Materials and their properties

Corso Materiali intelligenti e Biomimetici
1/03/2018

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Lamb 67


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BANG!
STONE AGE
BANG!
BRONZE AGE
BANG!
IRON AGE
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BANG!
DARK AGE
BANG!
MODERN AGE
BANG!
CRASH!
COMPUTER AGE
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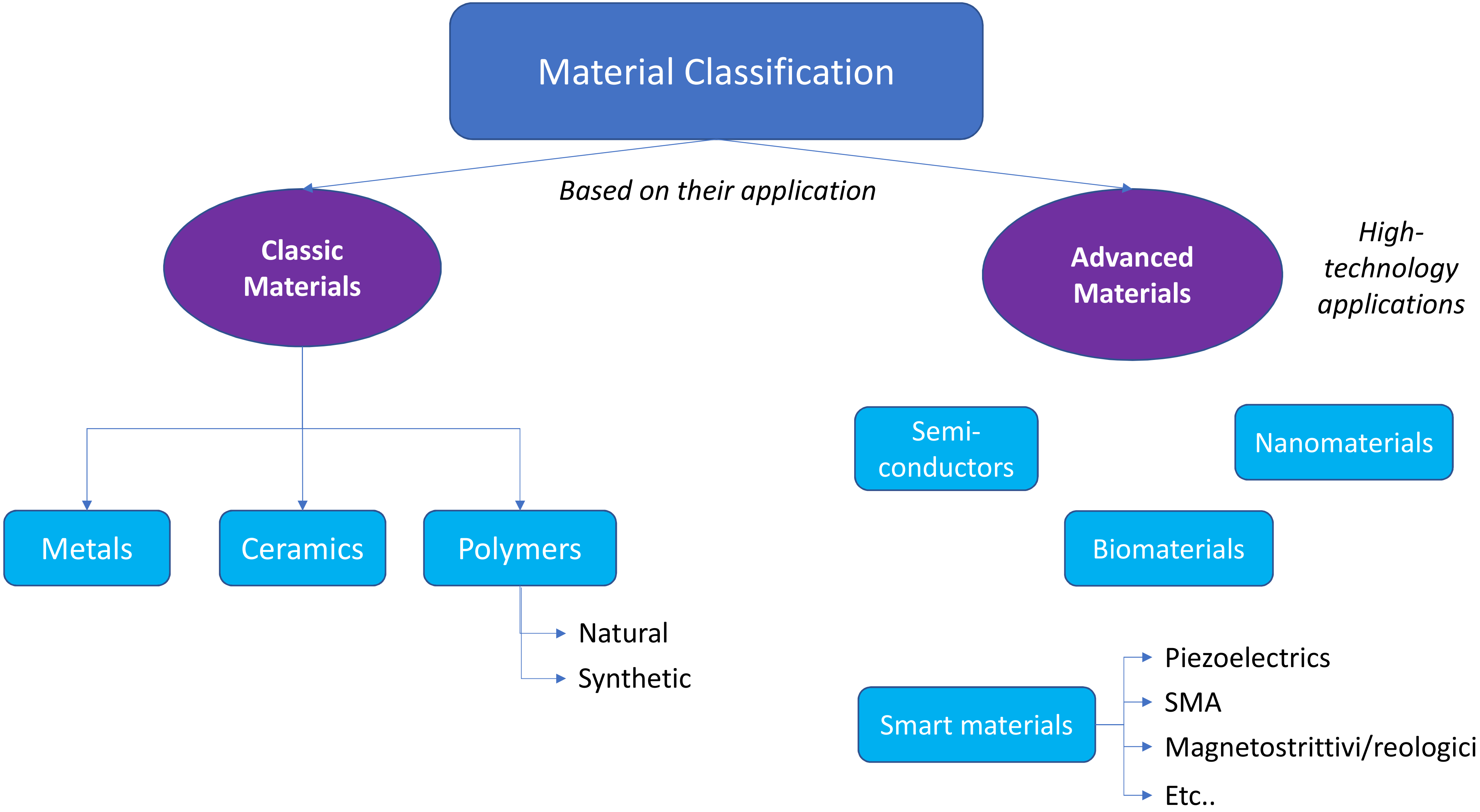
By T. Bui & G. Johnson



Material Classification

Based on their application

Classic Materials

- Metals
- Ceramics
- Polymers
  - Natural
  - Synthetic

Advanced Materials

High-technology applications

- Semi-conductors
- Nanomaterials
- Biomaterials
- Smart materials
  - Piezoelectrics
  - SMA
  - Magnetostrittivi/reologici
  - Etc..

From the previous lesson…

1. **They are able to react to an external stimuli (doing something ‘intelligent’, i.e. useful)**

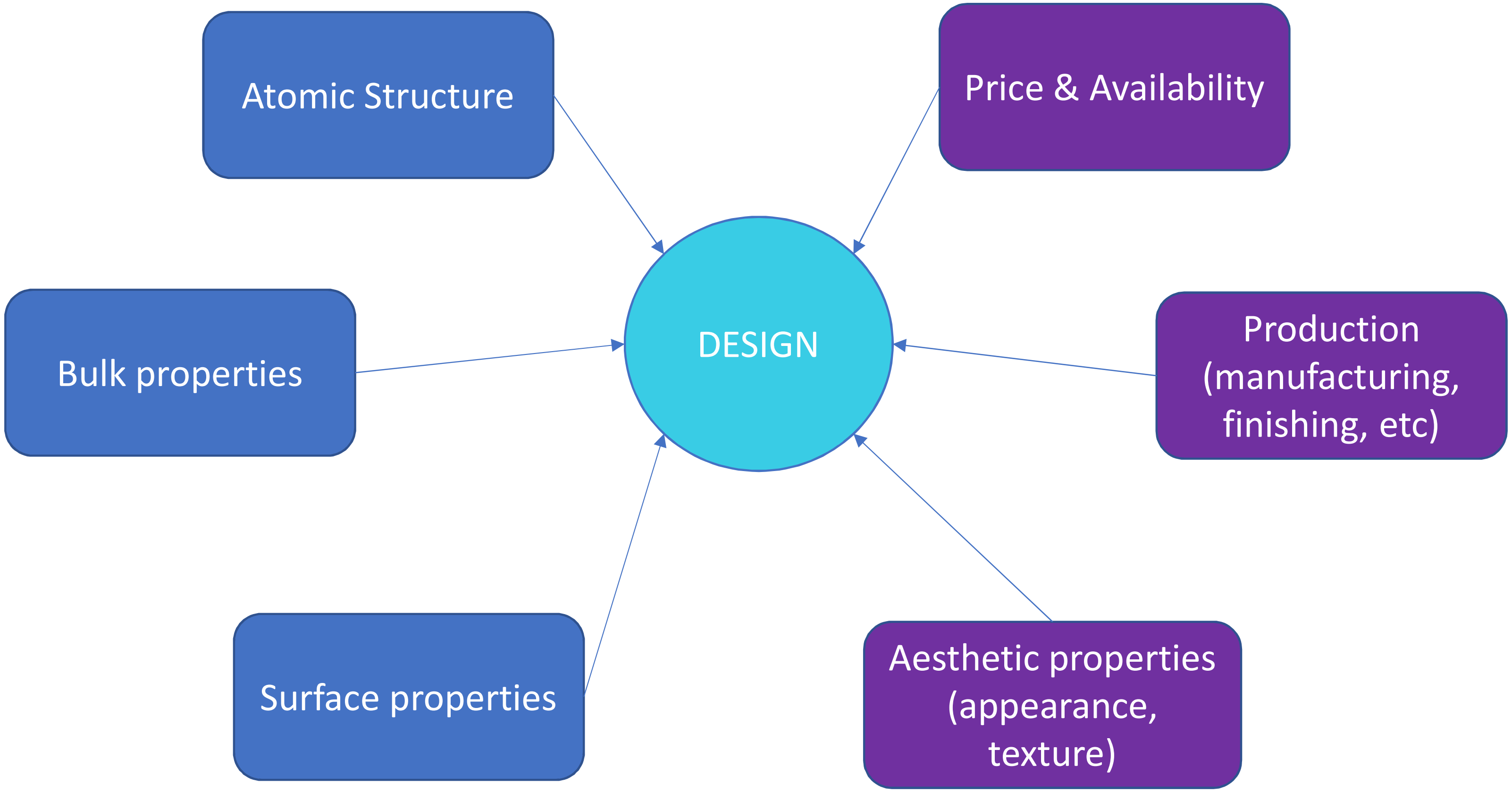
   These materials with one or more **property can be significantly altered in a controlled fashion** by external stimuli. Thus this material has *built-in or intrinsic sensor(s), actuator (s) and control mechanism (s) by which it is capable of sensing a stimulus, responding to it* in a predetermined manner and reverting to its original state as soon as the stimulus is removed.

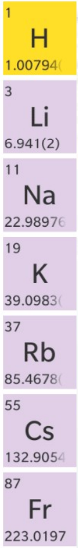
2. **Smart material vs. Smart structure**

Intrinsic properties

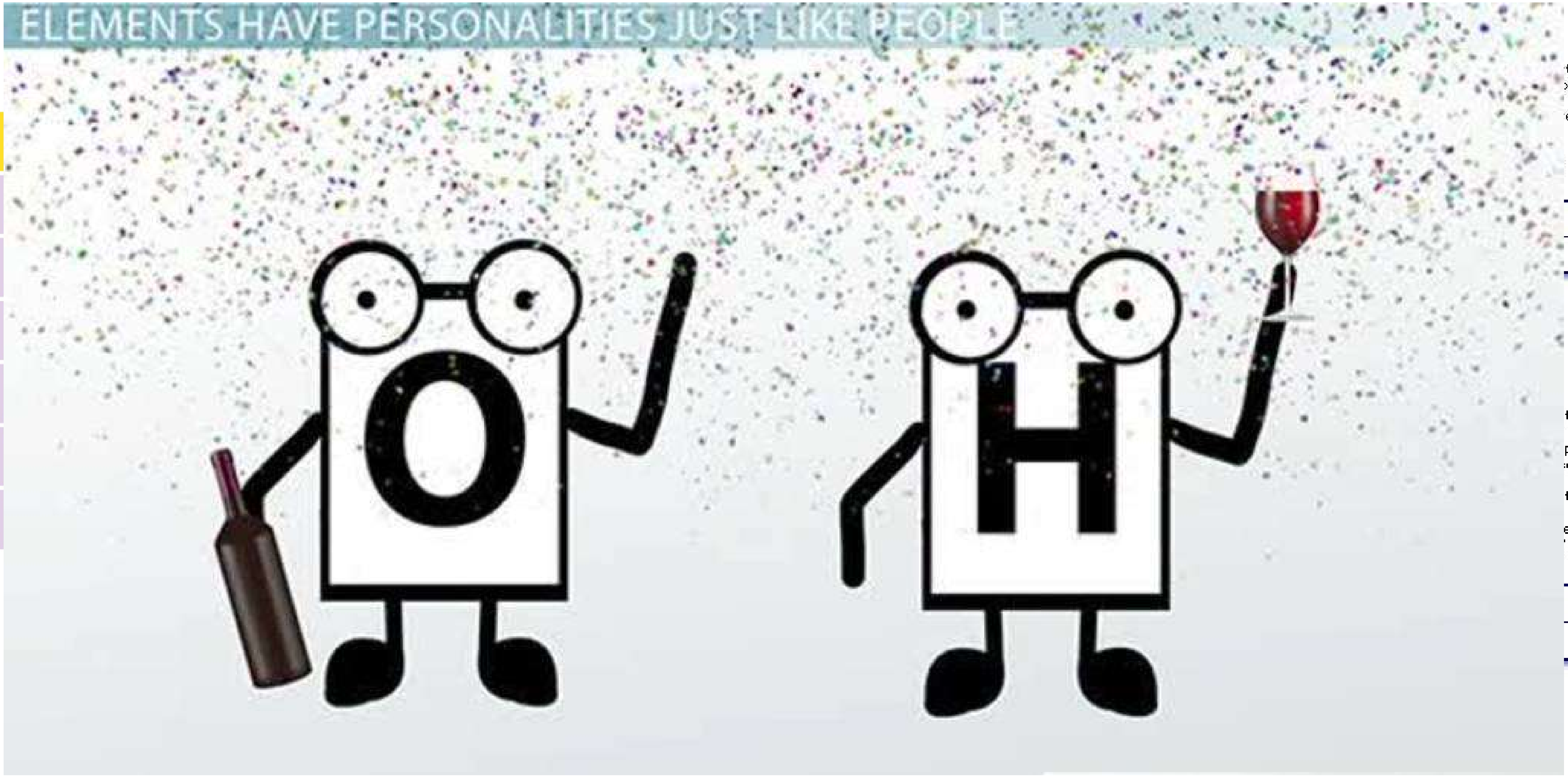
a physical property that does not depend on the amount of the material

Attributive properties





1	H	1.00794
3	Li	6.941(2)
11	Na	22.98976
19	K	39.0983
37	Rb	85.4678
55	Cs	132.9054
87	Fr	223.0197



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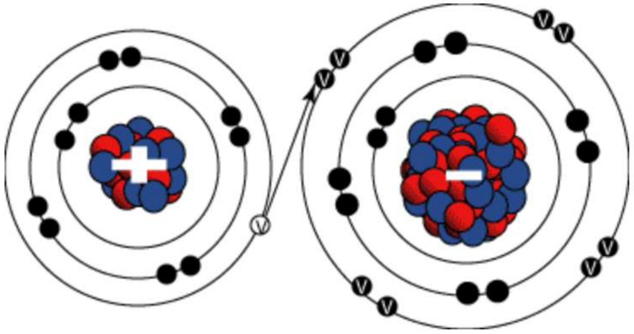
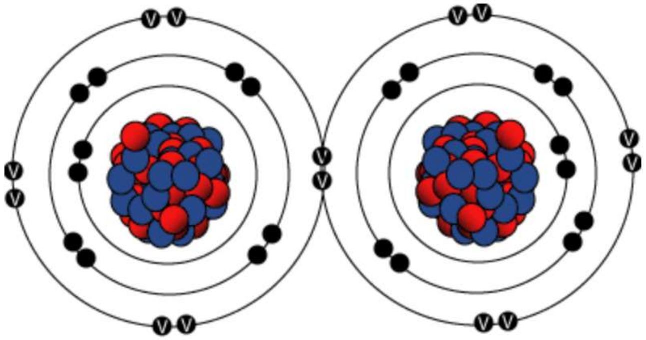
The atomic structure primarily affects the chemical, physical, thermal, electrical, magnetic, and optical properties.

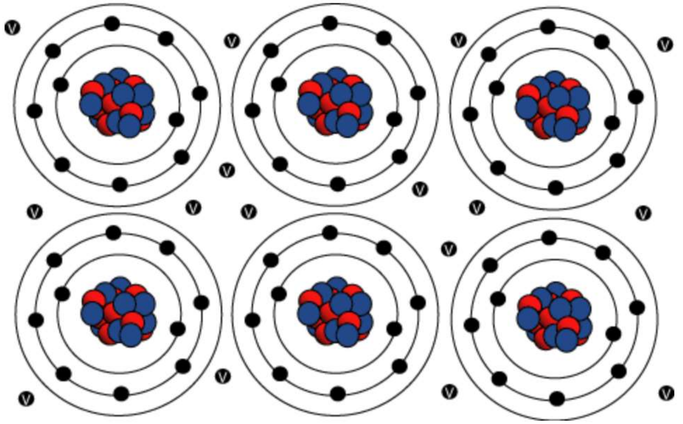
Atomic Bonding



Ionic bonding occurs between charged particles. To become stable, the metal atom wants to get rid of one or more electrons in its outer shell.

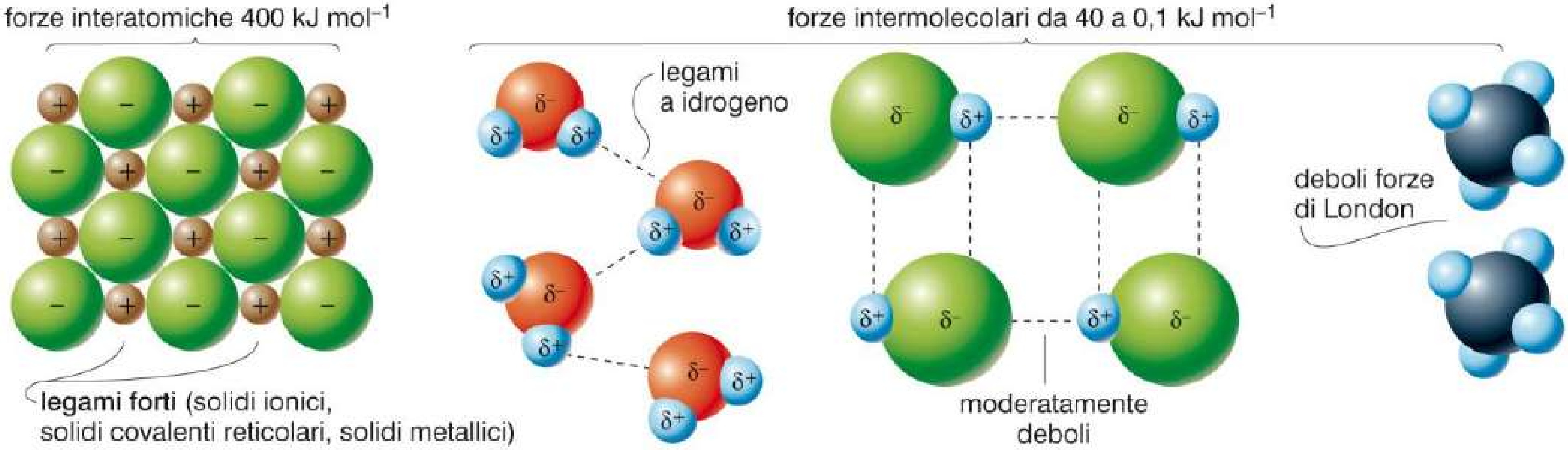


A **covalent bond** is formed by atoms sharing two or more electrons. Consequently, both atoms are held near each other since both atoms have a share in the electrons.



Metallic Bond is formed between metallic elements, which contains only 1 to 3 electrons in the outer shell. The bond between these electrons and the nucleus is relatively weak. So, the outer electrons leave individual atoms to become part of common “electron cloud.”

Forze intermolecolari

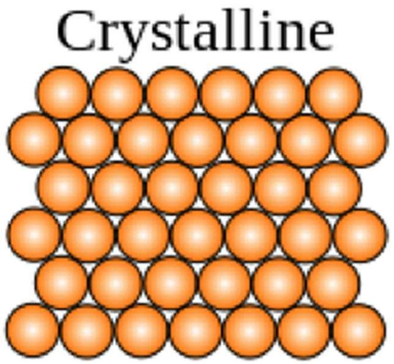


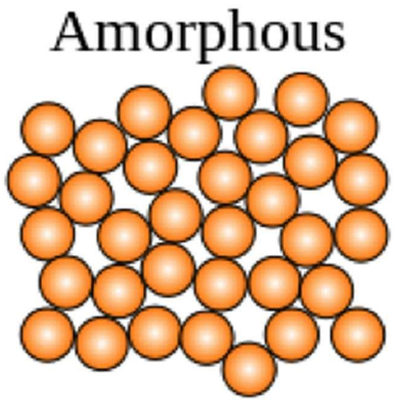
Solid state matter

Matter can be found at the solid state when **attraction between atoms is stronger then thermal agitation**.
In this state, chemical bonding force particles in fix position:

ordinate

casual





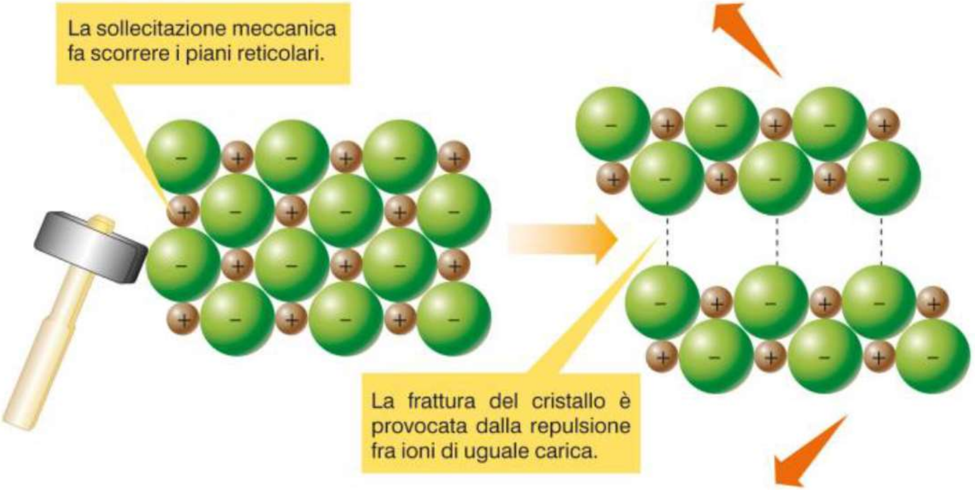
On the basis of the chemical bonding solids can be classified as: Ionic, colavent, metallic, molecular

Solidi Ionici

Nei solidi ionici ogni ione è attratto dagli altri di segno opposto che *si sistemano secondo orientazioni imposte dalle rispettive dimensioni*. Infatti, anioni e cationi hanno dimensioni molto diverse, ma solitamente più grande è un catione (o un anione) maggiore è il numero di anioni (o cationi) con cui esso può venire in contatto.

Si origina così una struttura in cui gli *ioni sono fortemente vincolati tra loro* con conseguenti:

- **alti punti di fusione**
- **elevata durezza**
- **fragilità** (superfici di frattura molto nette disposte secondo piani in cui il vincolo tra gli ioni è minore)
- **scarsa conduzione** allo stato solido (gli ioni sono vincolati nelle posizioni fisse e non possono muoversi), ma sono buoni conduttori allo stato fuso o in soluzione acquosa perché gli ioni divengono liberi di muoversi in seguito della rottura dei legami ionici
- **trasparenza** (gli elettroni non si muovono da atomo ad atomo e tendono ad interagire meno con i fotoni)



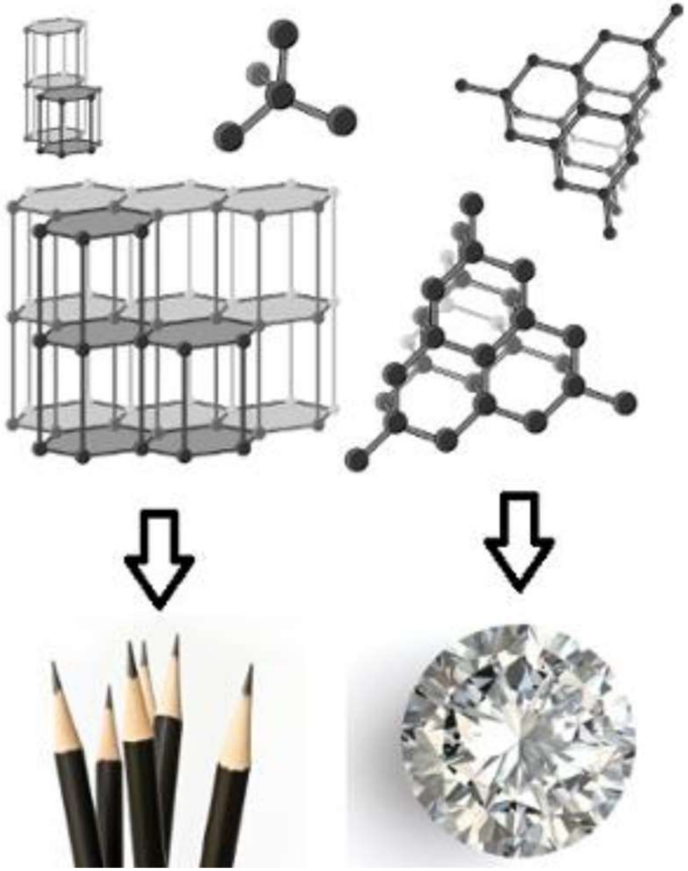
La sollecitazione meccanica fa scorrere i piani reticolari.

La frattura del cristallo è provocata dalla repulsione fra ioni di uguale carica.

Solidi Covalenti

Sono costituiti da atomi tutti uniti tra loro da legami covalenti, molto forti, per cui mostrano anch’essi **elevata durezza ed alti punti di fusione**.

Diamante e grafite sono costituiti da carbonio puro, ma le loro **proprietà** sono nettamente **diverse proprio a causa della disposizione degli atomi nel reticolo cristallino**. Nel diamante gli atomi di carbonio si dispongono in una struttura tridimensionale altamente compatta la cui cella elementare è rappresentata da un tetraedro che forma un reticolo cubico, mentre nella grafite essi costituiscono una struttura planare formata da esagoni. I diversi strati sono tenuti insieme da una nuvola elettronica simile a quella che caratterizza il legame metallico. *Ne segue che il diamante è duro ed isolante, mentre la grafite è facilmente sfaldabile e buona conduttrice di elettricità*.

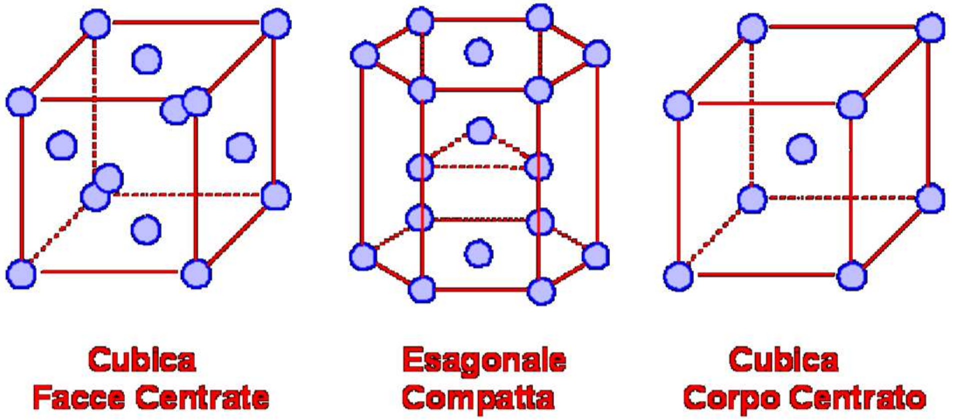


Solidi Metallici

In questi solidi gli elettroni messi in comune dagli atomi permeano come un “gas” gli spazi tra gli ioni positivi che si sono formati. Gli atomi presenti hanno le stesse dimensioni e si dispongono in modo da occupare il minor spazio possibile in reticoli.

La struttura a ioni immersi in un “gas” di elettroni spiega la **buona conducibilità termica e elettrica** dei metalli e la loro eccezionale **deformabilità** (interi blocchi di atomi possono scorrere tra di loro senza che si rompa il reticolo cristallino).

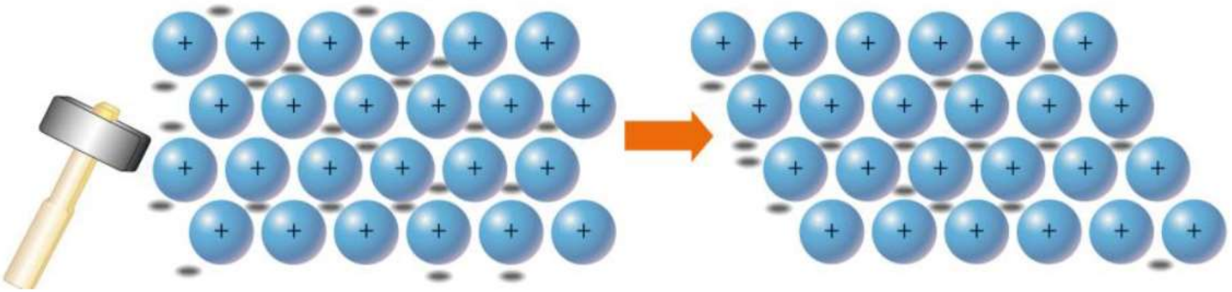
La **lucentezza** si spiega considerando che la luce incidente sulla superficie del metallo fa oscillare alla sua stessa frequenza gli elettroni liberi presenti nel cristallo. Questi, emettono a loro volta radiazioni alla stessa frequenza della luce incidente.



ferro, cromo, molibdeno, tungsteno

zinco, cobalto, magnesio

nichel, rame, argento, platino e oro



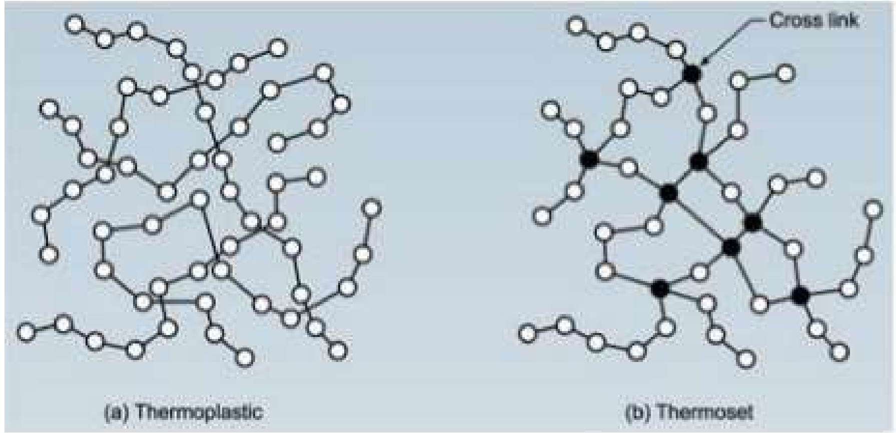
Solidi Molecolari

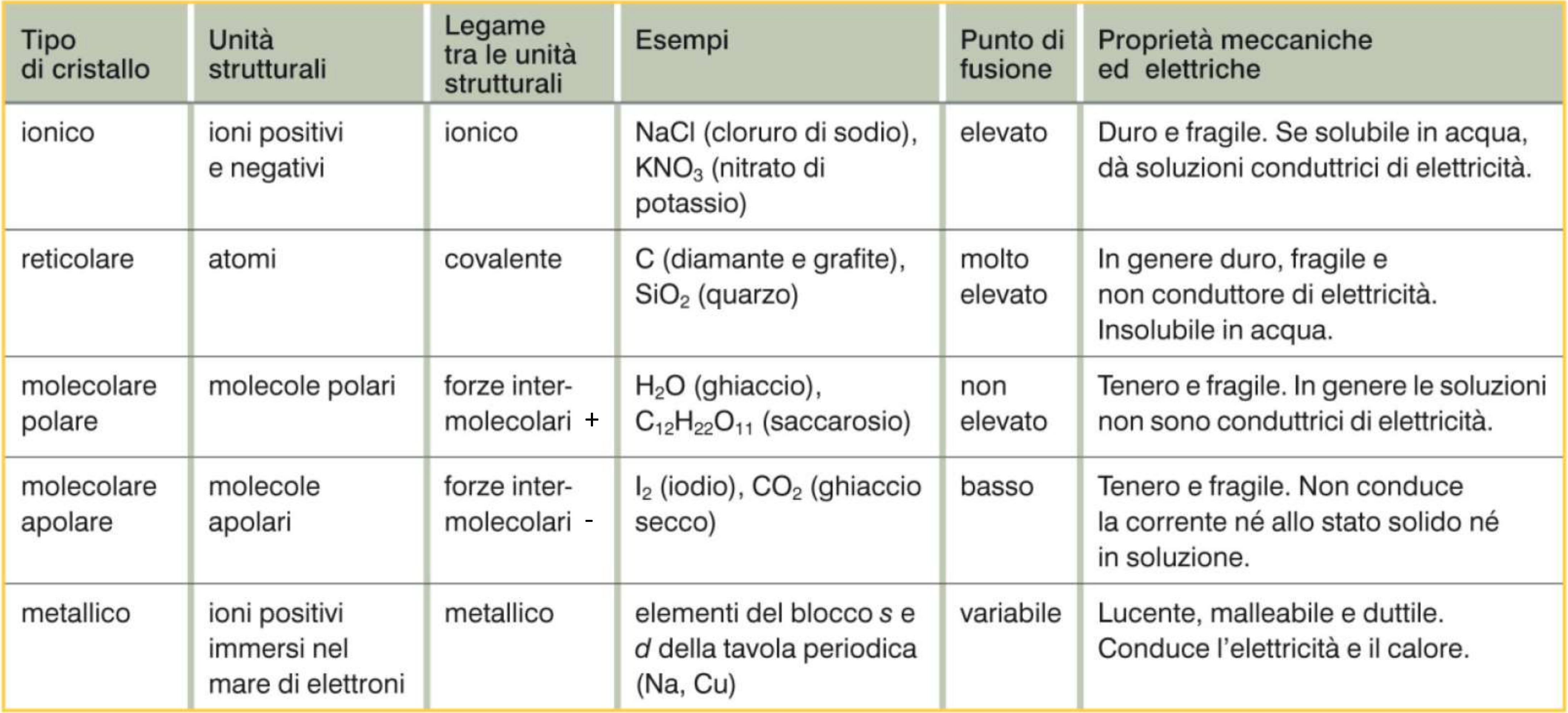

Le sostanze costituite da molecole apolari presentano deboli legami tra le molecole (forze di van der Waals) e forti legami tra gli atomi; sono **tenere e basso-fondenti** (Es: Zolfo). **Non conducono** corrente né allo stato solido né allo stato liquido.

Le sostanze costituite da molecole polari hanno invece legami intermolecolari più forti (dalle interazioni dipolo – dipolo ai legami a idrogeno) per cui hanno punti di fusione e di ebollizione maggiori. Ne sono esempi il ghiaccio e lo zucchero.

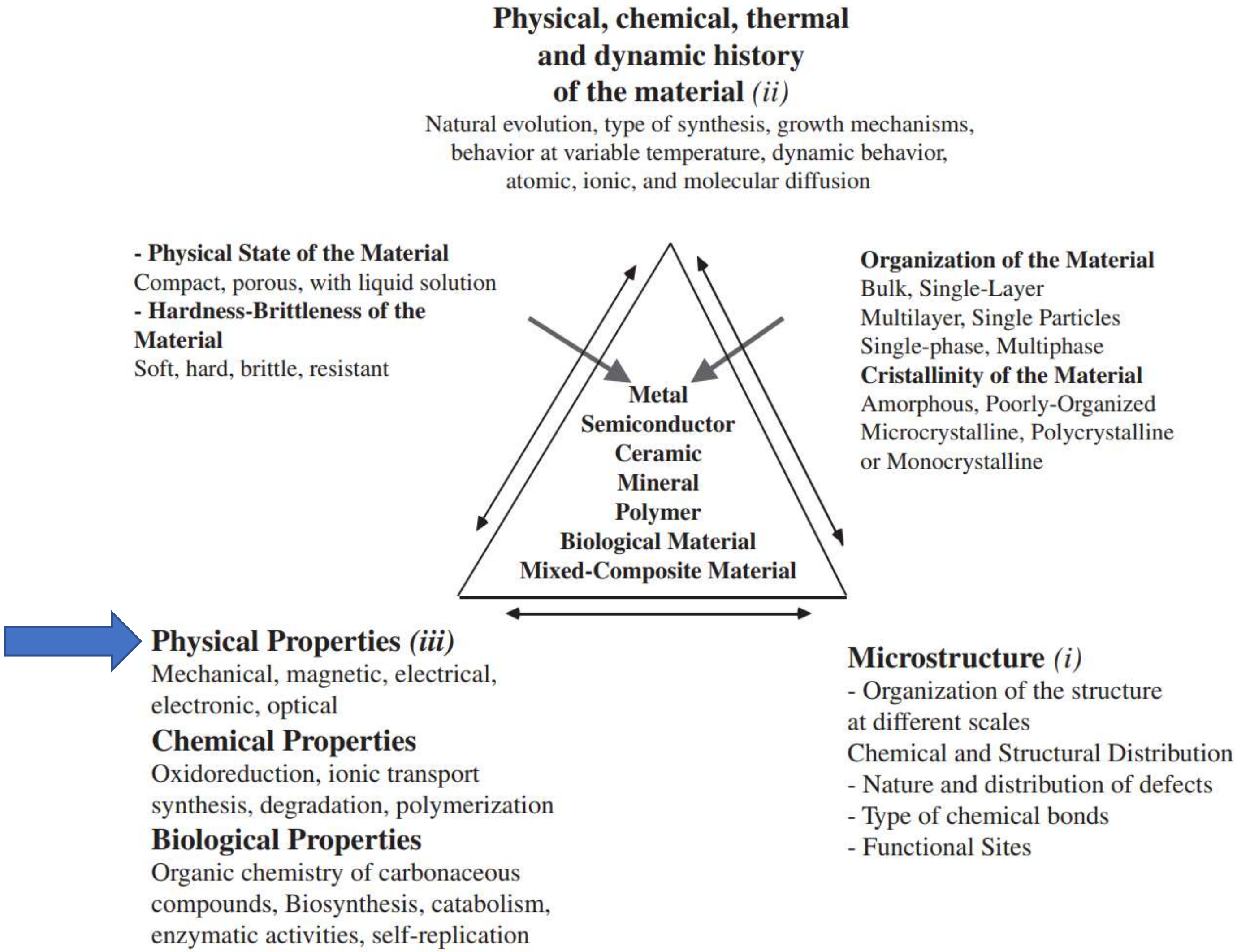
I *materiali polimerici* possono essere:

- **Termoplastici**, in presenza presenti di legami deboli tra catene che vengono facilmente rotti dal calore;
- **Termoindurenti**, in presenza di legami covalenti tra catene. Non possono essere sciolti e lavorati facilmente.





Tipo di cristallo	Unità strutturali	Legame tra le unità strutturali	Esempi	Punto di fusione	Proprietà meccaniche ed elettriche
ionico	ioni positivi e negativi	ionico	NaCl (cloruro di sodio), KNO_3 (nitrato di potassio)	elevato	Duro e fragile. Se solubile in acqua, dà soluzioni conduttrici di elettricità.
reticolare	atomi	covalente	C (diamante e grafite), SiO_2 (quarzo)	molto elevato	In genere duro, fragile e non conduttore di elettricità. Insolubile in acqua.
molecolare polare	molecole polari	forze intermolecolari +	H_2O (ghiaccio), $C_{12}H_{22}O_{11}$ (saccarosio)	non elevato	Tenero e fragile. In genere le soluzioni non sono conduttrici di elettricità.
molecolare apolare	molecole apolari	forze intermolecolari -	I_2 (iodio), CO_2 (ghiaccio secco)	basso	Tenero e fragile. Non conduce la corrente né allo stato solido né in soluzione.
metallico	ioni positivi immersi nel mare di elettroni	metallico	elementi del blocco *s* e *d* della tavola periodica (Na, Cu)	variabile	Lucente, malleabile e duttile. Conduce l'elettricità e il calore.



Physical, chemical, thermal and dynamic history of the material *(ii)*

Natural evolution, type of synthesis, growth mechanisms,
behavior at variable temperature, dynamic behavior,
atomic, ionic, and molecular diffusion

- Physical State of the Material
Compact, porous, with liquid solution
- Hardness-Brittleness of the Material
Soft, hard, brittle, resistant

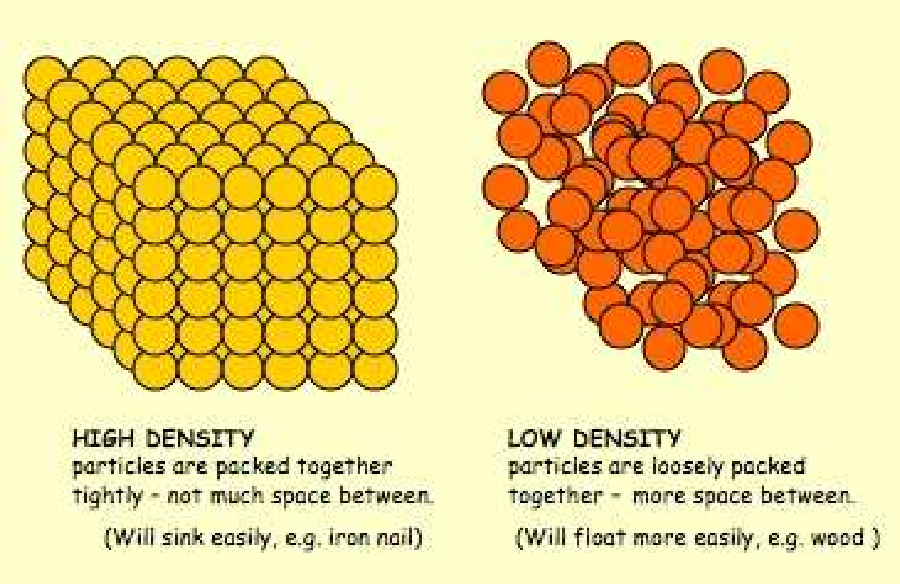
Organization of the Material
Bulk, Single-Layer
Multilayer, Single Particles
Single-phase, Multiphase
Cristallinity of the Material
Amorphous, Poorly-Organized
Microcrystalline, Polycrystalline
or Monocrystalline

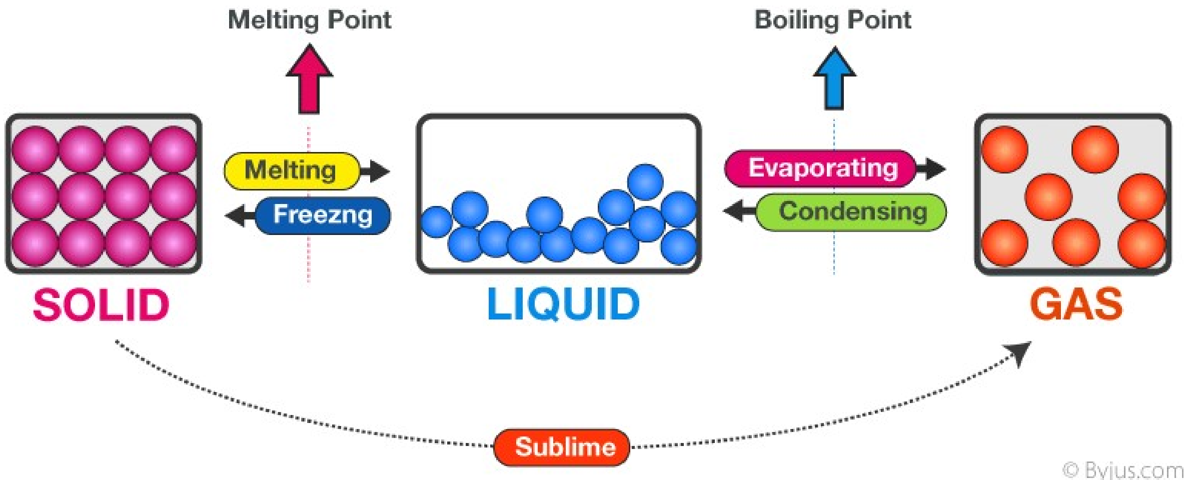
Metal
Semiconductor
Ceramic
Mineral
Polymer
Biological Material
Mixed-Composite Material

Physical Properties *(iii)*
Mechanical, magnetic, electrical,
electronic, optical
Chemical Properties
Oxidoreduction, ionic transport
synthesis, degradation, polymerization
Biological Properties
Organic chemistry of carbonaceous
compounds, Biosynthesis, catabolism,
enzymatic activities, self-replication

Microstructure *(i)*
- Organization of the structure
at different scales
Chemical and Structural Distribution
- Nature and distribution of defects
- Type of chemical bonds
- Functional Sites

General Physical Properties





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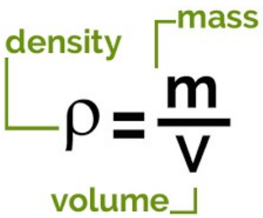
- Density:



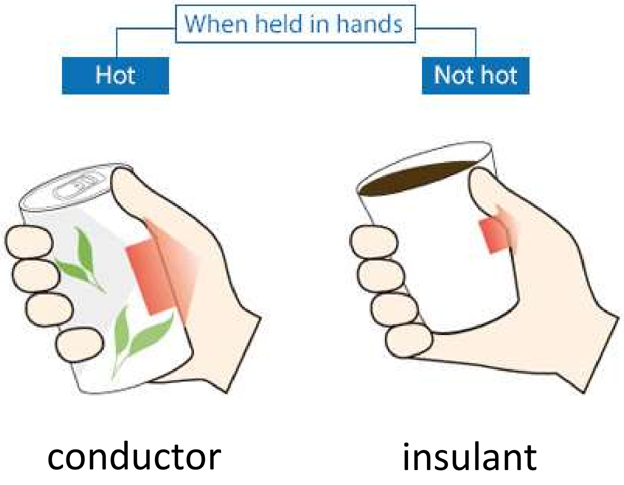
$$\rho = \frac{m}{V}$$

- Phase Transformation Temperatures:
  Phase transitions from solid to liquid, and from liquid to vapor absorb heat. The phase transition temperature where a solid changes to a liquid is called the **melting point**. The temperature at which the vapor pressure of a liquid equals 1 atm (101.3 kPa) is called the **boiling point**.

Thermal Properties

- Thermal Conductivity (k):

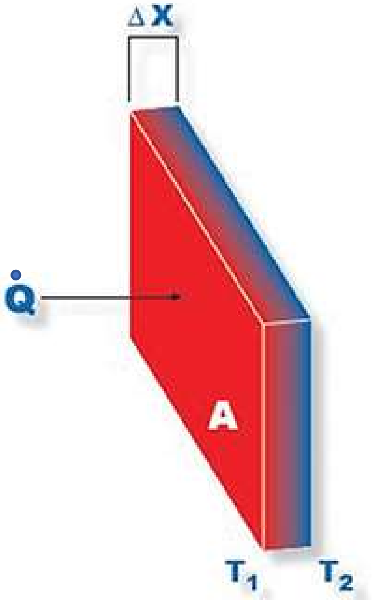
It is the intrinsic property of a material which relates its *ability to conduct heat*. Heat transfer by **conduction involves transfer of energy within a material without any motion of the material as a whole**. Conduction takes place when a temperature gradient exists in a solid (or stationary fluid) medium. Conductive heat flow occurs in the direction of decreasing temperature because higher temperature equates to higher molecular energy or more molecular movement. Energy is transferred from the more energetic to the less energetic molecules when neighboring molecules collide.



Thermal conductivity is defined as the *quantity of heat (Q) transmitted through a unit thickness (L) in a direction normal to a surface of unit area (A) due to a unit temperature gradient (ΔT)* under steady state conditions and when the heat transfer is dependent only on the temperature gradient. In equation form this becomes the following:

Thermal Conductivity = heat flow × distance / (area × temperature gradient)

$$K = \frac{\dot{Q} \bullet \Delta X}{A(T_2 - T_1)}$$



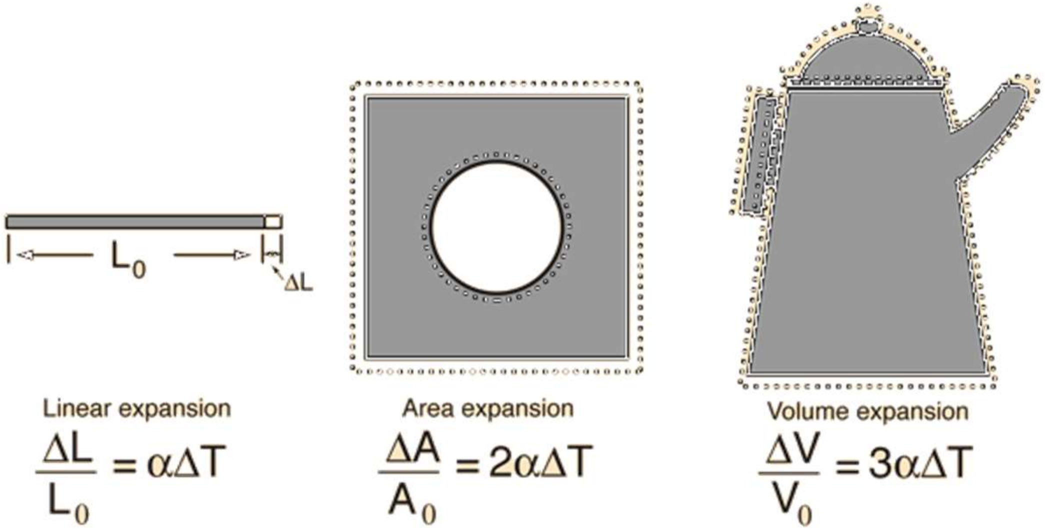
Thermal Properties

- Linear Coefficient of Thermal Expansion:

When heat is added to most materials, the average amplitude of the **atoms vibrating** within the material increases. This, in turn, **increases the separation between the atoms** causing the material to expand.

The linear coefficient of thermal expansion *α describes the relative change in length of a material per degree temperature change*.

Thermal expansion (and contraction) must be taken into account when designing products with close *tolerance fits* as these tolerances will change as temperature changes if the materials used in the design have different coefficients of thermal expansion. It should also be understood that thermal expansion can cause *significant stress* in a component if the design does not allow for expansion and contraction of components. The phenomena of thermal expansion can be challenging when designing bridges, buildings, aircraft and spacecraft, but it can be put to beneficial uses. For example, thermostats and other *heat-sensitive sensors* make use of the property of linear expansion.



Optical Properties

- Refraction:

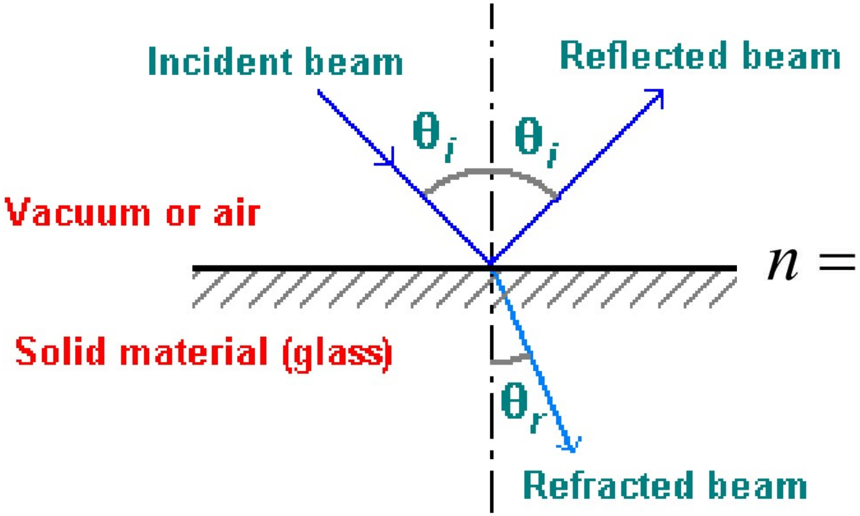
when light photons are transmitted through a material, they causes polarization of the electrons and in turn the speed of light is reduced and the beam of light changes direction.
The refraction index represents the **interaction of light with electrons** of the constituent atoms, thus *'n' increases with electron density or polarizability*.

- Reflectivity:

it is defined as **fraction of light reflected at an interface**.
The high reflectivity of metals, on the order of 0.90-0.95, is one reason that they are opaque. High reflectivity is desired in many applications including mirrors, coatings on glasses, etc.

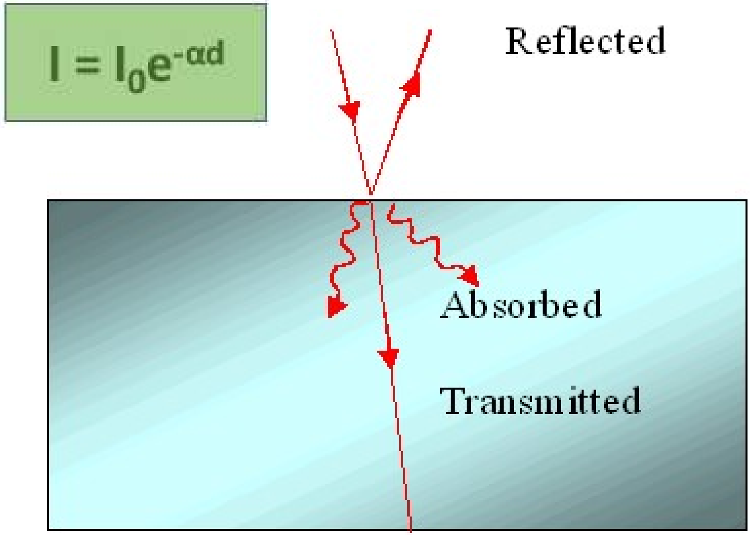
- Absorption:

When a light beam in impinged on a material surface**, portion of the incident beam that is not reflected by the material or transmitted through the material is absorbed**. The fraction of beam that is absorbed is *related to the thickness of the materials and the manner in which the photons interact with the material's structure (α=absorption coefficient)*.



$$n = \frac{c_0}{c}$$

$$I = I_0 e^{-\alpha d}$$



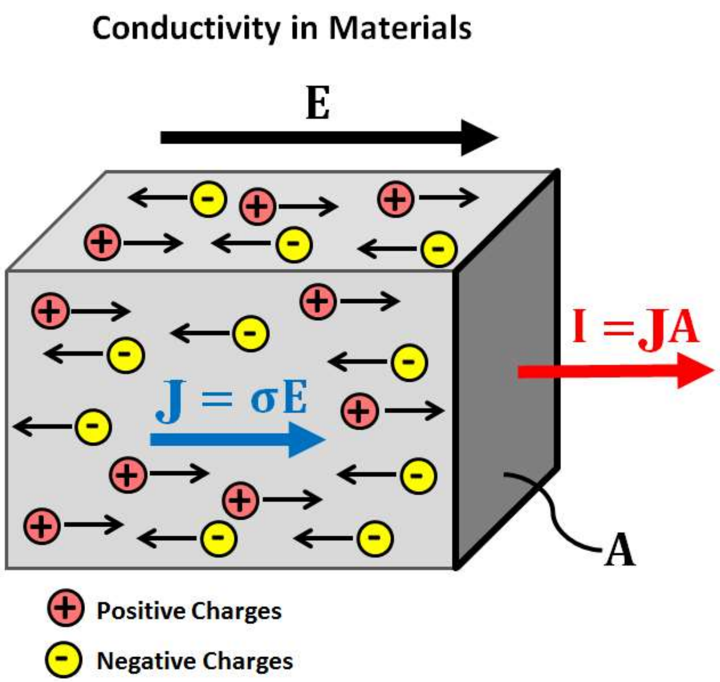
Electrical Properties

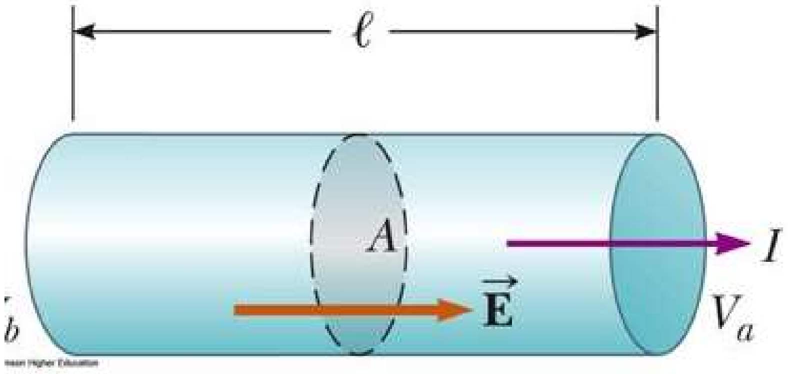
- Electrical Conductivity:

It is a measure of how well a material allow **the movement of an electric charge**. It is the *ratio of the current density to the electric field strength*.

- Electrical Resistivity

It is the reciprocal of conductivity, i.e. the **opposition of a body or substance to the flow of electrical current** through it (electrical energy can be dissipated as heat, light, etc). The amount of resistance depends on the type of material. Materials with low resistivity are good conductors of electricity and materials with high resistivity are good insulators.





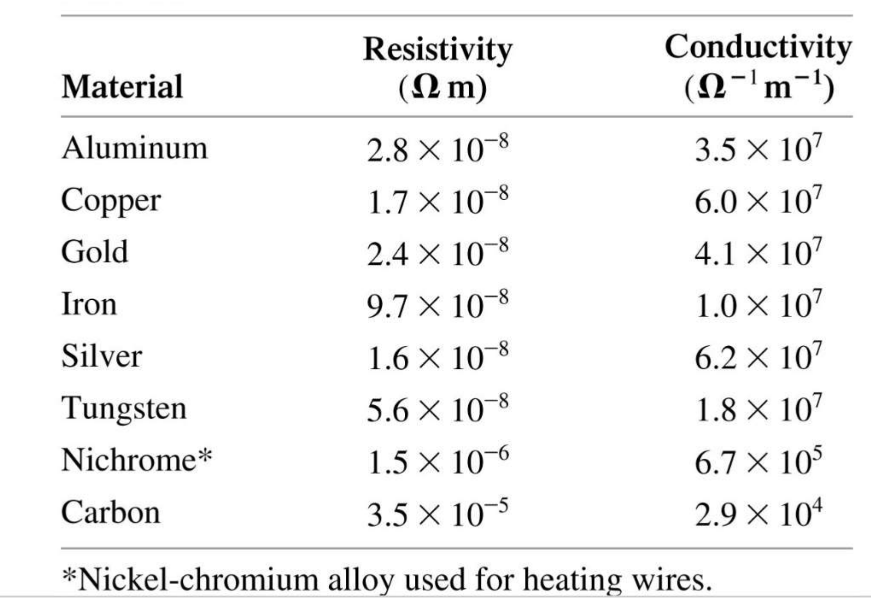
Electrical Properties

- Temperature Coefficient of Resistivity

The **conductivity and resistivity of material is temperature dependent** (normally, material resistivity increases as temperature increases). The reason that resistivity increases with increasing temperature is that the *number of imperfection in the atomic lattice structure increases with temperature and this hampers electron movement*. Additionally, thermal energy causes the atoms to vibrate about their equilibrium positions. At any moment in time many individual lattice atoms will be away from their perfect lattice sites and this interferes with electron movement.

$$R1 = R2\ [1 + a\ (T1 - T2)]$$

Where:
R1 = resistivity value adjusted to T1
R2 = resistivity value known or measured at temperature T2
a = Temperature Coefficient
T1 = Temperature at which resistivity value needs to be known
T2 = Temperature at which known or measured value was obtained



Material	Resistivity (Ω m)	Conductivity (Ω^{-1} m^{-1})
Aluminum	2.8×10^{-8}	3.5×10^{7}
Copper	1.7×10^{-8}	6.0×10^{7}
Gold	2.4×10^{-8}	4.1×10^{7}
Iron	9.7×10^{-8}	1.0×10^{7}
Silver	1.6×10^{-8}	6.2×10^{7}
Tungsten	5.6×10^{-8}	1.8×10^{7}
Nichrome*	1.5×10^{-6}	6.7×10^{5}
Carbon	3.5×10^{-5}	2.9×10^{4}

*Nickel-chromium alloy used for heating wires.

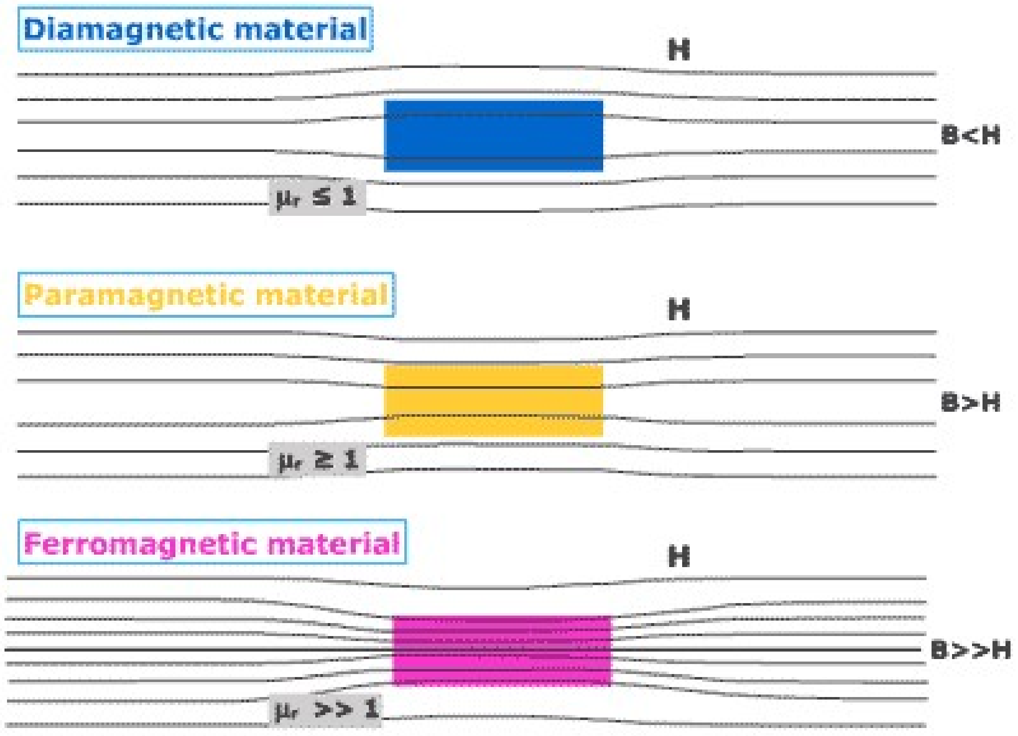
Magnetic Properties

- Magnetic Permeability:

It indicates **how easily a material can be magnetized**. It is a constant of *proportionality that exists between magnetic induction and magnetic field intensity*.

µ0=1.257 x 10-6 Henry per meter (H/m) in free space (vacuum)
µr = µ / µ0 (permeability is often expressed in relative terms)

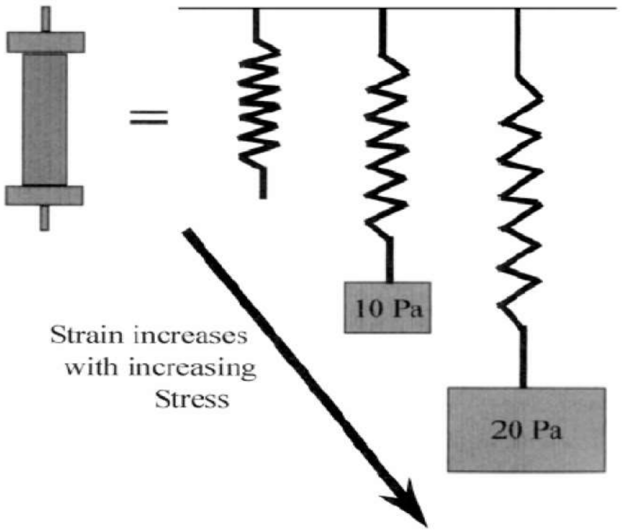
Materials that cause the lines of flux to move farther apart, resulting in a decrease in magnetic flux density compared with a vacuum, are called **diamagnetic;**
materials that concentrate magnetic flux by a factor of more than one but less than or equal to ten are called **paramagnetic** (non-ferrous metals such as copper, aluminum);
materials that concentrate the flux by a factor of more than ten are called **ferromagnetic** (iron, steel, nickel).

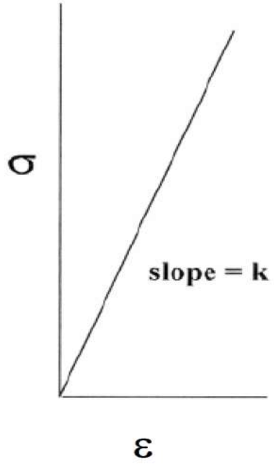


Mechanical Properties

- The **elastic modulus** (E) represents the resistance of a material to deformation (**stiffness**). The reciprocal of E (J) is known as **compliance**.

$$J = \frac{1}{E}$$

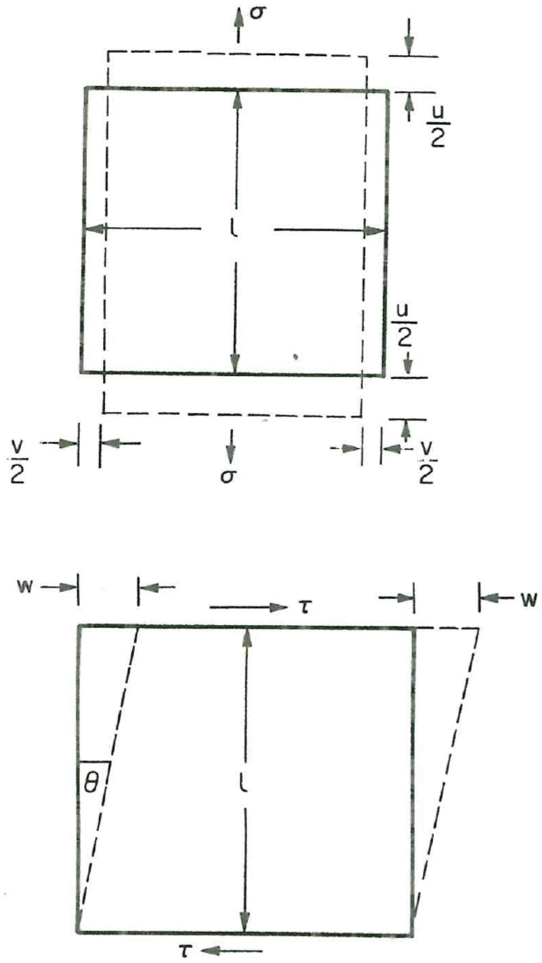




Stress is directly proportional to deformation:

$$\sigma = E \cdot \varepsilon$$

Elastic modulus vs. Shear modulus



Nominal tensile strain,

$$\epsilon_n = \frac{u}{l}$$

Nominal lateral strain,

$$\epsilon_n = -\frac{v}{l}$$

Poisson's ratio,

$$\nu = -\frac{\text{lateral strain}}{\text{tensile strain}}$$

Engineering shear strain,

$$\gamma = \frac{w}{l} = \tan\theta$$

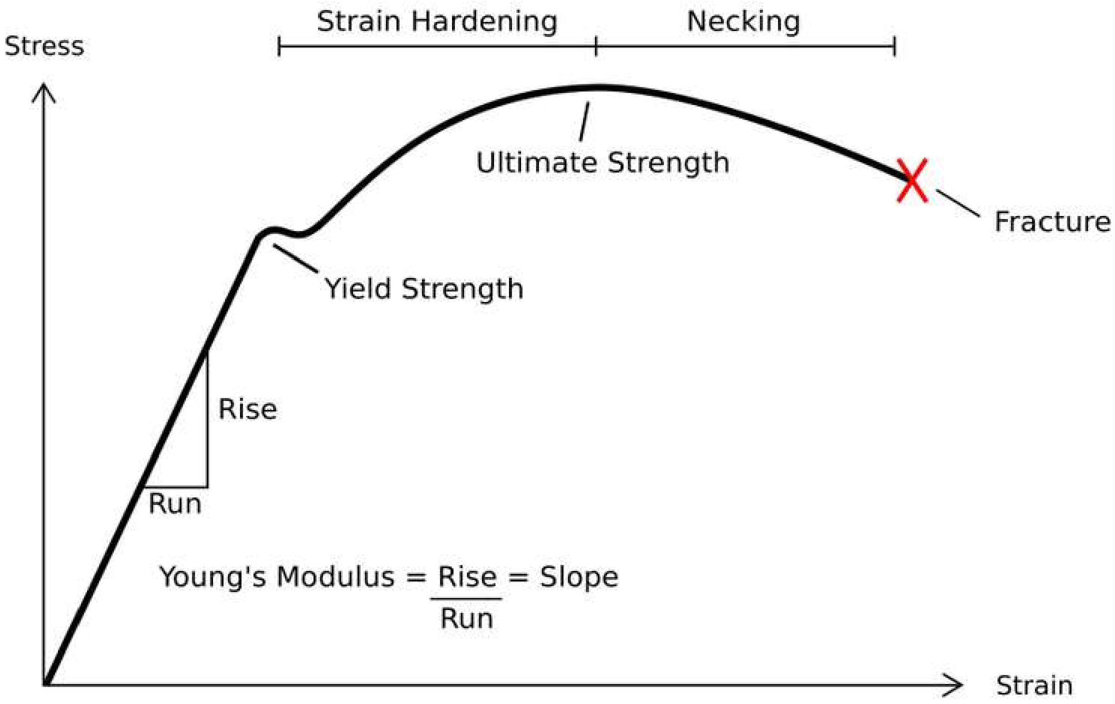
$$E = 2G(1+\nu)$$

Elastic modulus

Shear modulus

G = τ /γ

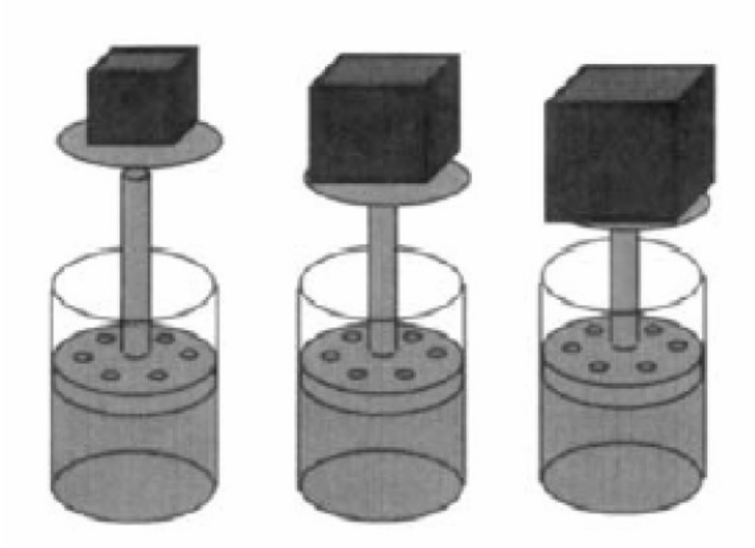
Elastic response

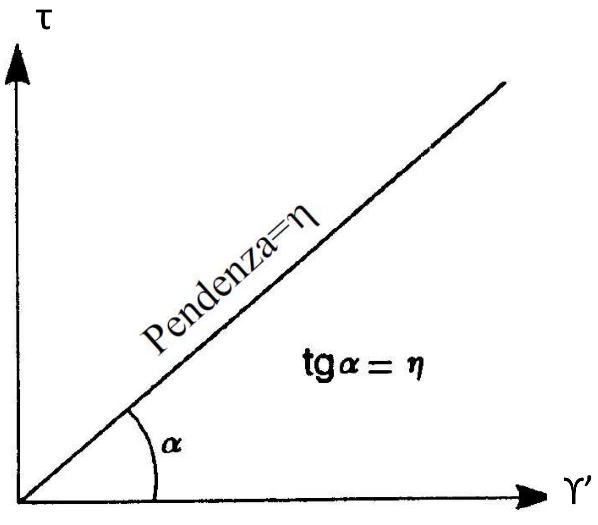


An elastic material has a linear response until a critical stress value (yield stress), then it becames not linear until the failure of the sample.

Mechanical Properties

- **Viscosity** represents the resistance of a material to flow

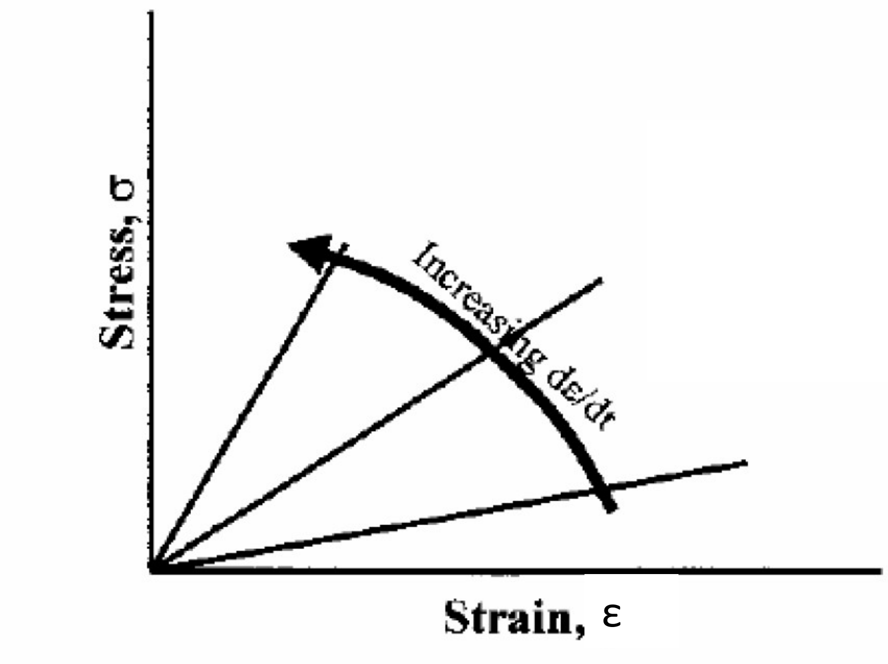




$$\tau = \eta \gamma'$$

Mechanical Properties

- **Viscoselasticity** is related to material with time-dependent properties



Time dependency:
The **apparent stiffness** of the material increases with increasing testing velocity

Deborah number

‘’Le montagne si scioglieranno davanti al Signore, Dio di Israele ‘’ - Libro dei Giudici (5,-5)

‘’But Deborah knew two things. First, that the mountains flow, as everything flows. But, secondly, that they flowed before the Lord, and not before man, for the simple reason that man in his short lifetime cannot see them flowing, while the time of observation of God is infinite.’’
M.Reiner, The Deborah Number, Physics today, 62 (1964)

The perception of a material is dependent from **observation time**.

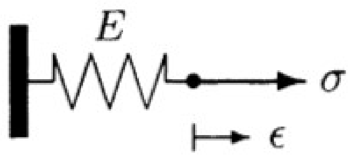
$$De = \frac{\tau}{t} \begin{cases} De \gg 1 \ (\boldsymbol{\tau}_{SR} \gg t) & \text{Slow response (solid like materials)} \\ De \ll 1 \ (t \gg \boldsymbol{\tau}_{SR}) & \text{Instantaneous response (liquid like materials)} \\ De \approx 1 \ (\boldsymbol{\tau}_{SR} \approx t) & \text{Intermediate response (viscoelastic materials)} \end{cases}$$

How can we describe viscoelastic behaviour?

Lumped parameter models

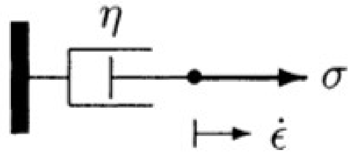
SPRING: ELASTIC SOLID

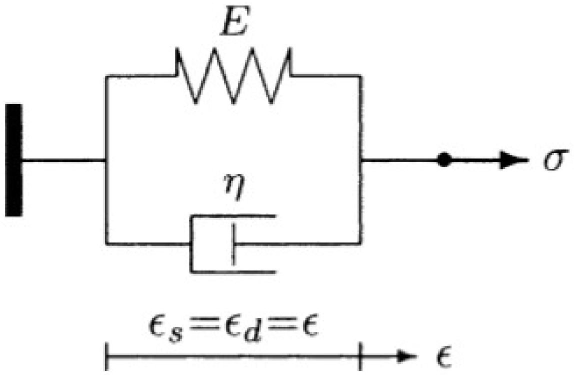
$$\sigma = E\,\epsilon$$



DASHPOT: VISCOUS FLUID

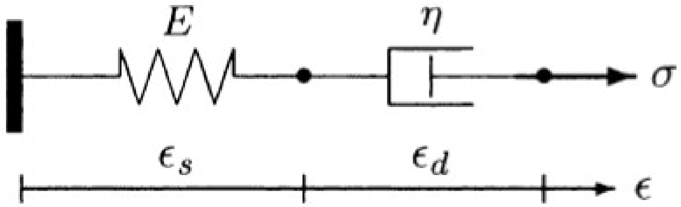
$$\sigma = \eta\,\dot{\epsilon}$$





Kelvin–Voight model

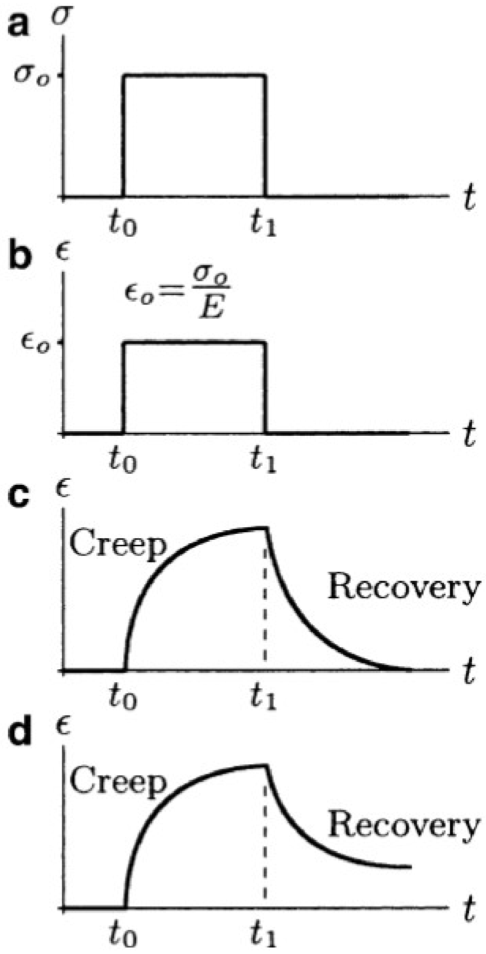
$$\sigma = E\varepsilon + \eta\frac{\mathrm{d}\varepsilon}{\mathrm{d}t}.$$



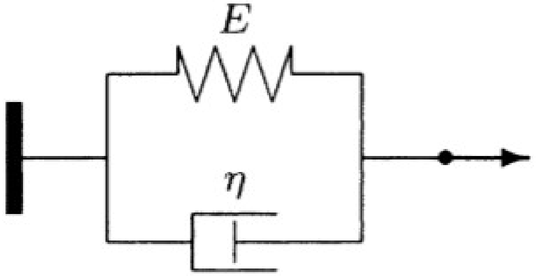
Maxwell model

$$\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

Creep



Creep and recovery



Stimulus = **stress step σ_0** (a)

Response:

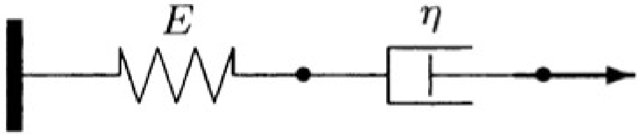
- (b) elastic material -> **constant strain** at time t0. At time t1, the material will instantly and **completely recover the deformation**.
- (c) viscoelastic solid -> a **strain gradually increasing** between times t0 and t1. At time t1, gradual recovery will start. The *recovery will eventually be complete.*
- (d) viscoelastic liquid -> complete recovery will never be achieved and there will be a **residue of deformation** left in the material

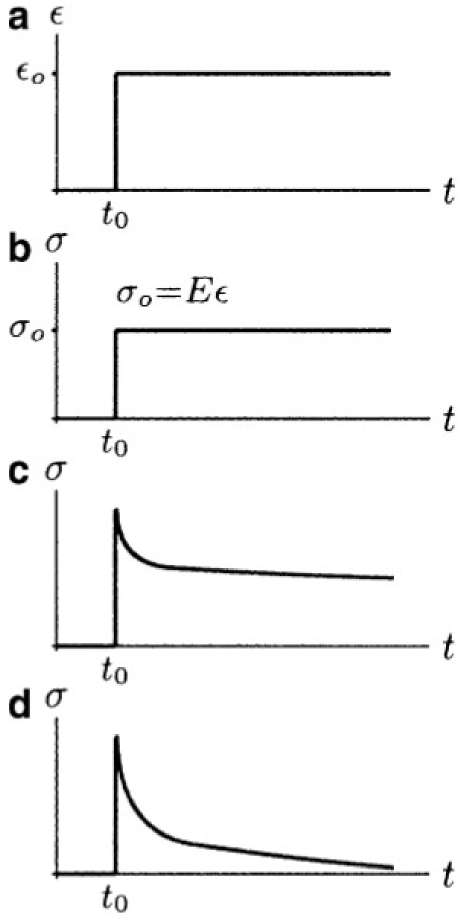
$$\varepsilon(t) = \frac{\sigma_0}{E}\left(1 - e^{-tE/\eta}\right)$$

Retardation time (τ_C): The strain achives to (1-1/e) of its final value

i.e. when $t=\tau$, $\varepsilon(\tau) = \varepsilon_{\text{equilibrium}}(1-e^{-1}) = \varepsilon_{\text{equilibrium}} * 0.67$

Stress Relaxation





Stress relaxation

Stimulus = **strain step ε_0** (a)

Response:

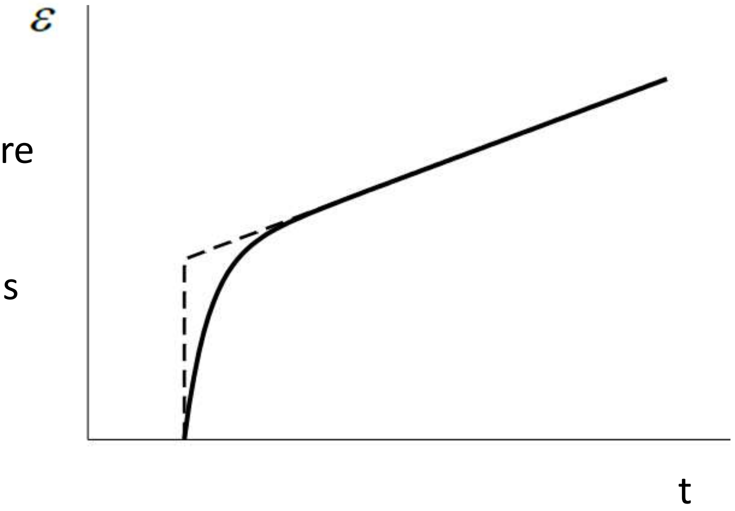
- (b) elastic material -> constant stress
- (c) viscoelastic solid -> **initial high stress that will decrease over time**, but stress level will **never reduce to zero**
- (d) viscoelastic liquid -> initial high stress that will decrease over time, and the stress will **eventually reduce to zero**

$$\sigma(t) = \varepsilon_0 E e^{-tE/\eta}$$

Relaxation time (τ_{SR}): The force drops to 1/e of its initial value

i.e. when $t=\tau$, $\sigma(\tau) = \sigma_0 e^{-1} = \sigma_0 * 0.33$

Creep and SR equations



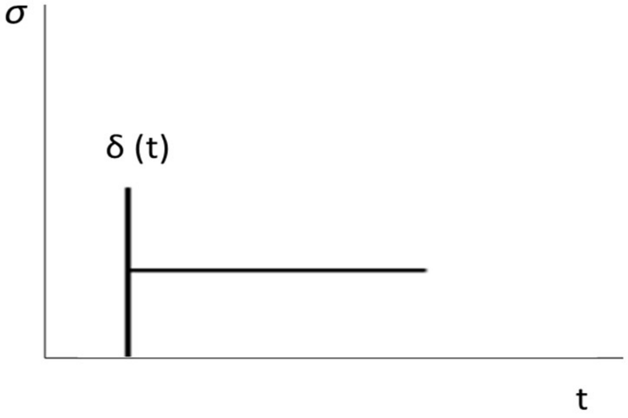
- Creep -> Voigt

  because Maxwell does not describe correctly creep answer: the answer is more edgy and **does not describe the transition between short time** (elastic) **and long time behavior** (viscous)**.**
  Maxwell does not describe well all the situations in which the applied stimulus is a stress.

$$\varepsilon(t) = \sigma_0\left(\frac{t}{\eta} + \frac{1}{E}\right)$$

- SR -> Maxwell

$$\sigma(t) = \varepsilon_0 \eta . \delta(t) + \varepsilon_0 E$$



Universal Testing Machine

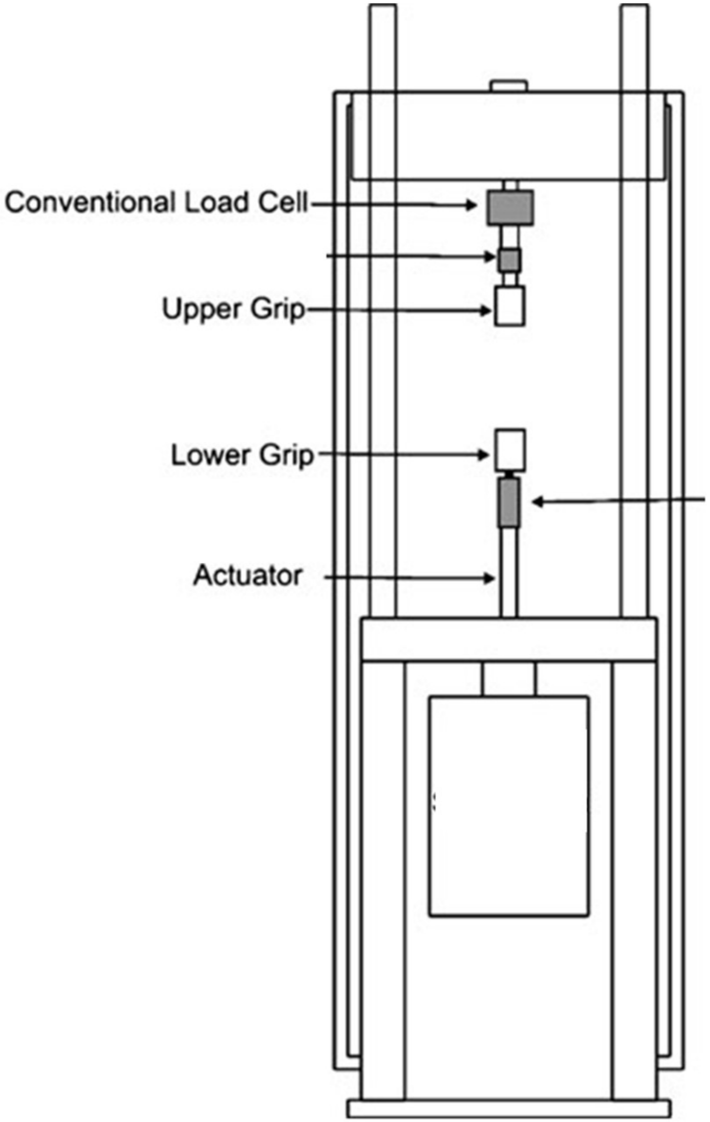
Bulk Mechanical Properties

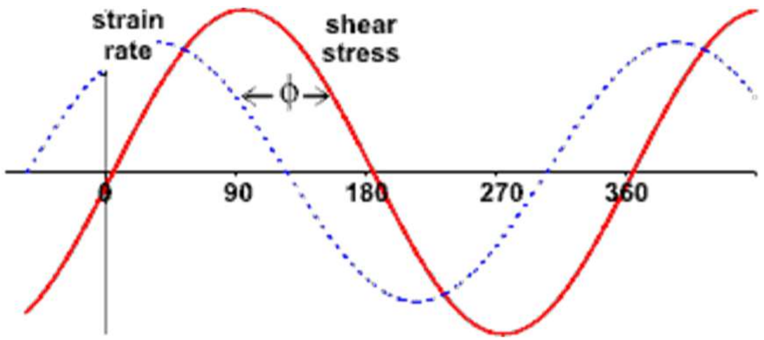
Universal testing machines (UTM):

Compression and tensile tests

Main components:

- Load cell (different maximum loads)
- Actuator
- Sample holding system





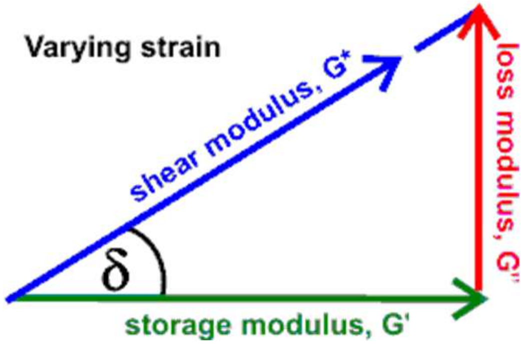
Stimulus = **strain sinusoid**

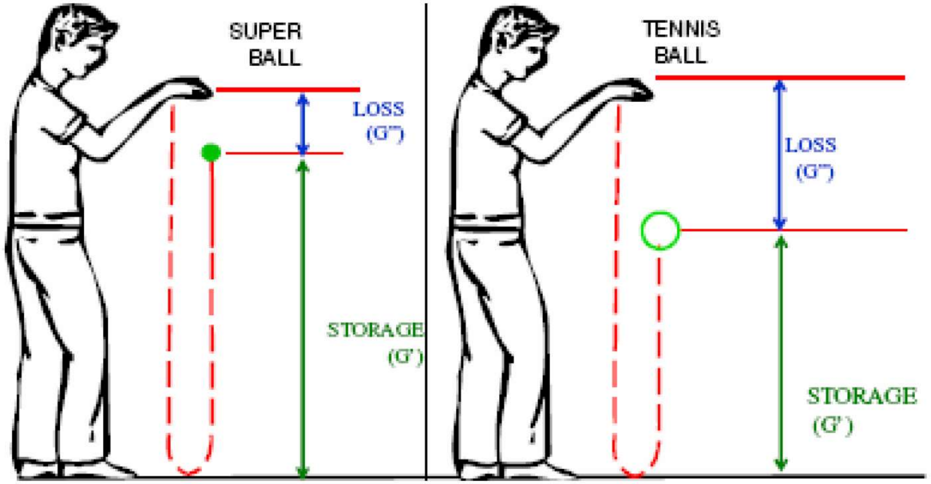
Response = stress sinusoid:

- ϕ= 0 for ideally elastic material (all energy stored in the material)
- ϕ= 90° for an ideally viscous liquid (all energy dissipated)

shear stress = shear strain ^{x} sin(ωt + ϕ)
shear stress = viscous stress - i ^{x} elastic stress

complex shear moduls
G* = G' + iG′′

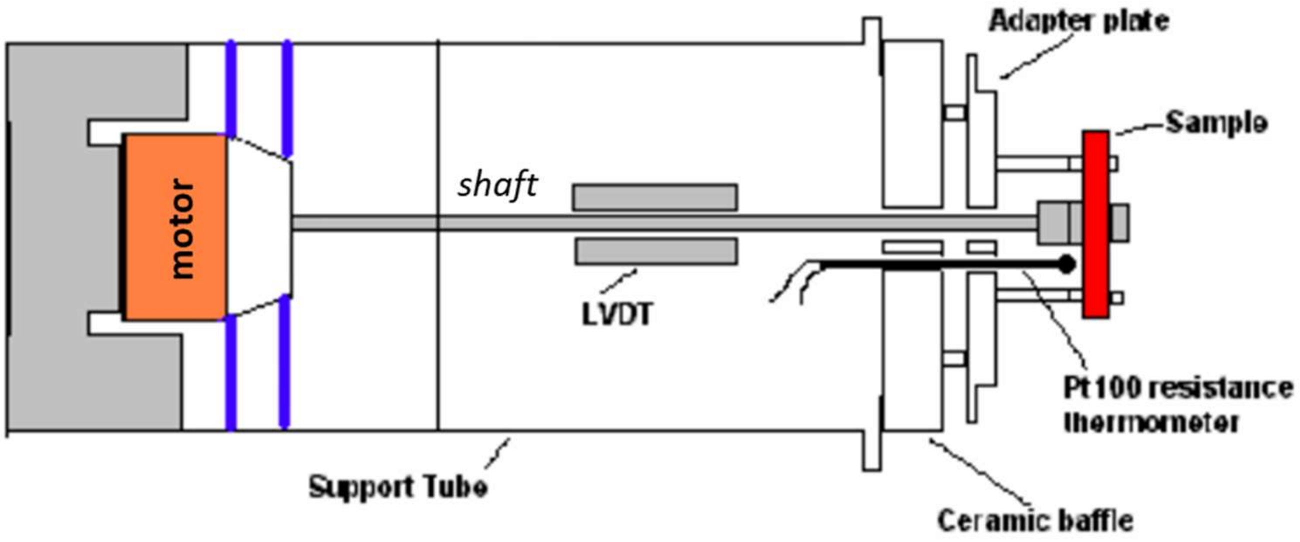




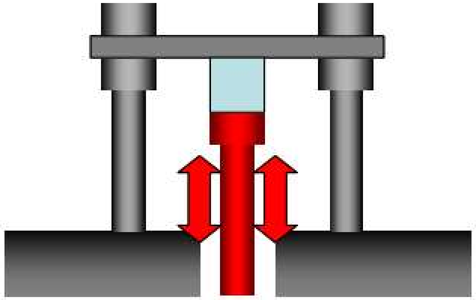
(Dynamic Mechanical Analysis)

Dynamic Mechanical Analyser

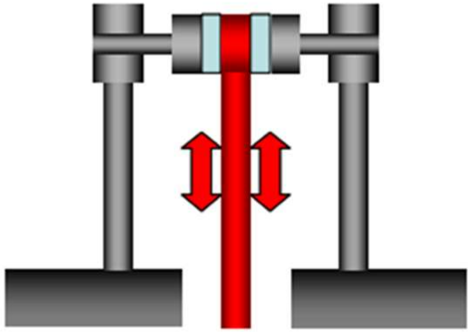
Bulk Mechanical Properties



The stress is transmitted through the drive shaft onto the sample which is mounted in a clamping mechanism. As the sample deforms, the amount of displacement is measured by the LVDT positional sensor.



Compression



Shear

Bulk vs. Surface Properties

- Mechanical
  - *elastic modulus & viscoelastic properties*
- Thermal
  - *Thermal expansion coefficient*
- Optical
  - *absorption/transmission*
- Electrical/Magnetic

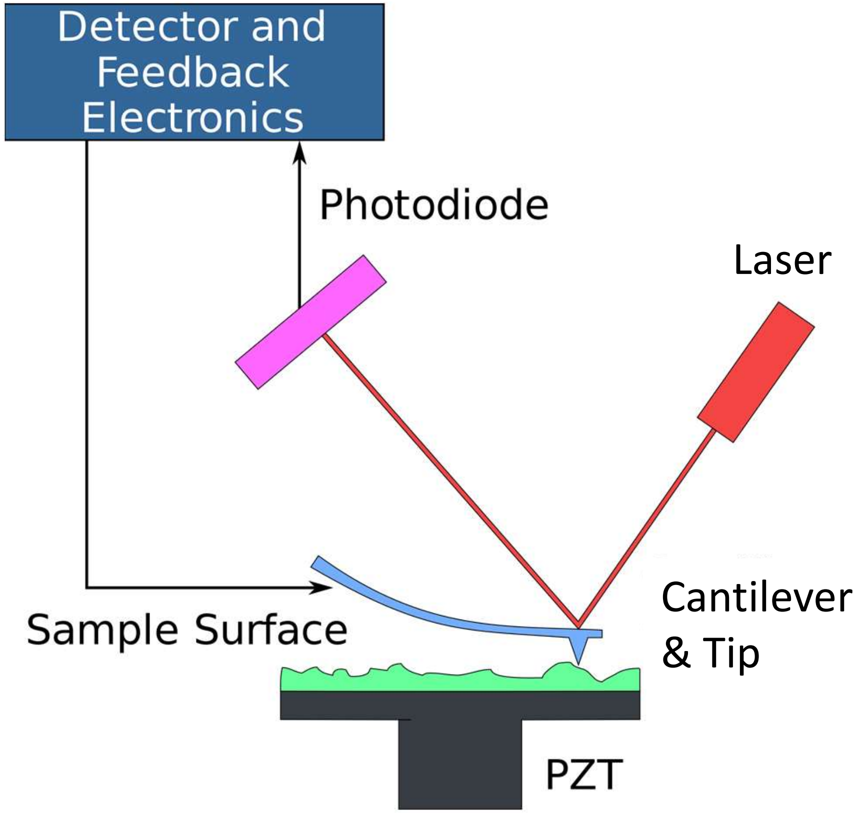
- Mechanical
  - *surface stiffness*
- Optical
  - *reflection*
- Roughness
- Chemistry
- Wettability
- Surface energy

How to measure surface properties

- Contact angles -> wettability (directly), surface energy (indirectly)
- Electron spectroscopy for chemical analysis (ESCA) -> chemical properties
- Atomic force microscopy -> topography, mechanics (up to 0.1 nm)
- Nanoindentation -> mechanics (um)

Mechanical
Surface
Properties

AFM



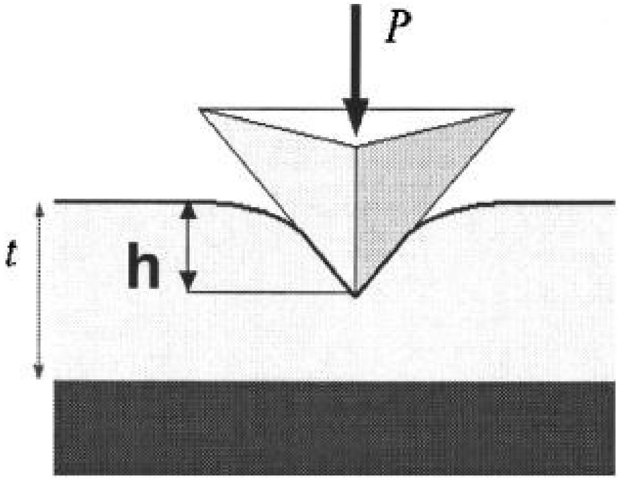
The tip is scanned laterally across the surface, and the vertical movements of the tip are recorded and used to construct a quantitative **3 dimensional topographic map**.

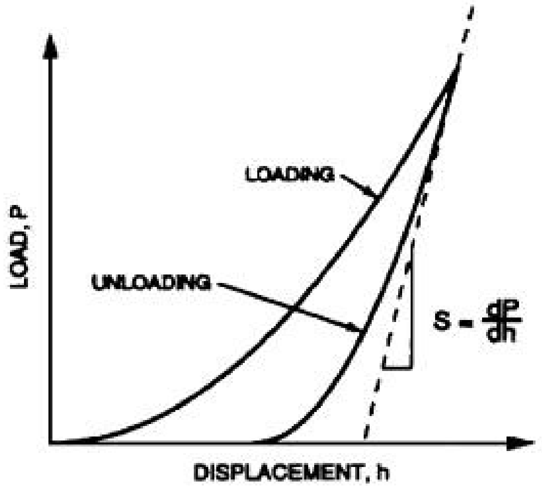
- lateral resolution: typically 5-15 nm
- vertical resolution: 0.1nm

Other information:
- Surface roughness measurements
- Investigation of local mechanical properties

(i.e. stiffness, adhesion, friction)

Nanoidentation





The slope of the curve (dP/dh) upon unloading is indicative of the **stiffness S** of the contact. This value generally includes a *contribution from both the material being tested and the response of the tip itself.*

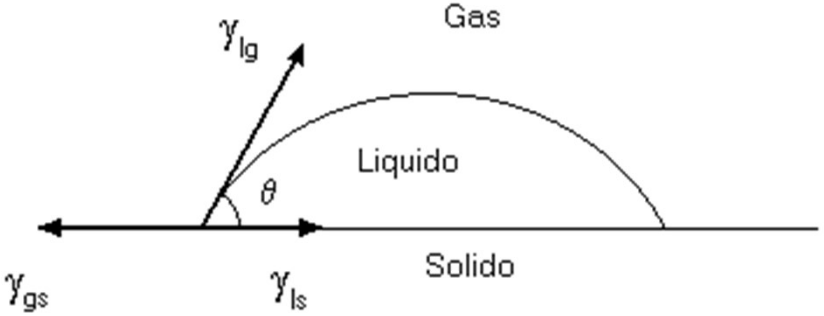
Reduced elastic modulus

$$E_r = \frac{1}{\beta}\frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A_p(h_c)}}$$

$$1/E_r = (1-\nu_i^2)/E_i + (1-\nu_s^2)/E_s\,.$$

Tip: known mechanical properties, typically very hard material (Ei>>Es)

Contact angle

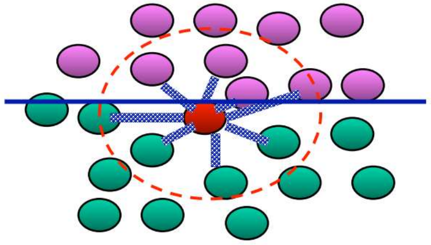


$$\gamma_{gs} = \gamma_{ls} + \gamma_{lg}\cos\theta$$

Superficial tension of a solid in a specific environment

Superficial tension between solid-liquid

Superficial tension of liquid in a specific environment

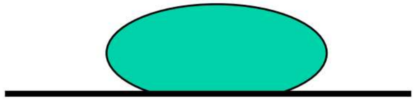


Solido. Adesione

Liquido. Coesione

Adesione > Coesione
Liquido bagna

$0 < \theta < 90°$

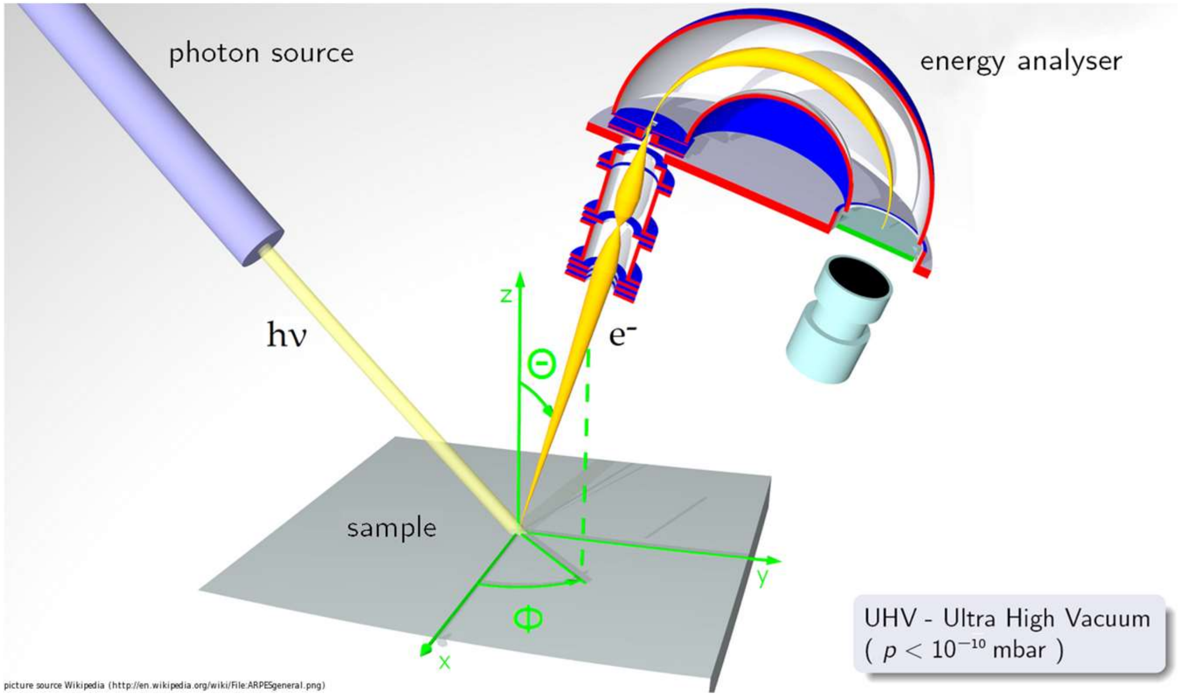


Adesione < Coesione
Liquido non bagna

$90° < \theta < 180°$

Electron Spectroscopy for Chemical Analysis (ESCA)

This technique is based on the **Photoelectric Effect:** when a material is irradiated with x-rays, photoelectrons are subsequently ejected from atoms in the near surface (*1-10 nm)*.



picture source Wikipedia (http://en.wikipedia.org/wiki/File:ARPESgeneral.png)

information about: elemental composition, concentrations and chemical environments (i.e. oxidation states) of surface and near surface atoms.

Esercizi

1) Data un barra di acciaio con E=200GPa, G=77GPa,l=100mm, d=2mm compressa con una F=500N; calcolare: allungamento verticale e laterale
2) Considerare un test di creep con s0=7kPa, d_eq=600um, d0=400um (considerando t0=1s); h=10mm; ricavare i parametri concentrati del modello (E, tau)
3) Calcolare la resistenza di un pezzo di alluminio a 25°C con sezione quadrata (l=1m) e lunghezza 10m, sapendo che la sua resistività a 20°C è a pari a 2.706e-8 Ohm*m e che il coefficiene di espansione termica=0.0043°C.

https://padlet.com/lu_cacopardo/6cqcl59eo9jv