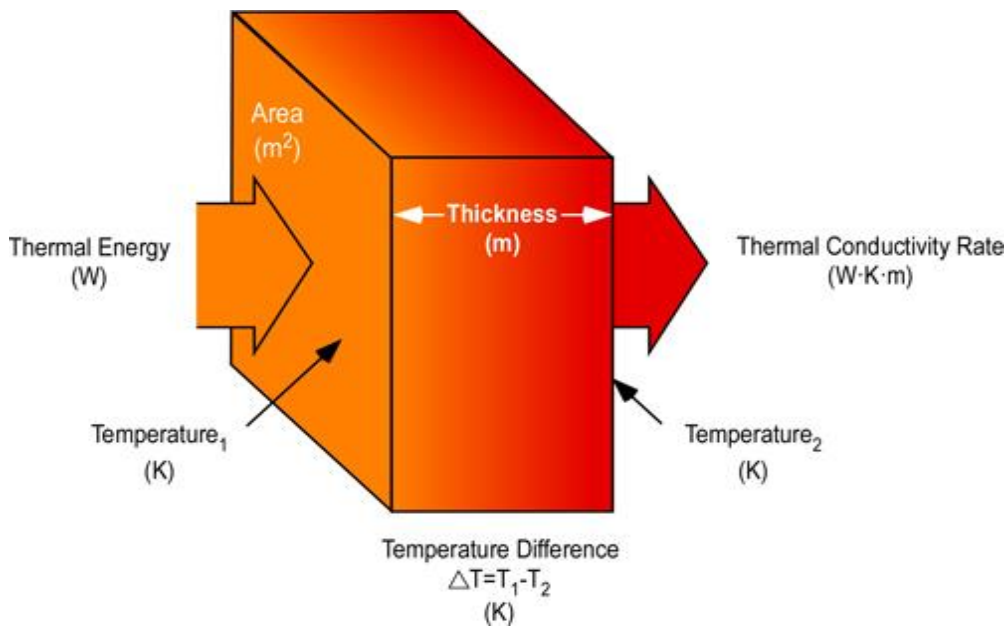
- **Relations between elastic modulus**

For homogeneous isotropic materials simple relations exist between elastic constants (Young's modulus E, shear modulus G, bulk modulus K, and Poisson's ratio ν) that allow calculating them all as long as two are known

$$\boldsymbol{E = 2G(1+\nu) = 3K(1-2\nu)}$$

2.6 Thermal conductivity

k_t : Heat-transfer rate per unit area divided by the temperature gradient



<Heat transfer through conduction>

$$q = -k_t A \frac{dT}{dx}$$

<Fourier's law>

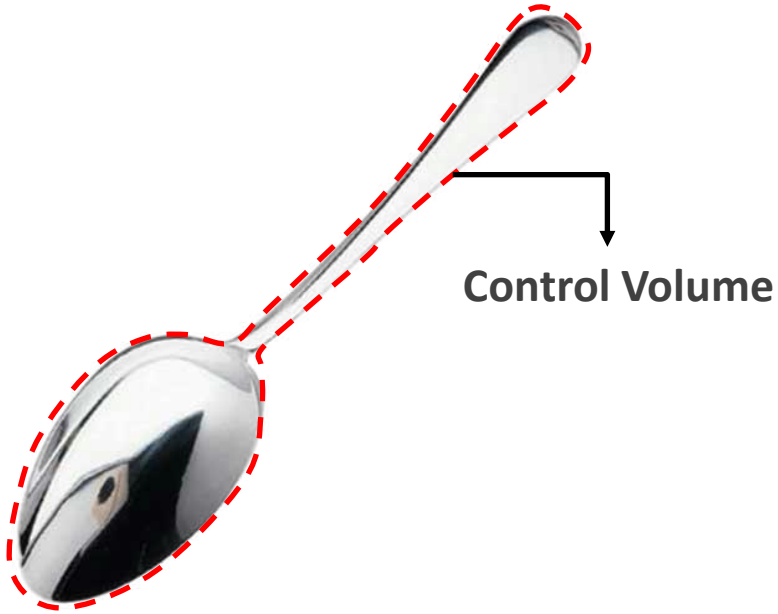
$$k_t = \left[\frac{W}{m \cdot K}\right]$$

2.6 Thermal conductivity

<A stainless spoon in hot water>

$$\delta Q = du + \delta W$$

<1st law of thermodynamics>

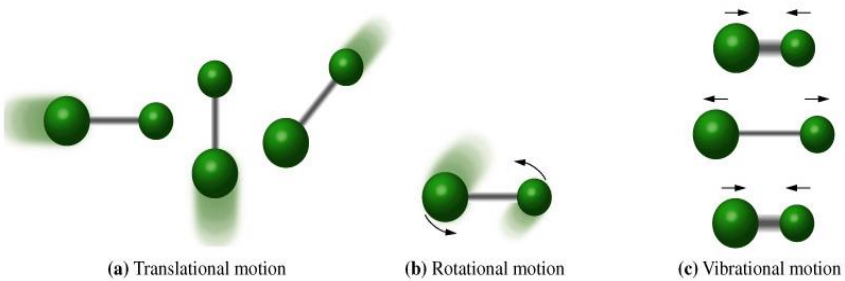


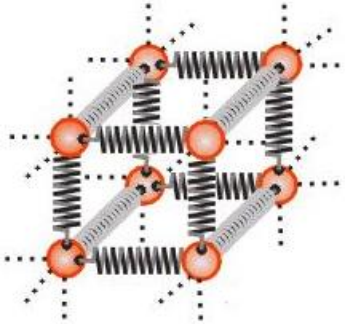
2.6 Thermal conductivity

- **Internal energy (u)**

$$\delta Q = du + \cancel{\delta W}$$

: 1st law of thermodynamics





Translational energy $\frac{1}{2}m({v_x}^2 + {v_y}^2 + {v_z}^2)$

Rotational energy $\frac{1}{2}I({w_x}^2 + {w_y}^2 + {w_z}^2)$

Vibrational energy $\frac{1}{2}(m\dot{x}^2 + kx^2)$

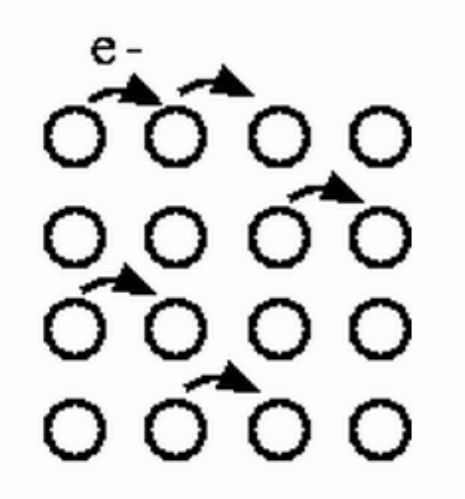
<Internal energy for dielectric molecule>

$$\frac{1}{2}(m(\dot{x}^2+\dot{y}^2+\dot{z}^2) + k(x^2+y^2+z^2))$$

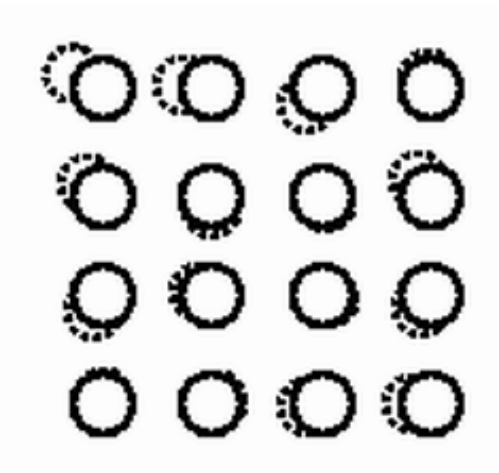
<Internal energy for solid>

2.6 Thermal conductivity

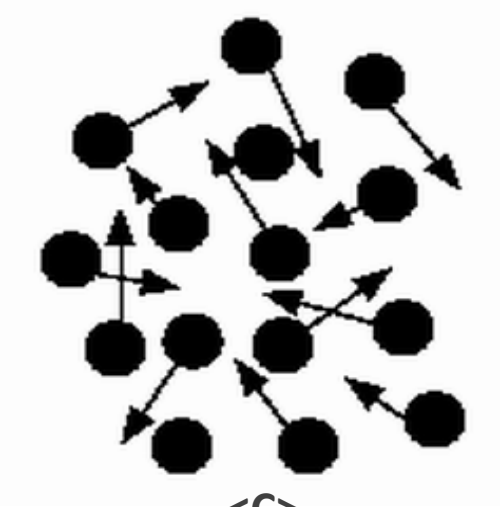
- **Three different mechanisms for conduction in materials**



<A>



<B>



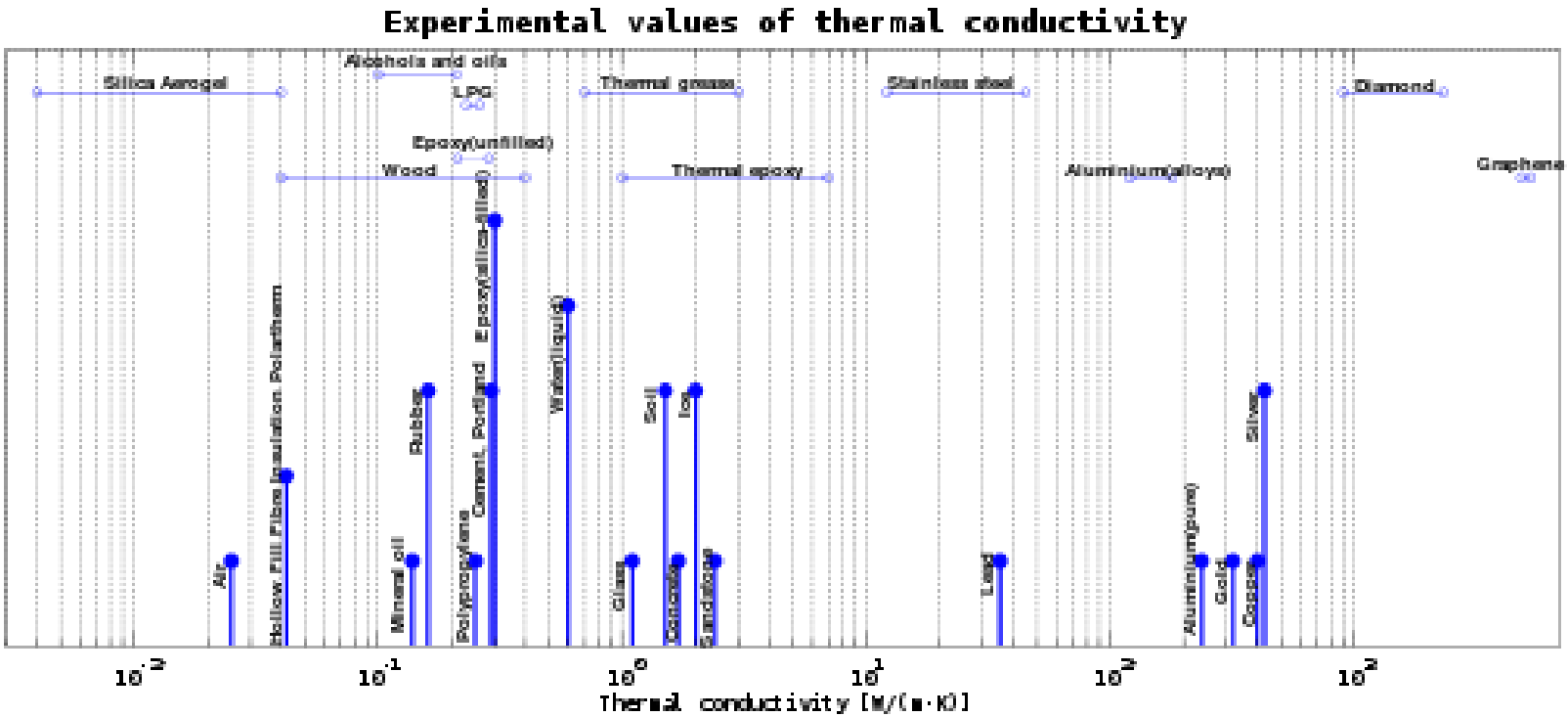
<C>

<A> : Electron motion (metallic conductor)

<B> : Lattice vibration-energy transport (phonon motion; only have energy)

<C> : Molecular motion (gases)

2.6 Thermal conductivity



Experimental values of thermal conductivity

2.6 Thermal conductivity

- **Gases thermal conductivity**

$$k_t = \frac{1}{8}(9\gamma - 5)\rho c_v \bar{v}\lambda \ (Eucken, 1913)$$

γ: specific heat ratio

ρ: density of material

c_v: specific heat at constant volume

$\bar{v}$: average particle velocity

λ: mean free path of particles

2.6 Thermal conductivity

- **Gases thermal conductivity**

$$\bar{v} = \left(\frac{8 g_c R T}{\pi}\right)^2 \quad (Present, 1958)$$

g_c: $1\ kg \cdot m/N \cdot s^2$

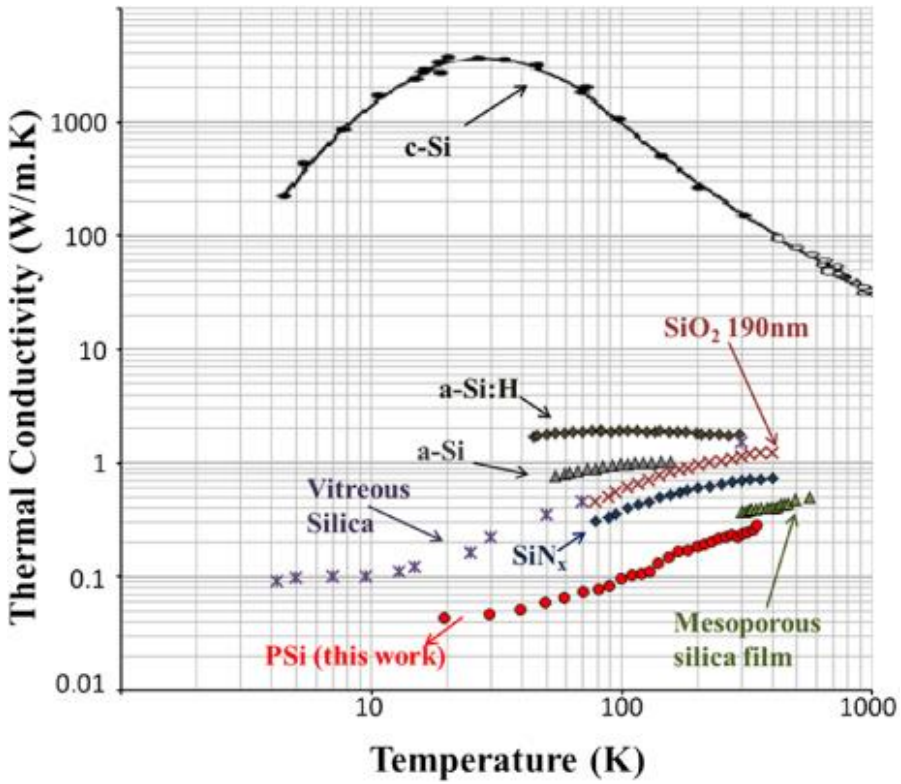
R: R_u/M, R_u= 8.31434 $\frac{J}{mol} \cdot K$

M: molecular weight of the gas

T: absolute temperature of the gas

2.6 Thermal conductivity

- **Gases thermal conductivity**



Comparison of the thermal conductivity of porous Si (this work) with that of bulk crystalline silicon (Glassbrenner and Slack 1964), a-Si (Lee et al 1991), a-Si : H (Cahill et al 1989) and different other C-MOS compatible films (mesoporous silica (Shin et al 2008), vitreous silica (Smith et al 1978) and silicon nitride (Lee and Cahill 1997)).

2.6 Thermal conductivity

- **Solids thermal conductivity**

$$k_t = \frac{1}{3}\rho c_v \bar{v} \lambda$$

ρ: density of material

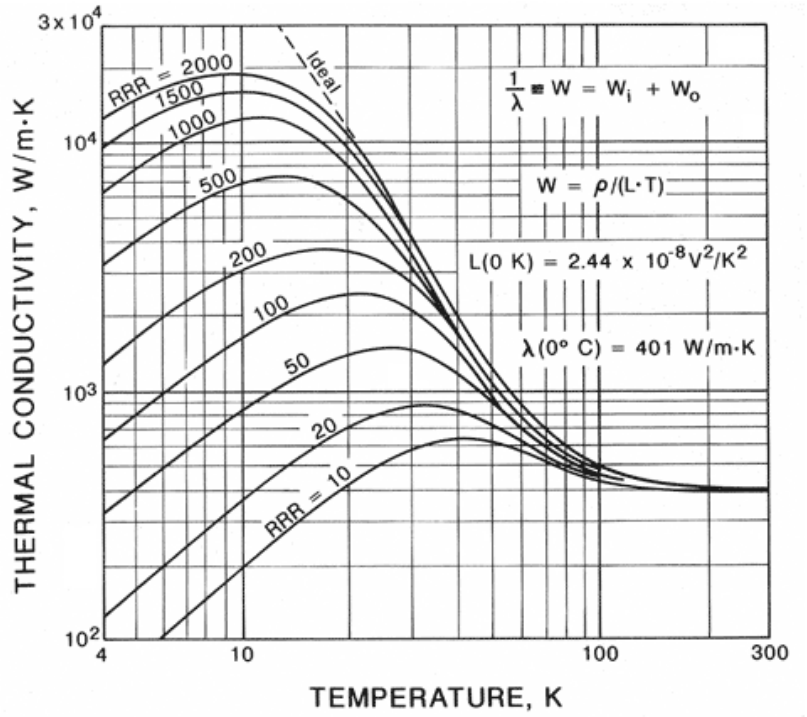
c_v: specific heat at constant volume

$\bar{v}$: average particle velocity

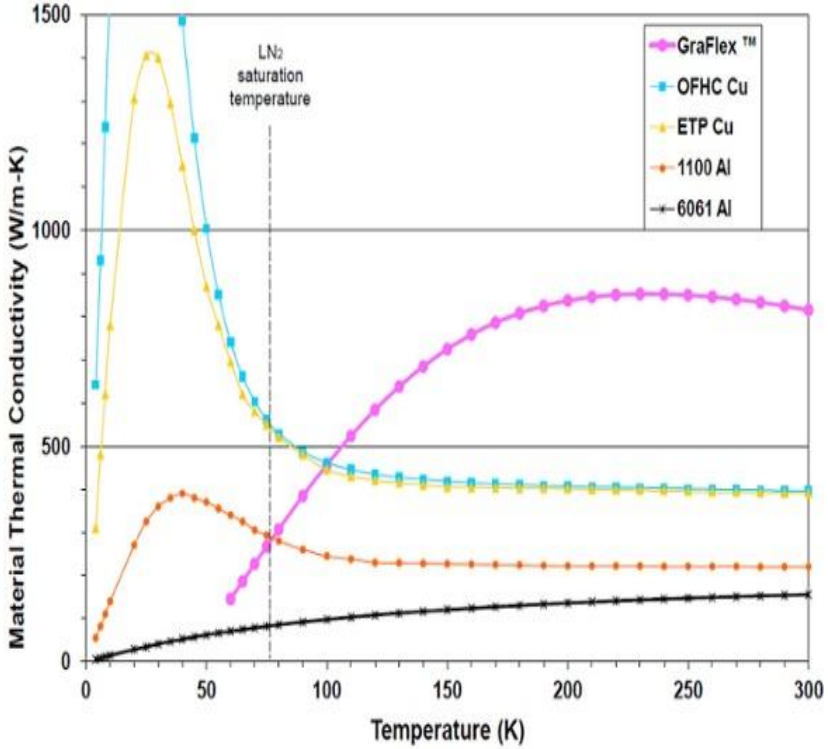
λ: mean free path of particles

2.6 Thermal conductivity

- **Solids thermal conductivity**



Thermal conductivity of copper alloys



Graphite Thermal Conductivity vs Al and Cu Straps

2.7 Specific heats of solids

- **Specific heat**

The energy required to change the temperature of the substance by one degree!

- C_p When constant pressure
- C_v When constant volume

Debye specific heat function

- **Debye model**

For solids, “Debye model” represents how the specific heats change under the temperature variation

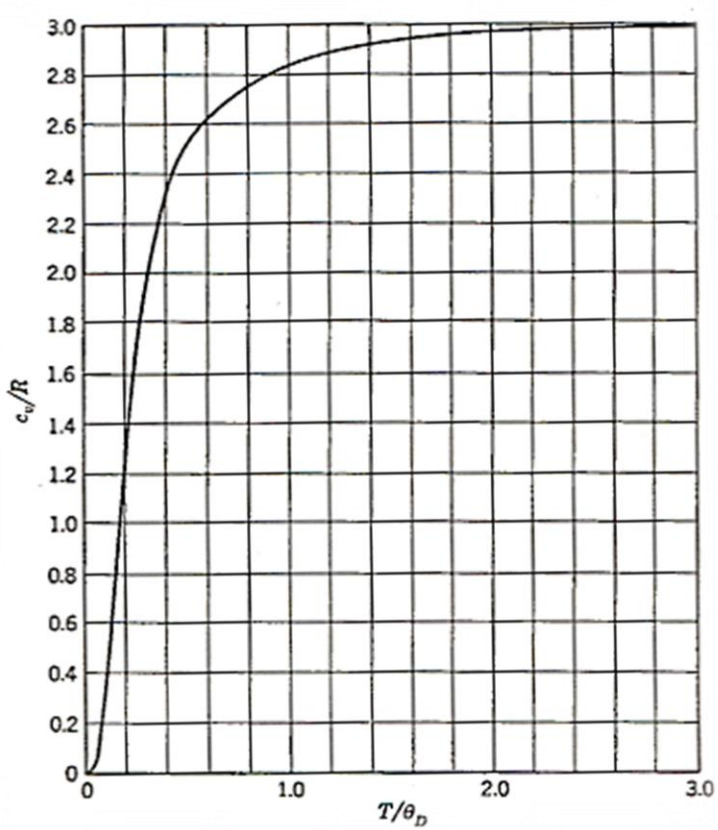
$$C_v = \frac{9RT^3}{\theta_D^3}\int_0^{\theta_D/T}\frac{x^4 e^x dx}{(e^x-1)^2} = 3\mathrm{R}\left(\frac{T}{\theta_D}\right)^3 D\left(\frac{T}{\theta_D}\right)$$

θ_D : Debye Characteristic temperature
$D(\mathrm{T}/\theta_D)$: Debye function

where, $\theta_D = \frac{hv_a}{k}\left(\frac{3N}{4\pi V}\right)^{1/3}$

h : Planck's constant
v_a : Speed of sound in the solid
k : $Boltzmann's\ constant$
N/V : $Number\ of\ atoms\ per\ unit\ volume\ for\ the\ solid$

Debye specific heat function



The Debye specific heat function

- $\frac{T}{\theta_D} > 3$, $\frac{C_v}{R} \approx 3$ (Dulong-Petit value)
- $\frac{T}{\theta_D} < \frac{1}{12}$, $\frac{C_v}{R} \propto T^3$

Specific heat affected by electrons

According to quantum theory,

$$C_{v,e} = \frac{4\pi^4 a m_e M R^2 T}{h^2 N_0 (3\pi^2 N/V)^{2/3}} = \gamma_e T$$

$a = Number\ of\ free\ electrons\ per\ atom$
$m_e = Electron\ effective\ mass$
$M = atomic\ weight\ of\ material$
$R = Specific\ gas\ constant\ for\ material$
$T = Absolute\ temperature$
$h = Planck's\ constant$
$N_0 = Avogadro's\ number$
$N/V = Number\ of\ free\ electrons\ per\ unit\ volume$
$\gamma_e = Electronic\ specific - heat\ coefficient$

Specific heat affected by electrons

Table. Electronic specific heat coefficients

Material	γ_e mJ/kg-K^2	γ_e Btu/lb$_m$-°R^2
Aluminum	50.4	6.69×10^{-6}
Beryllium	24.6	3.27×10^{-6}
Chromium	29.8	3.95×10^{-6}
Copper	11.0	1.46×10^{-6}
Gold	3.55	0.471×10^{-6}
Iron	89.9	11.9×10^{-6}
Nickel	124.0	16.5×10^{-6}
Niobium	94.9	12.6×10^{-6}
Platinum	34.0	4.51×10^{-6}
Silver	5.65	0.749×10^{-6}
Tantalum	32.3	4.29×10^{-6}
Titanium	74.1	9.83×10^{-6}
Zirconium	33.2	4.41×10^{-6}

By permission from Gopal (1966).

Ordinary temperature → γ_e is small (ignorable)

Low Temperature → γ_e becomes important!

2.8 Specific heat of liquids and gases

- **Specific heat of a material (equipartition theorem)**

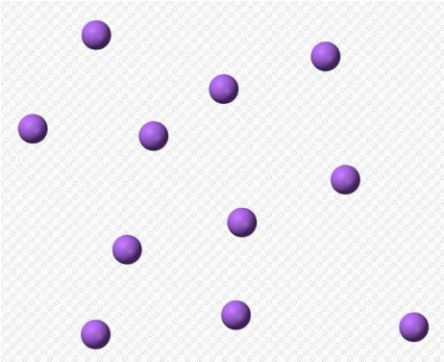
$$C_v = \frac{1}{2}Rf$$

(f : number of degrees of freedom)

① Monatomic gas

- Degree of freedom
  - Translational motion : 3
  - Rotational motion : 0
  - Vibrational motion : 0

$$\therefore C_v = \frac{3}{2}R$$



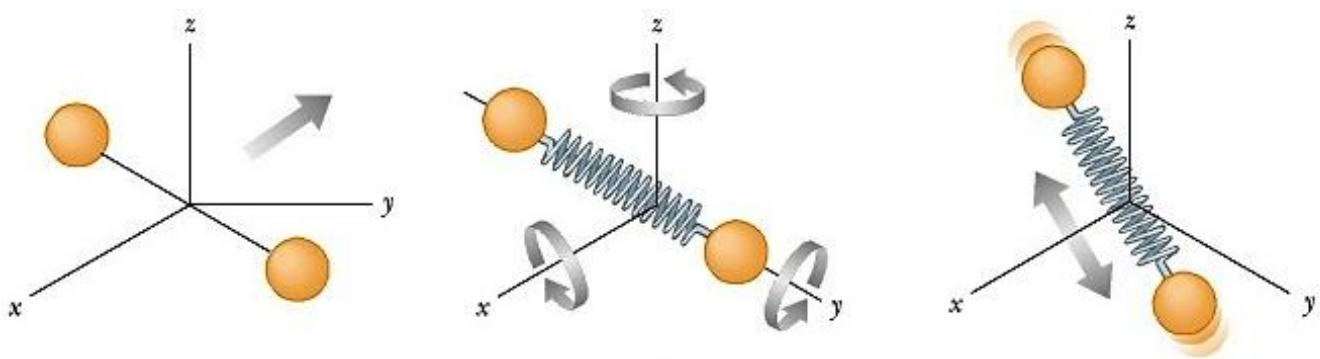
2.8 Specific heat of liquids and gases

② Diatomic gas

- Degree of freedom
  - Translational motion : 3
  - Rotational motion : 2
  - Vibrational motion : 2

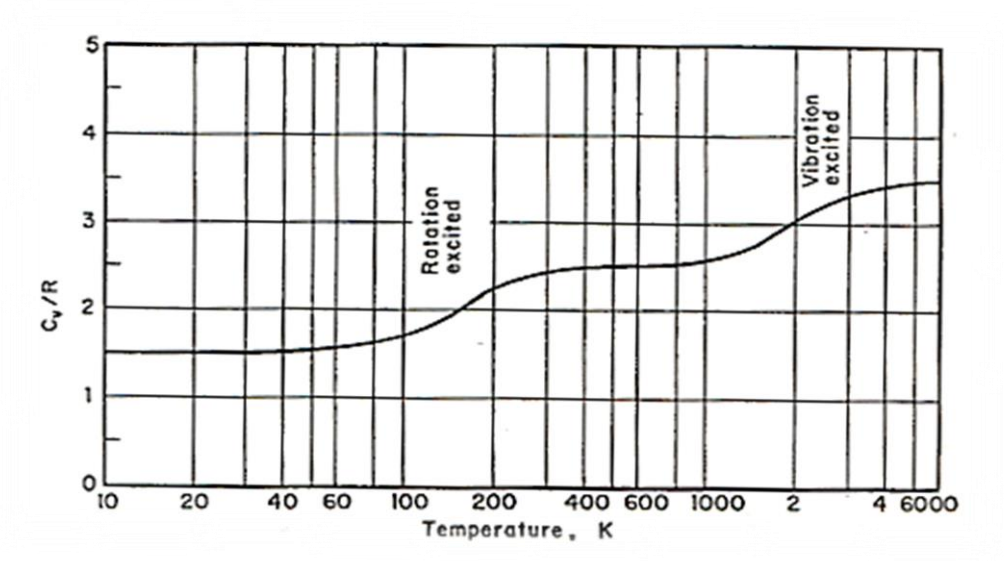
$$\therefore C_v = \frac{7}{2}R$$

(according to the classical theory)



2.8 Specific heat of liquids and gases

In the actual case, rotational, vibrational modes are quantized!



<Variation of the specific heat C_v for hydrogen gas>

0~10K	Translational motion only $(\frac{C_v}{R} = \frac{3}{2})$
10~1000K	Translational+Rotational motion $(\frac{C_v}{R} = \frac{5}{2})$
1000K~	Translational+Rotational+Vibrational motion $(\frac{C_v}{R} = \frac{7}{2})$

2.9 Coefficient of thermal expansion

- **Coefficient of thermal expansion**

  - For isotropic materials

$$\beta = 3\lambda_t$$

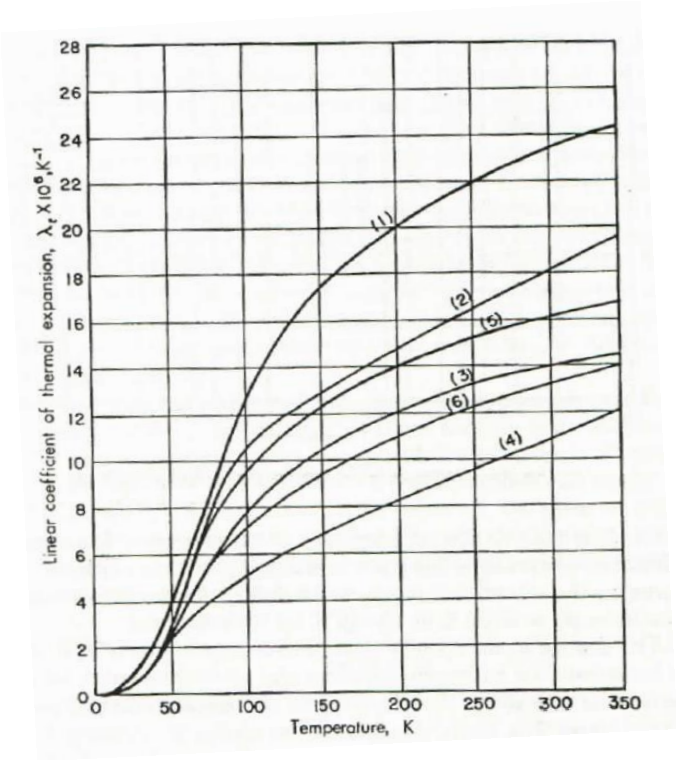
$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$ (in the vicinity of the critical point)

β is fractional change in volume per unit change in temperature

λ_t is the linear coefficient of thermal expansion

2.9 Coefficient of thermal expansion

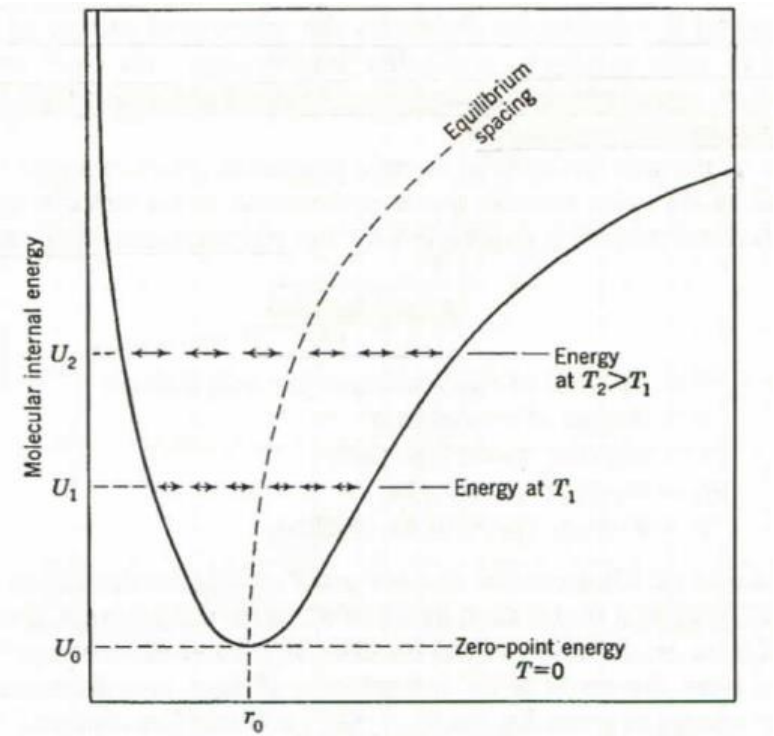
- **The temperature variation of the linear coefficient for thermal expansion for several materials**



Linear coefficient of thermal expansion for several materials at low temperature:
(1) 2024-T4 aluminum (2) beryllium copper (3) K Monel
(2) (4) titanium (5) 304 stainless steel (6) C1020 carbon steel

2.9 Coefficient of thermal expansion

- **The intermolecular potential-energy curve**



Variation of the intermolecular potential energy for a pair of molecules

2.9 Coefficient of thermal expansion

- **The intermolecular forces**

  - The intermolecular potential-energy curve is not symmetrical. Therefore, as the molecule acquires more energy, its mean position relative to its neighbors becomes larger, that is, the material expands.

  - The coefficient of thermal expansion increases as temperature is increased.

2.9 Coefficient of thermal expansion

- **Coefficient of thermal expansion**

  - For crystalline solids, the Gruneisen relation

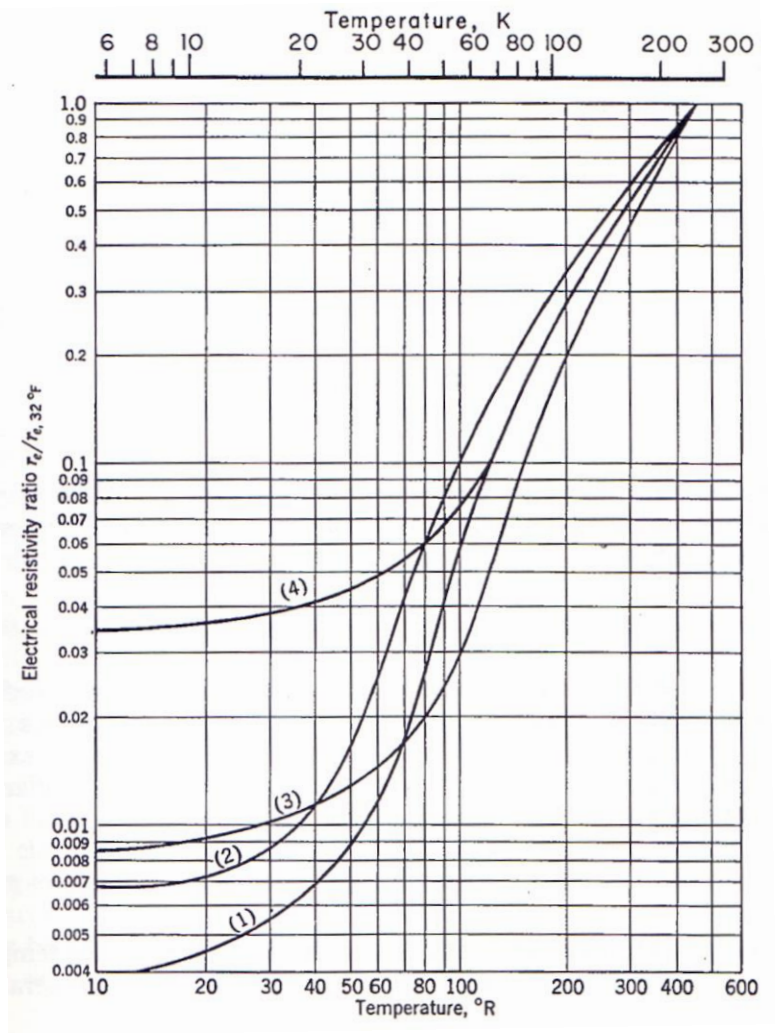
$$\beta = \frac{\gamma_G c_v \rho}{B}$$

ρ is the density of the material
B is the bulk modulus
γ_G is the Gruneisen constant

Material	γ_G
Aluminum	2.17
Copper	1.96
Gold	2.40
Iron	1.60
Lead	2.73
Nickel	1.88
Platinum	2.54
Silver	2.40
Tantalum	1.75
Tungsten	1.62

Values of the Gruneisen constant for selected solids

2.10 Electrical conductivity



$$k_e = \frac{I/_{Area}}{dV/_{dx}} = \frac{I/_A}{V/_I} = \frac{L}{RA}$$

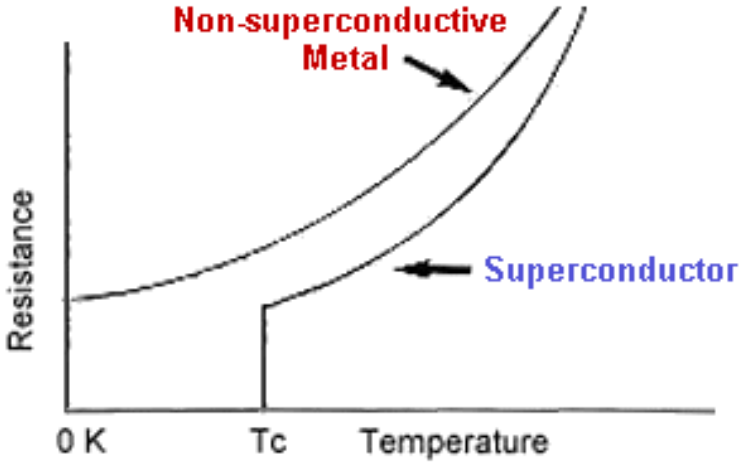
Electrical resistivity, $\rho = \frac{1}{k_e}$

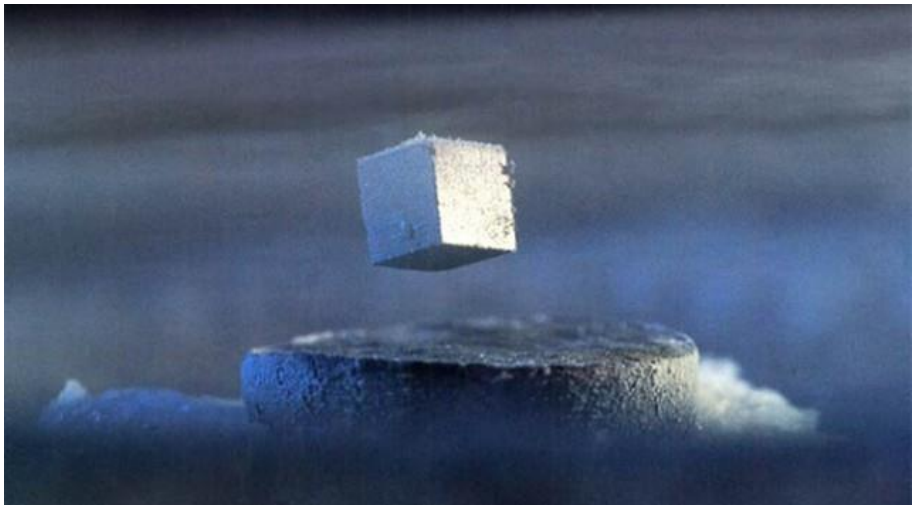
As T ↓, Vibrational E ↓

$$q = kA\frac{dT}{dx} \qquad I = k_e A\frac{dV}{dx}$$

2.11 Superconductivity

- Only at very low T
- Disappearance of all electric resistance
- Appearance of perfect diamagnetism





Paramagnetism ~ magnet
diamagnetism ~ repel
ferromagnetism ~ stick

2.11 Superconductivity

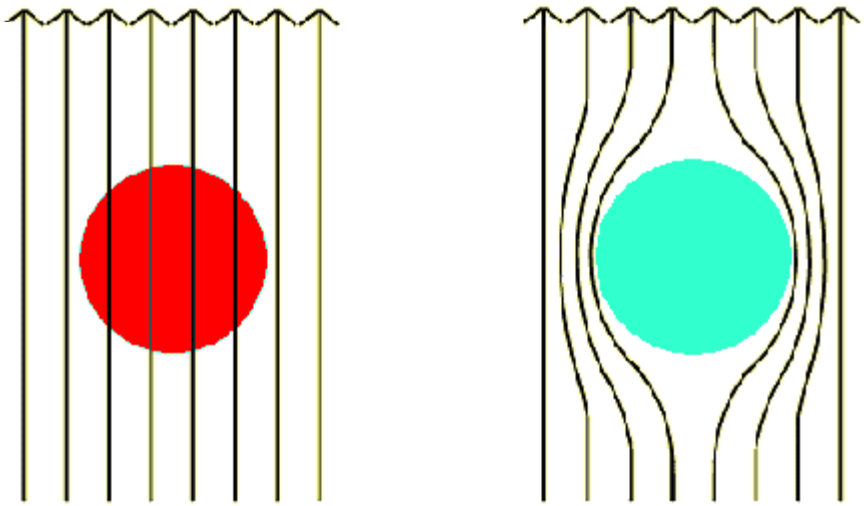
T : $T < T_o$

$\mathcal{H}$: $\mathcal{H}_o$(Critical field)

└ magnetic field strength required to destroy superconductivity

I : I_c(Critical current)

└ upper limit to the electric current without destroying superconductivity



Normal Superconducting

2.11 Superconductivity

- **Applications**

MRI (Magnetic Resonance Imaging)
High magnetic field stability

2.11 Superconductivity

- **Video: Levitating Superconductor on a Möbius strip**

The Royal Institution - Levitating Superconductor on a Möbius strip
https://www.youtube.com/watch?v=zPqEEZa2Gis

2.12 Cryogenic fluid property

$LN_2 (liquid\ N_2)$

→ Clear, Colorless
→ N.B.P. (Normal Boiling Point) : $77K$
→ Produced by the distiliation of air
→ Small heat of vaporization

2.12 Cryogenic fluid property

Usage of $LN_2(liquid\ N_2)$

Quick freezing of food, Drying etc.

2.12 Cryogenic fluid property

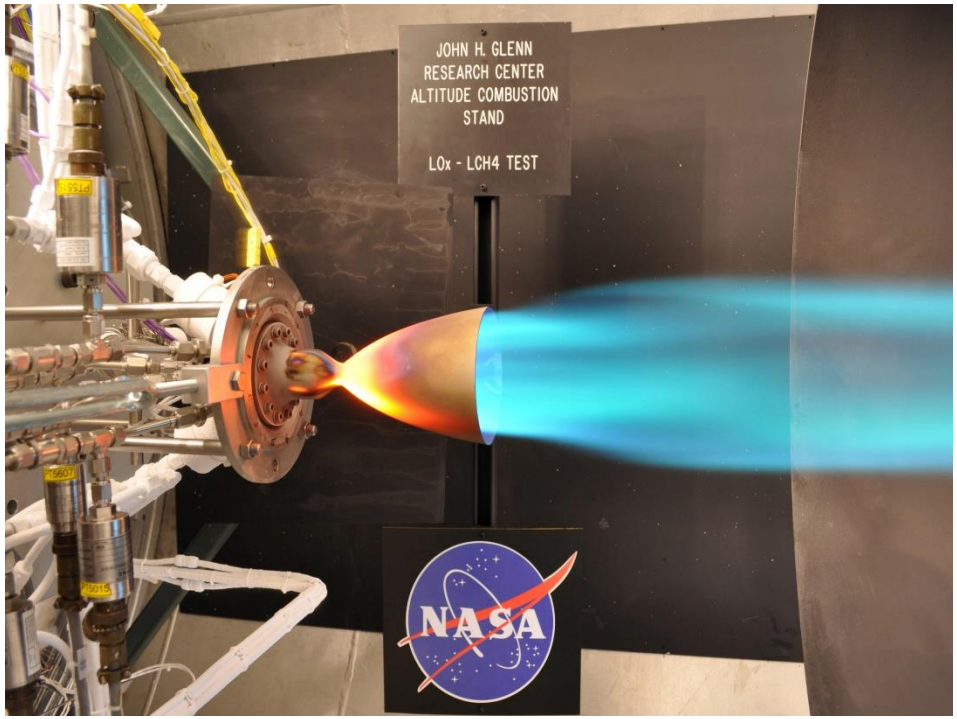
$LO_2 (liquid\ O_2)$

→ Slightly magnetic (paramagnetic)
→ N.B.P. (Normal Boiling Point) : $90K$
→ Produced by the distiliation of air
→ Slightly magnetic (paramagnetic)

2.12 Cryogenic fluid property

Usage of $LO_2(liquid\ O_2)$

Fuel of rocket, welding etc.



2.13 H_2

N.B.P. = $20.3K$

Types of hydrogen atom

$H - H \quad H - D$

$D - D \quad T - T$

	H hydrogen	D deuterium	T tritium
$proton$	1	1	1
$neutron$	0	1	2
$electron$	1	1	1

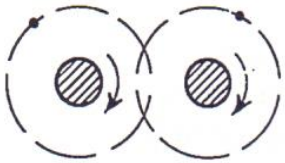
2.13 H_2

N.B.P. = $20.3K$

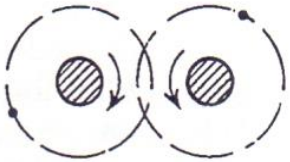
Types of hydrogen molecules

$ortho - H_2$
(Spins aligned, high energy)

$para - H_2$
(Opposite spins, low energy)

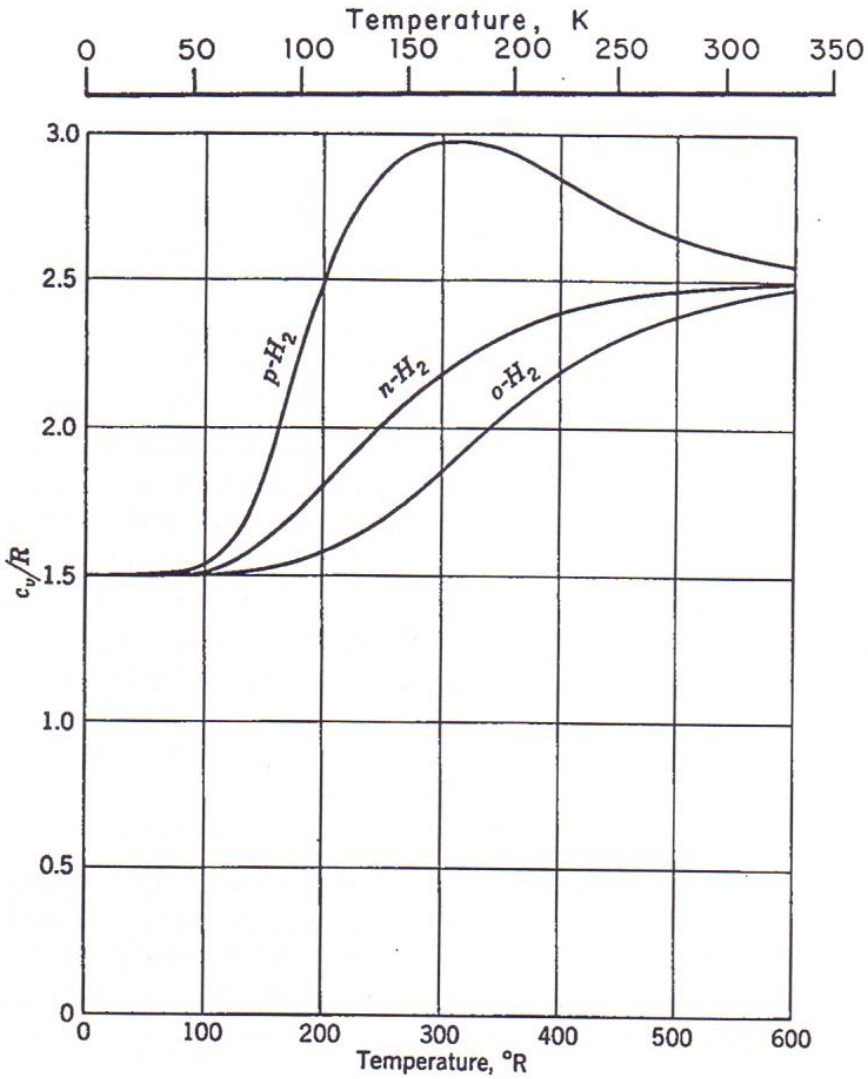


Ortho-hydrogen



Para-hydrogen

2.13 H_2

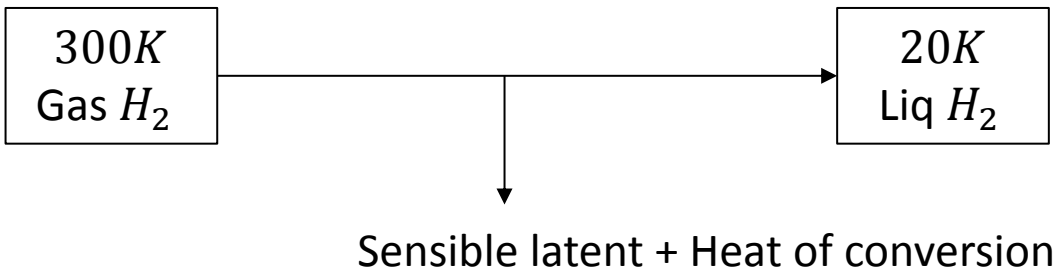

Temperature, K
0
50
100
150
200
250
300
350
3.0
2.5
2.0
1.5
1.0
0.5
0
c_v/R
p-H_2
n-H_2
o-H_2
0
100
200
300
400
500
600
Temperature, °R

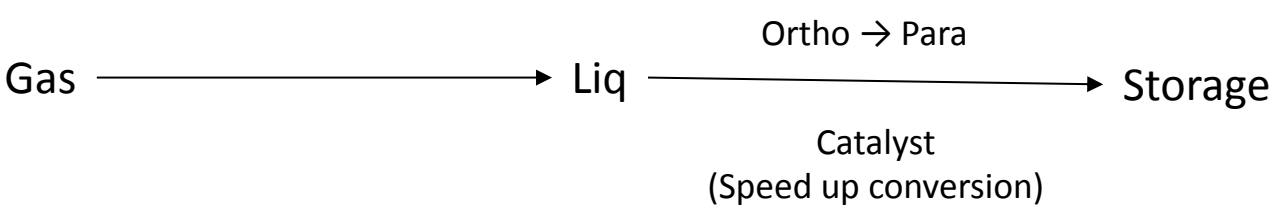
2.13 H_2

$ortho - H_2 \rightarrow$
$para - H_2 + \Delta\alpha\ (heat\ of\ conversion)$
$70.3kJ/kg$
Latent heat $44.3kJ/kg$

At high temperature is a mixture of $75\%\ ortho - H_2$ and $25\%\ para - H_2$
As temperature is cooled to the normal boiling point of hydrogen, the $ortho - H_2$ concentration decreases from $75\ to\ 0.2\%$

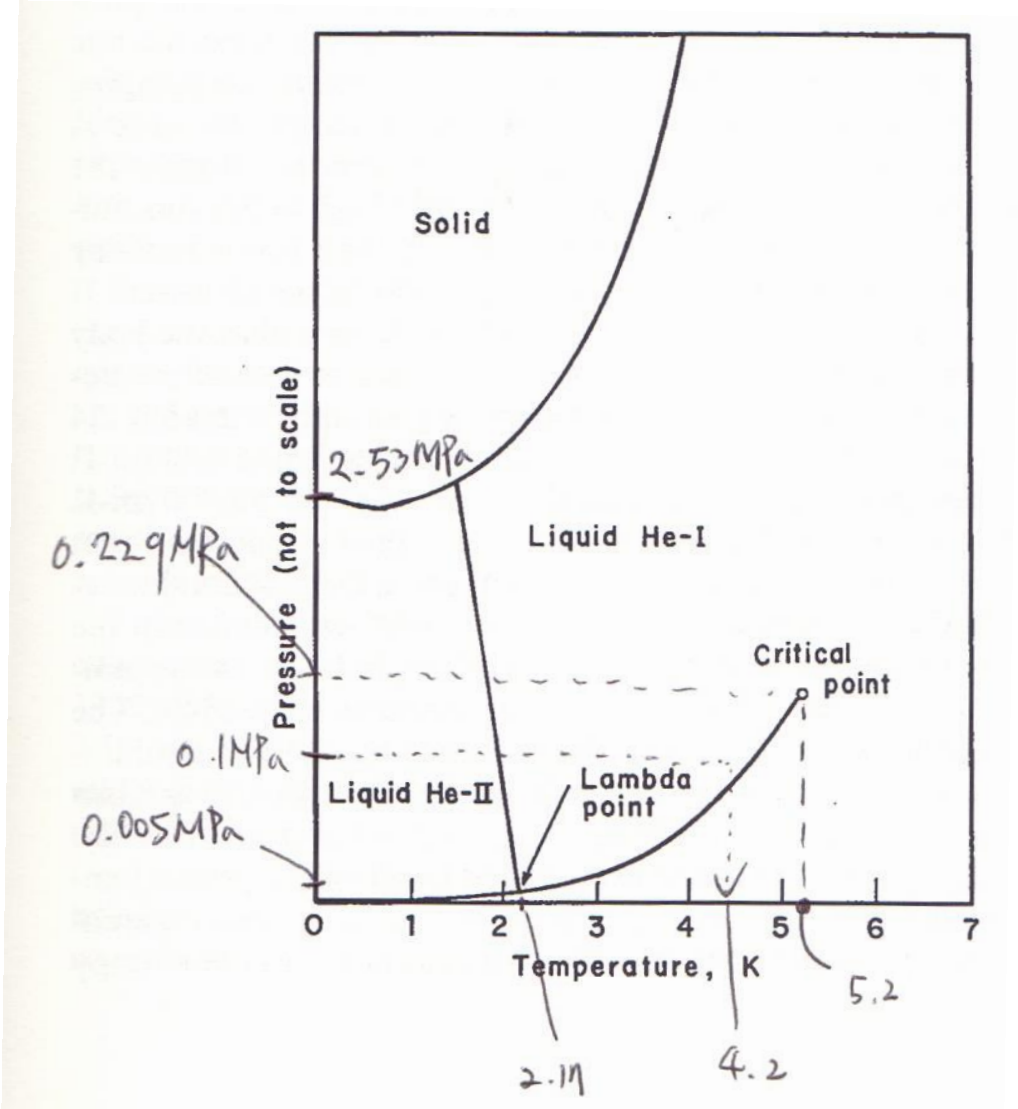
2.13 H_2


300K
Gas H2
20K
Liq H2
Sensible latent + Heat of conversion


Gas
Liq
Ortho → Para
Storage
Catalyst
(Speed up conversion)

2.13 He^4

- Difficult to liquefy
- N.B.P. = $4.2K$
- No triple point



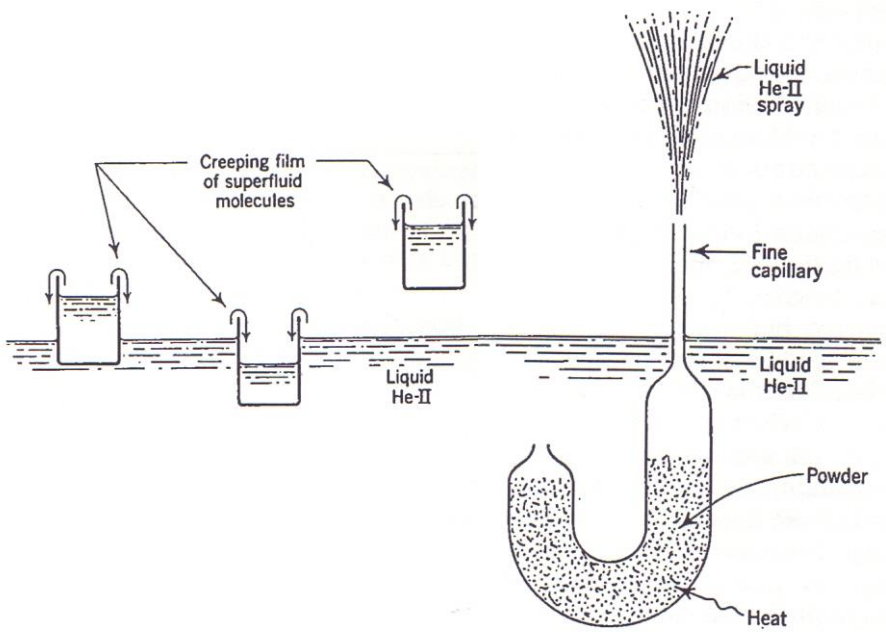
2.13 He^4

$He - \mathrm{I}$: Normal fluid

$He - \mathrm{II}$: Super fluid

└ act as if it has zero viscosity

$$\left(viscosity,\ \tau = \mu \frac{dV}{dr}\right)$$



Behavior of superfluid

2.13 He^4

- **Video: Superfluid helium**

BBC - Ben Miller experiments with superfluid helium - Horizon: What is One Degree? - BBC Two
https://www.youtube.com/watch?v=9FudzqfpLLs

2.14 He^3

- N.B.P. = $3.19K$
- Super fluid transition = $3.5mK$