Corso Materiali Intelligenti e Biomimetici

12/03/2020

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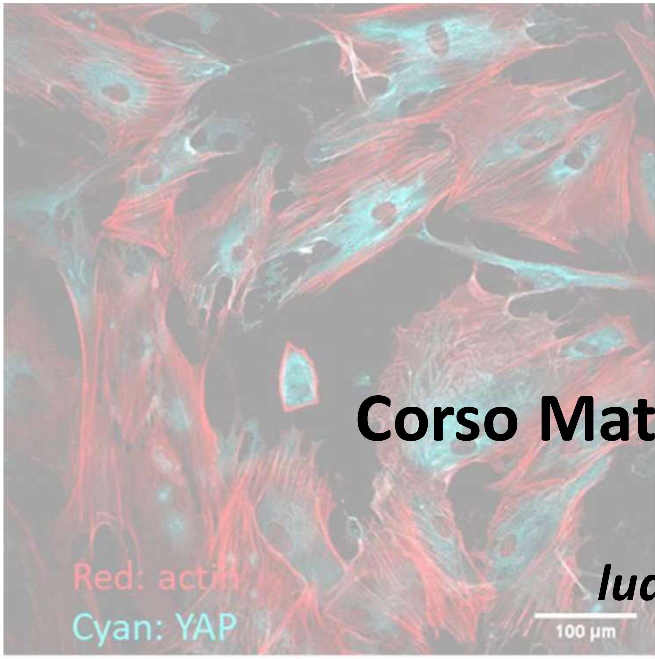

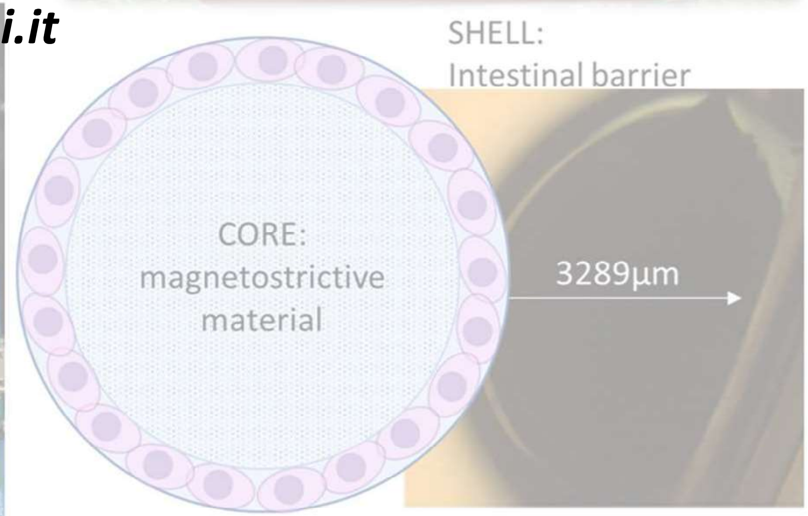

Organizzazione Corso Materiali Intelligenti e Biomimetici *A.A. 2019/20*

Orario:

Giovedì 2h: Teoria -> 11.30 - 13.30
Venerdì 1h: esercitazione/applicazioni -> 15.30 - 16.30

Martedì 2h: DesignLab (1°anno) -> 12.30 - 14.30
Venerdì 2h si1: Comsol (2°anno) -> 16.30 - 18.30

Esame:

- 3/5 voto teoria (a comune) -> SCRITTO: domande teoria/esercizi -> 18 punti
- 2/5 voto lab (design 1°anno/ comsol 2°anno)

  <u>Design Lab:</u>
  report lab consegnato all'esame (report personale, progetto può essere svolto in gruppo) -> 6 punti
  domande a risposta multipla su teoria lab -> 6 punti

Martedì 3/03	organizzazione corso, introduzione ai materiali intelligenti
Martedì 10/03	
Giovedì 12/03	proprietà dei materiali intelligenti (e non)
Venerdì 13/03	
Giovedì 19/03	Piezoelettrici
Venerdì 20/03	
Giovedì 26/03	SMA
Venerdì 27/03	
Giovedì 2/04	Magnetoreologici, ferrofluidici, Magnetostrittivi
Venerdì 3/04	
Giovedì 16/04	Nanomateriali
Venerdì 17/04	
Giovedì 23/04	Materiali innovativi
Venerdì 24/04	
Giovedì 30/04	Polymers and Hydrogels in bioengineering
Giovedì 7/05	EAP
Venerdì 8/05	
Giovedì 14/05	Polimeri sensibili a pH
Venerdì 15/05	
Giovedì 21/05	Polimeri sensibili a T
Venerdì 22/05	
Giovedì27/05	Polimeri conduttivi
Venerdì 28/05	

Materiale Didattico:

http://www.centropiaggio.unipi.it/course/materiali-intelligenti

- 'Engineering Analysis of Smart Material Systems' – *Donald Leo*
- 'Smart Structure Theory' – *Chopra & Sihori*
- *papers*

(Smart) Materials and their Properties

Corso Materiali Intelligenti e Biomimetici

12-13/03/2020

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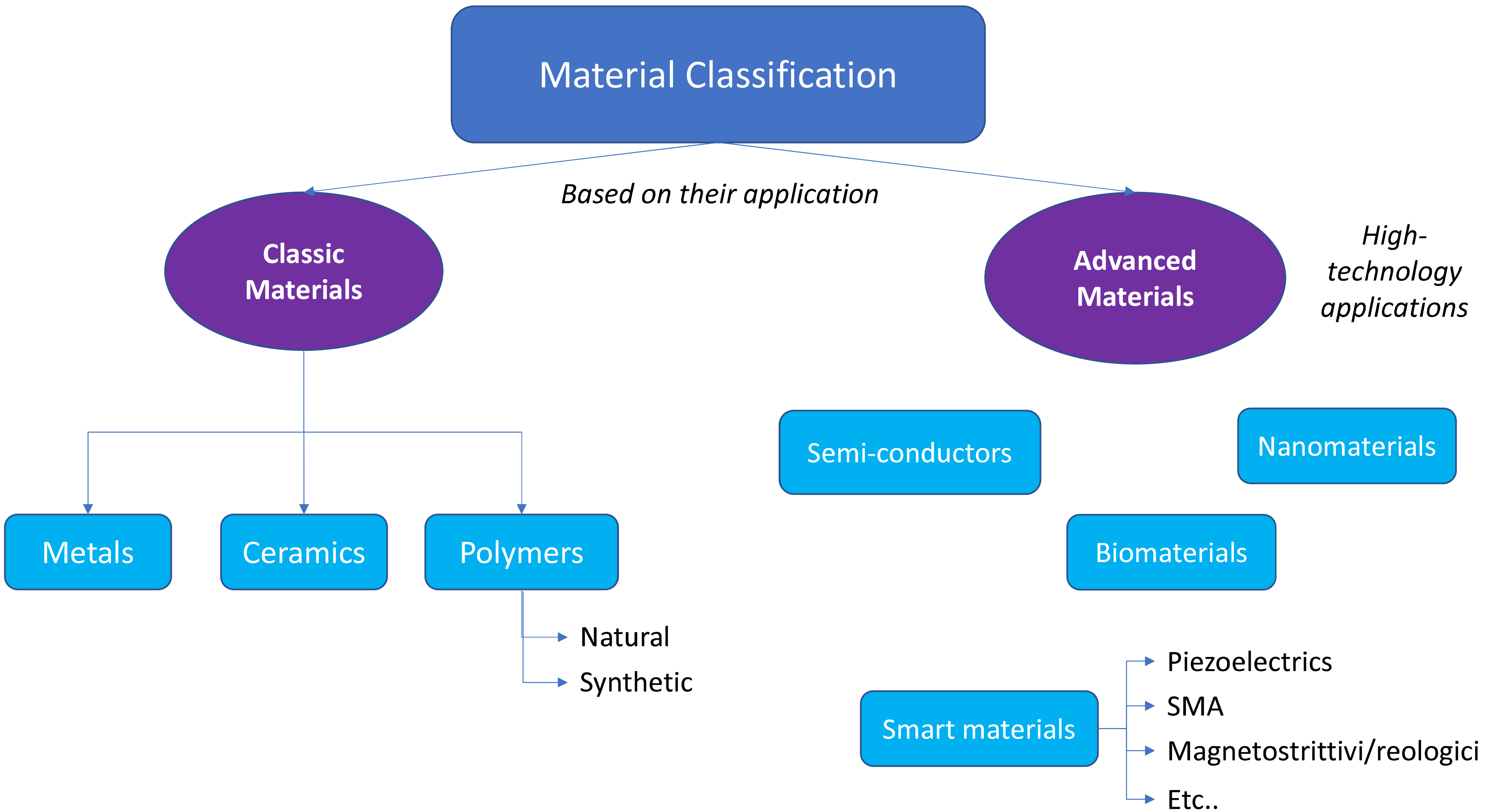
BANG!
STONE AGE
BANG!
BRONZE AGE
BANG!
IRON AGE
BANG!
DARK AGE
BANG!
MODERN AGE
BANG!
CRASH!
COMPUTER AGE


Material Classification
Based on their application
Classic Materials
Advanced Materials
High-technology applications
Metals
Ceramics
Polymers
Natural
Synthetic
Semi-conductors
Nanomaterials
Biomaterials
Smart materials
Piezoelectrics
SMA
Magnetostrittivi/reologici
Etc..

From the previous lessons…

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

   These materials has one or more **property can be significantly altered in a controlled fashion** by external stimuli.

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

Smart Materials

- We define **smart materials** as those that **convert energy between multiple physical domains**.
- A ***domain*** is any physical quantity that we can describe by a set of two state variables.

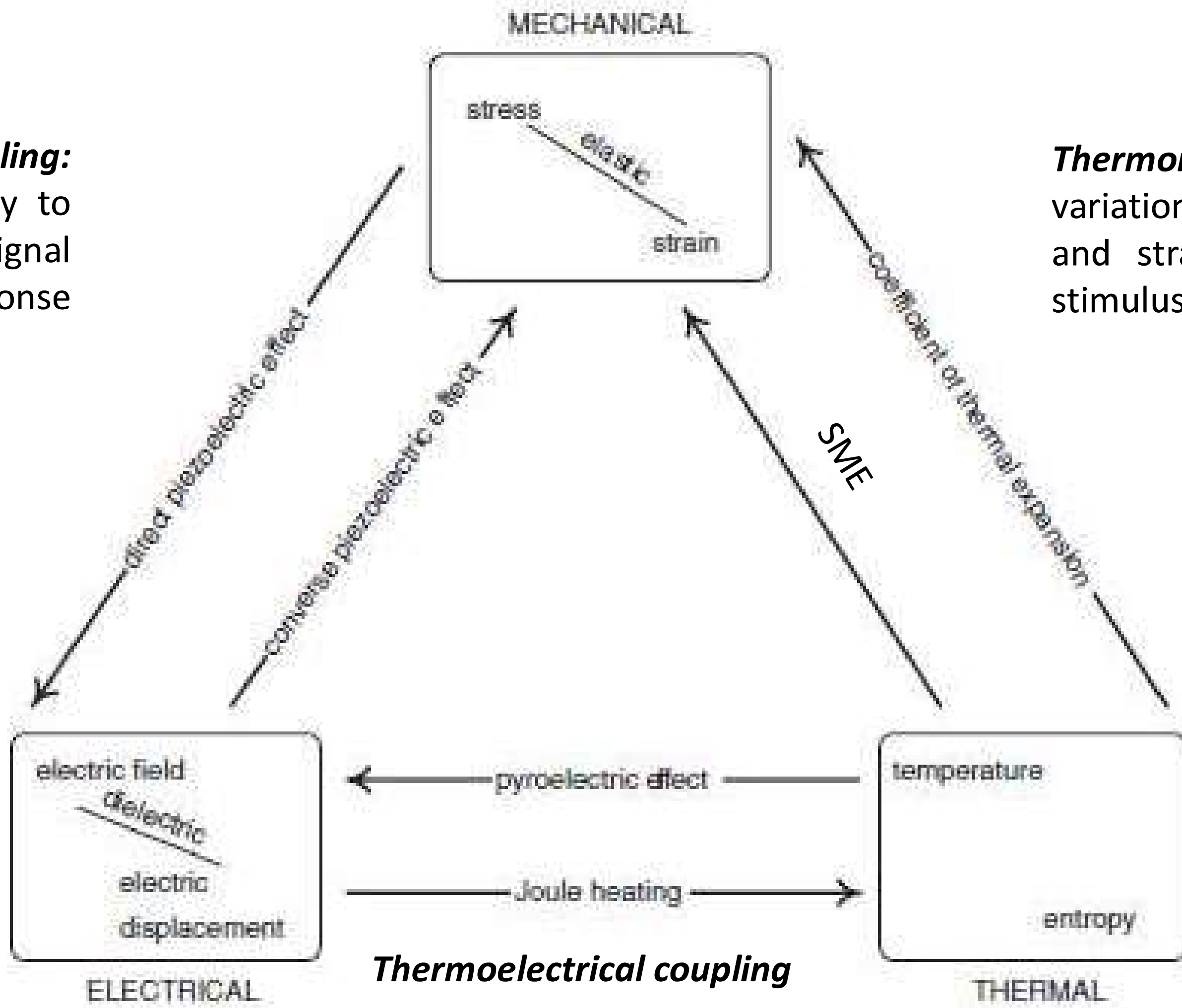
Mechanical	Electrical	Thermal	Magnetic	Chemical
Stress	Electric field	Temperature	Magnetic field	Concentration
Strain	Electric displacement	Entropy	Magnetic flux	Volumetric flux

Figure 1.1 Examples of physical domains and associated state variables.

Coupling occurs when a change in the state variable in one physical domain causes a change in the state variable of a separate physical domain.

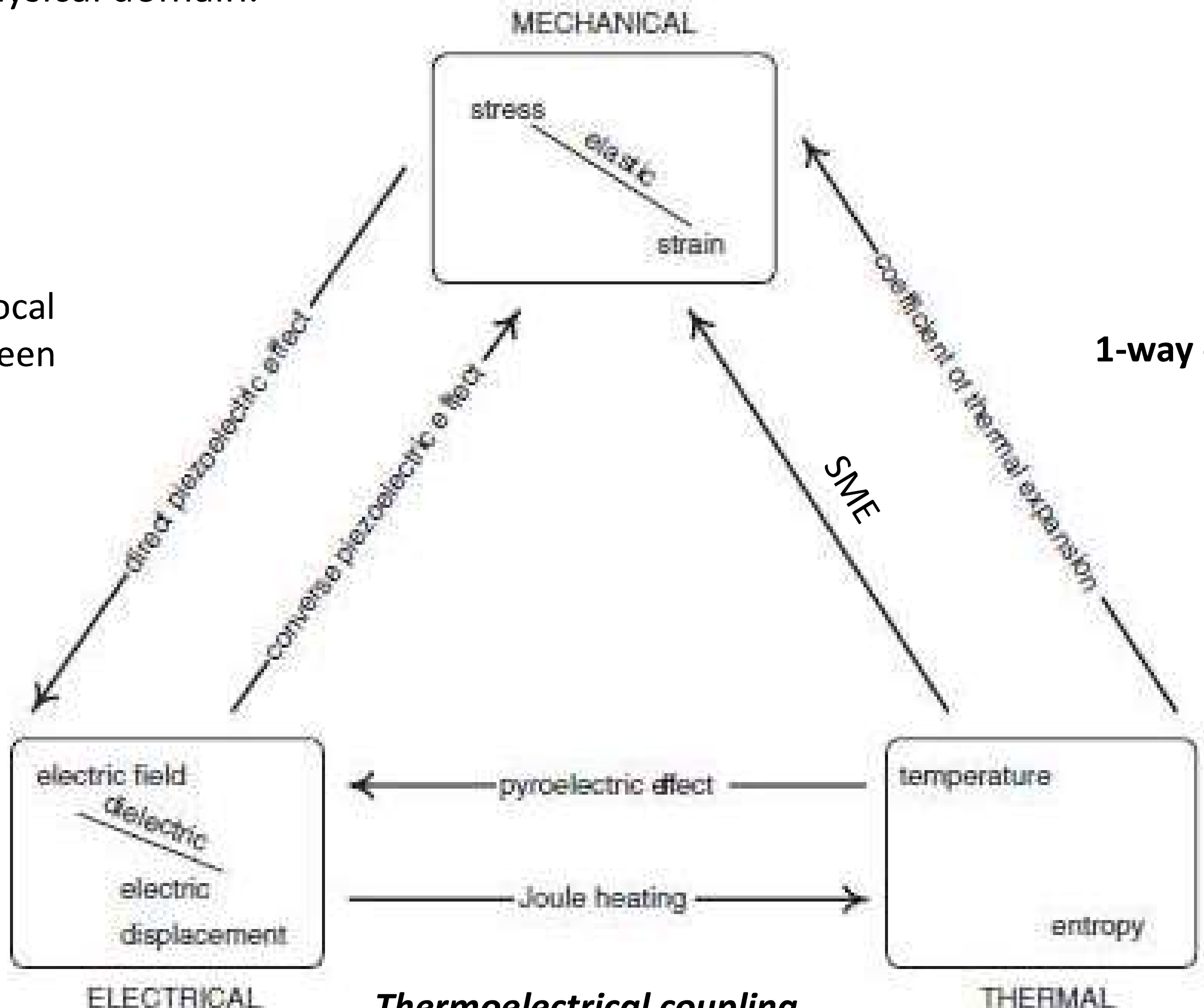
Electromechanical coupling: materials has the ability to convert an electrical signal into a mechanical response and vice versa

Thermomechanical coupling: variation in mechanical stress and strain due to a thermal stimulus



Coupling occurs when a change in the state variable in one physical domain causes a change in the state variable of a separate physical domain.

2-way coupling: a reciprocal relationship exists between the 2 domains



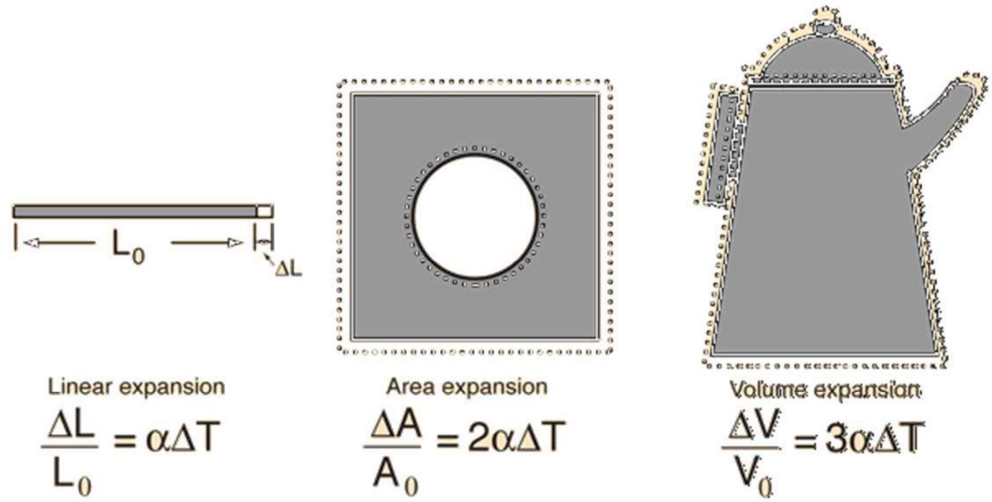
1-way coupling

Thermoelectrical coupling

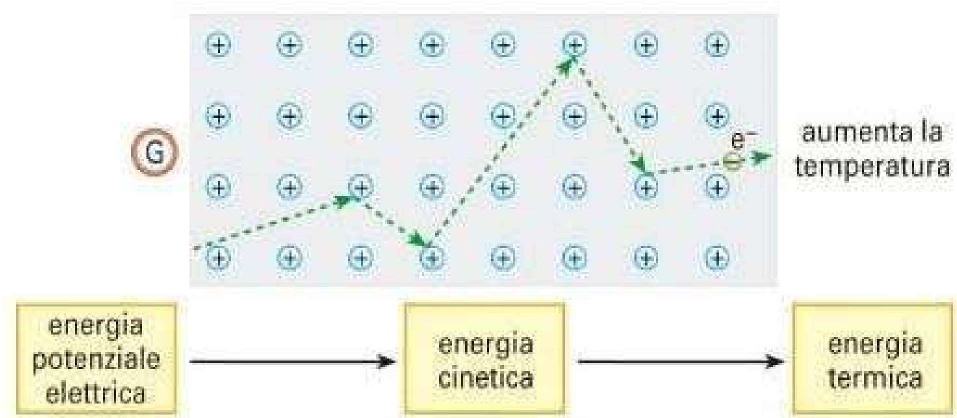
Thermomechanical coupling: *Thermal Expansion*

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.

Thermal expansion (and contraction) must be taken into account when designing products with close *tolerance fits* as these tolerances will change as temperature changes. 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. Thermostats and other *heat-sensitive sensors* make use of the property of linear expansion.



Thermoelectrical coupling: *Joule effect* & *Temperature Coefficient of Resistivity*



$$Q = R \cdot i^2 \cdot \Delta t$$

Q = calore sviluppato (J)
R = resistenza (Ω)
i = intensità di corrente (A)
Δt = tempo impiegato (s)

The *material resistance increases as temperature increases* -> thermal energy causes the atoms to vibrate about their equilibrium positions interfering with electron movement.

$\rho = \rho_0 [1 + \alpha (T - T_0)]$ α = temperature cofficent of resistivity

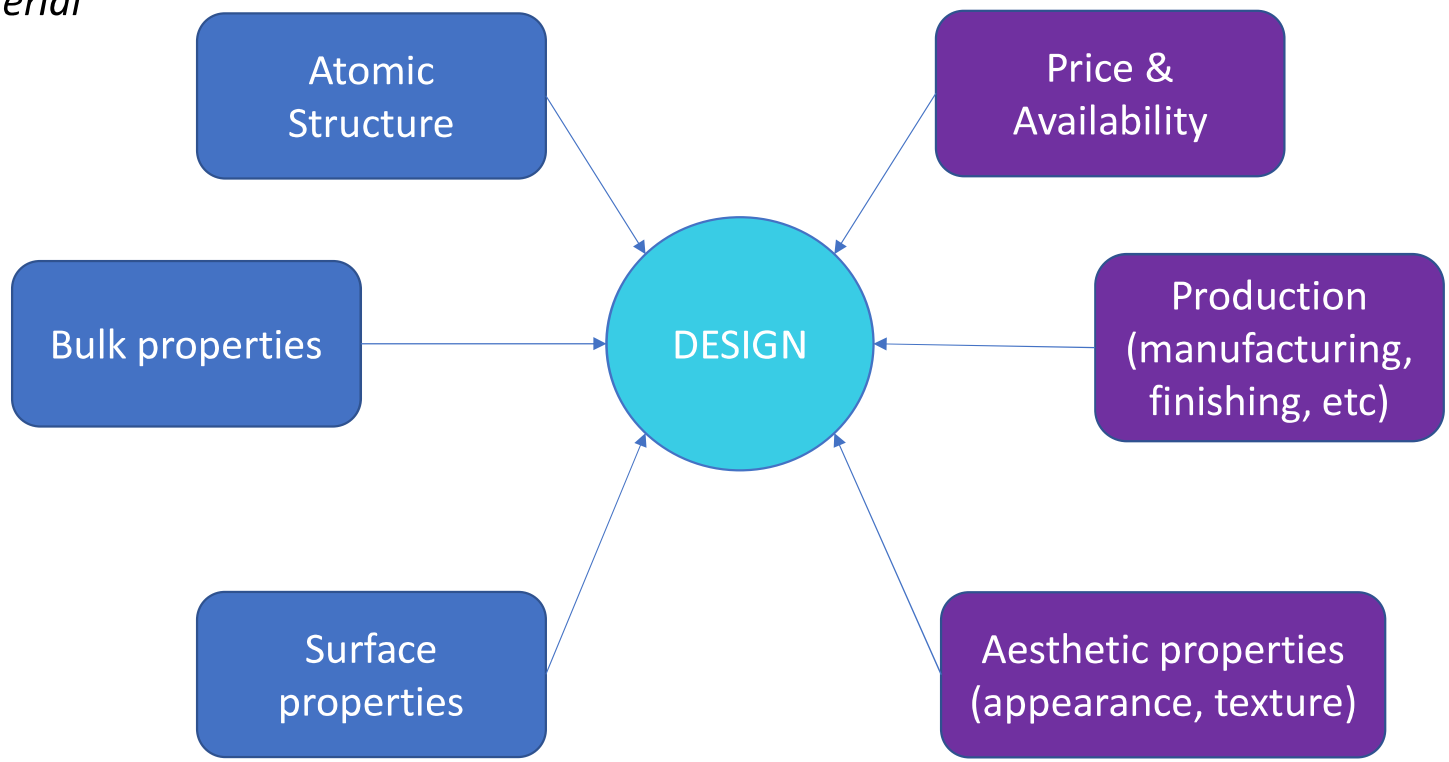
Material Properties in Engineering

Intrinsic properties

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

Extrinsic properties

(or attributive)



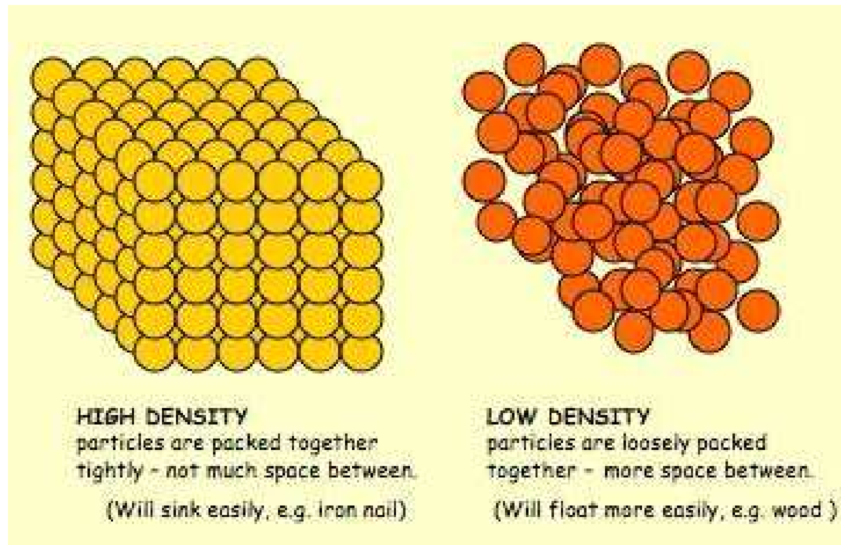
Material Properties in Engineering

Properties that are commonly used to compare engineering materials are:

1. **density:** the mass normalized to the volume (in SI units it is defined in terms of kg/m^3)

density, mass, volume

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

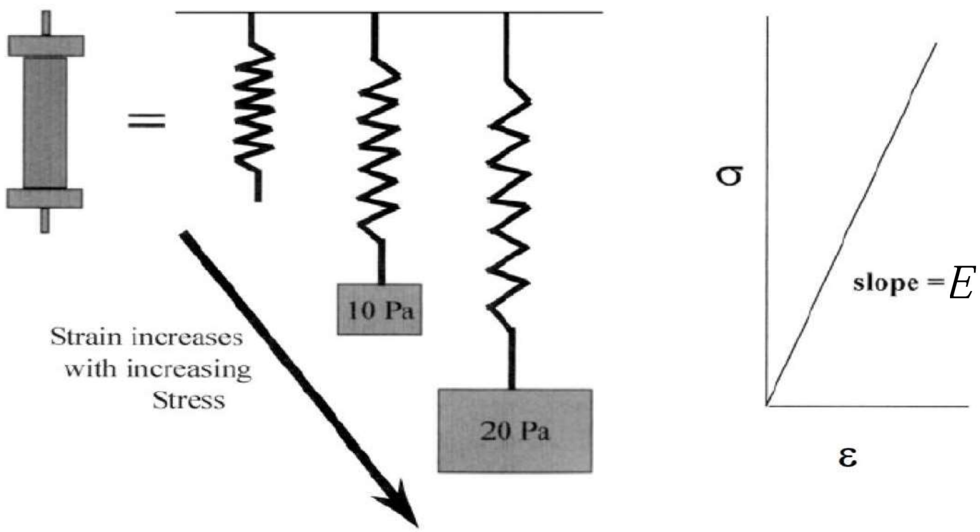


Low values for materials are approximately *0.01 kg/m3 for foams*, and high values can reach ≈ *20 kg/m3 for some metals and ceramics.*

Material Properties in Engineering

Properties that are commonly used to compare engineering materials are:

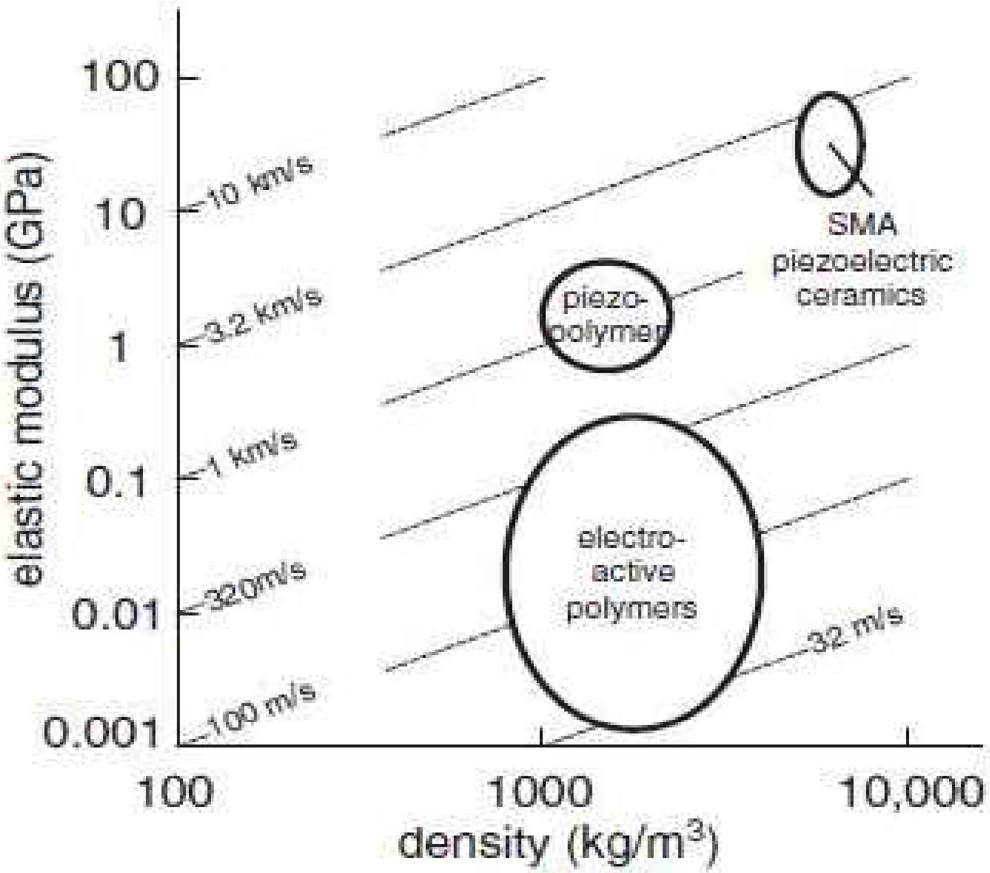
2. elastic modulus (E): relates the applied loads on a solid material to the resulting deformation (stress/strain)



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

In contrast, the variation in elastic modulus for materials spans approximately seven orders of magnitude, from approximately *1 kPa for soft foams* and elastomeric materials to almost *1000 GPa for certain ceramics*.

Smart Material Properties

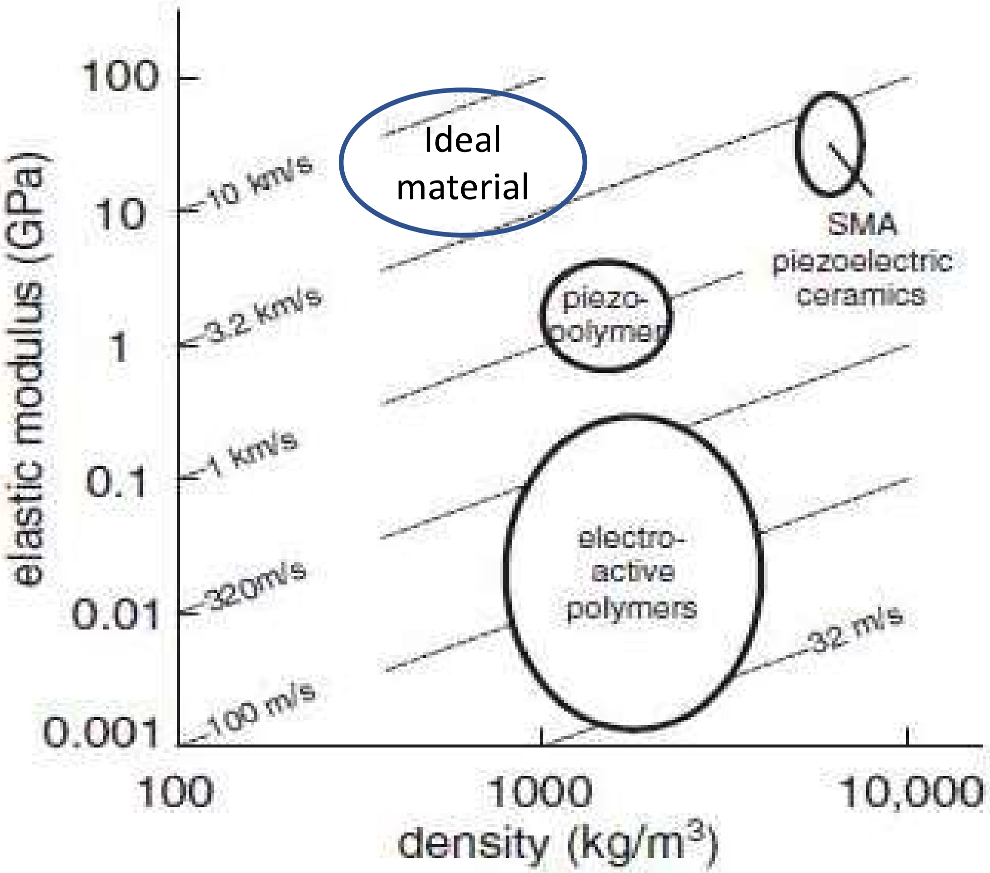


Piezoelectric materials and shape memory alloys:
modulus of 10 to 100 GPa
density 7000 to 8000 kg/m^3

Piezoelectric polymers are softer:
modulus is on the order of 1 to 3 Gpa
density of approximately 1000 to 2000 kg/m^3

Electroactive polymers are generally the softest and least dense smart materials:
modulus 1 to 500 Mpa
density 1000 to 3000 kg/m^3

Smart Material Properties



Engineering design often requires materials that have a *high modulus and are lightweight*. High-modulus lightweight materials would lie in the *upper left portion of the graph*.

A material property that relates to the modulus and density is the *wave speed*, defined as the **square root of the modulus normalized to the density**. The dashed lines represent *lines of constant wave speed*, and a higher wave speed indicates that the material has a *higher ratio of modulus to density*.

Generally values span from 10 m/s to over 1 km/s.

$$\text{WAVE SPEED} = \sqrt{\frac{\epsilon}{\rho}}$$

ϵ → modulo elastico

ρ → densità

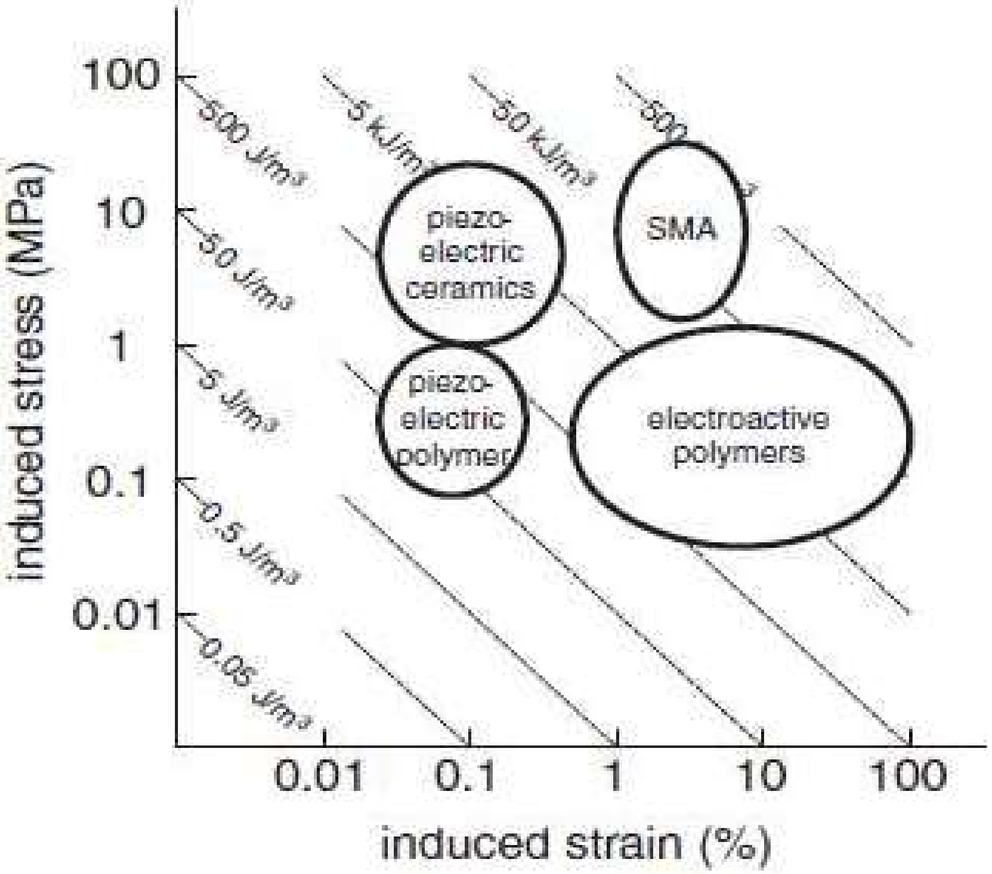
$$[\epsilon] = Pa = \frac{N}{m^2} = \frac{kg\ m}{m^2\ s^2}$$

$$[\rho] = \frac{kg}{m^3}$$

$$\Downarrow$$

$$\left[\sqrt{\frac{\epsilon}{\rho}}\right] = \sqrt{\frac{\cancel{kg}\ m}{\cancel{m^2}\ s^2} \cdot \frac{m^{\cancel{3}}}{\cancel{kg}}} = \sqrt{\frac{m^2}{s^2}} = \frac{m}{s}$$

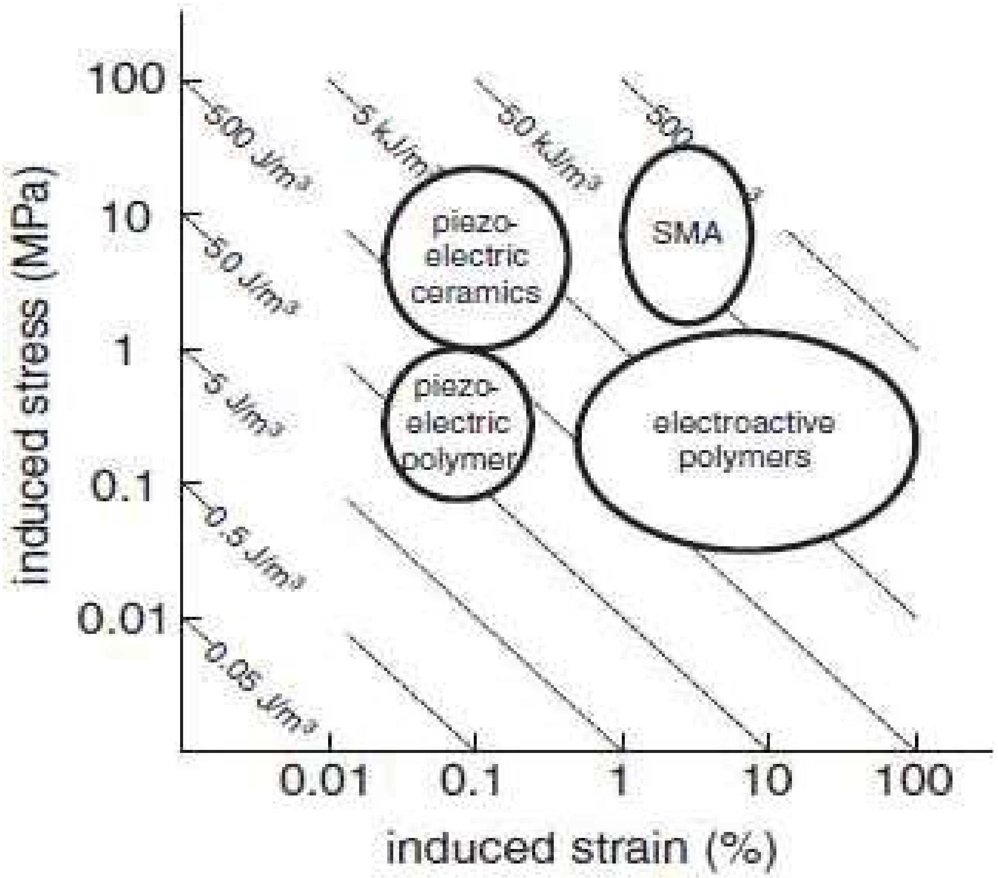
Smart Material Properties



Actuator materials are often compared in terms of the force and the motion that they can generate under an applied stimulus -> **stress/strain**

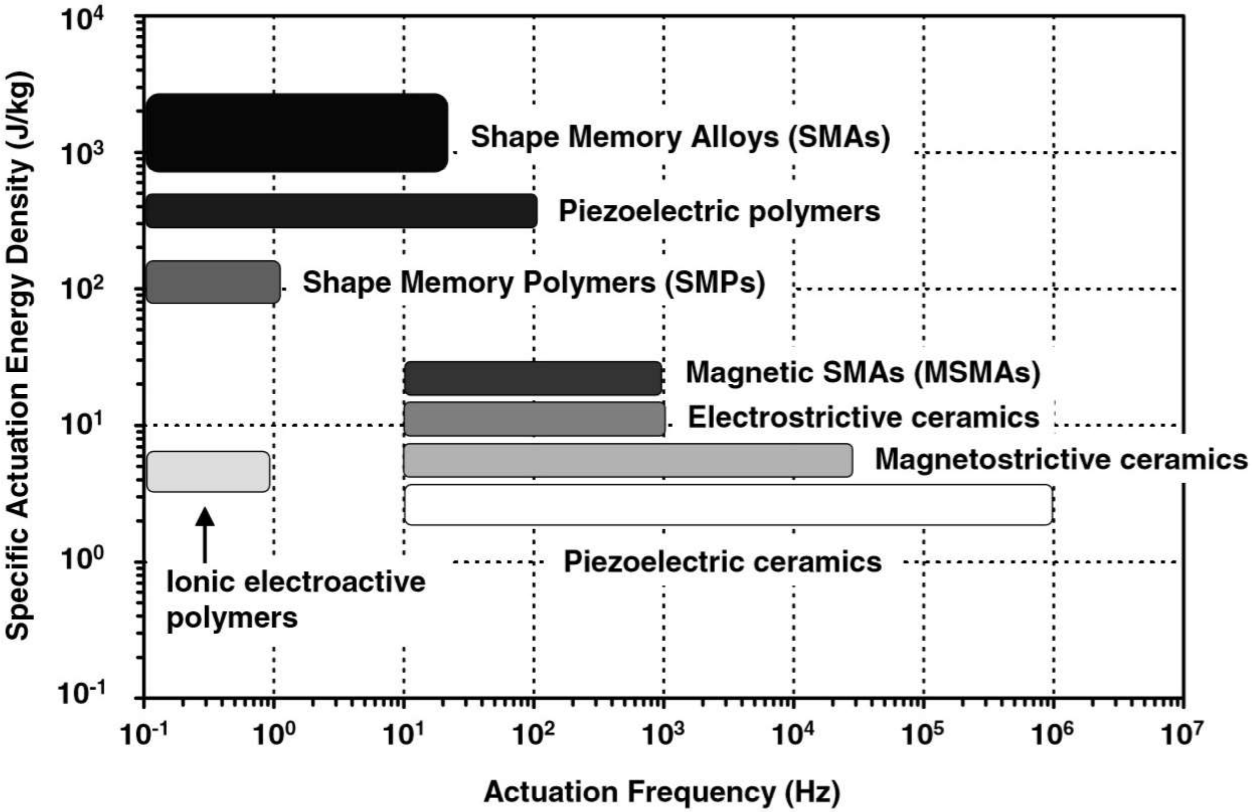
Piezoelectric ceramics generally occupy the upper left portion of the diagram because they produce *small strain and large stress*, whereas **electroactive polymer materials** generally occupy the lower right part of the diagram because they are *large strain–small stress materials*. **Shape memory alloys** are the materials that push farthest into the upper right part of the diagram, due to the fact they can produce *large stress and large strain*.

Smart Material Properties



Force and displacement are examples of *extrinsic properties* (i.e., those that are a function of the geometry of the material or device). As we shall see, it is often useful to compare materials by certain *intrinsic properties*: properties that do not depend on geometry. Stress is defined as the force applied per unit area, and strain is defined as a change in a dimension over the original size of the dimension.

The *product of the stress and strain* produced by a material is defined as the **volumetric energy density**. Thus, a material with a *higher energy density* will have a *larger capacity to do work per unit volume*.
Dashed lines represent lines of constant energy density -> materials in the upper right portion of the plot are materials that have higher energy density and thus have a larger work capacity per unit volume.



Piezoelectric materials generally have the *largest response speed of the materials,* which is governed by small changes in the molecular structure. Because these molecular changes occur on very small length scales, piezoelectric materials can respond very fast to changes in the stimulus applied. For example, it is possible to design a piezoelectric material that will change dimensions in a time scale on the order of microseconds.

The time response of **shape memory alloys**, on the other hand, is limited by the speed at which the stimulus can cause changes in the molecular structure of the alloy.

Volumetric energy density $U_v = \sigma \varepsilon$

stress $\left[\frac{N}{m^2} \cdot \frac{m}{m}\right] \Rightarrow \left[\frac{J}{m^3}\right]$

strain [adimensionale]

Specific " " " $\left[\frac{U_v}{\rho}\right] = \left[\frac{J}{m^3 \frac{kg}{m^3}}\right] = \left[\frac{J}{kg}\right]$

Table 1.1. *Comparison of actuators*

Actuators	Piezoceramic PZT	Piezofilm PVDF	Electrostrictive PMN	Magnetostrictive Terfenol-D	Shape Memory Nitinol
Ferroic class	Ferroelectric	Ferroelectric	Ferroelectric	Ferromagnetic	Ferroelastic
Field	Electric	Electric	Electric	Magnetic	Thermal
Maximum Free Strain %	0.1	0.07	0.1	0.2	8
Response time	μs	μs	μs	μs	s
Young's Modulus E (GPa)	68.9	2.1	117.2	48.3	27.6 for martensite 89.6 for austenite
Strain-voltage characteristic	First-order linear	First-order linear	Nonlinear	Nonlinear	Nonlinear

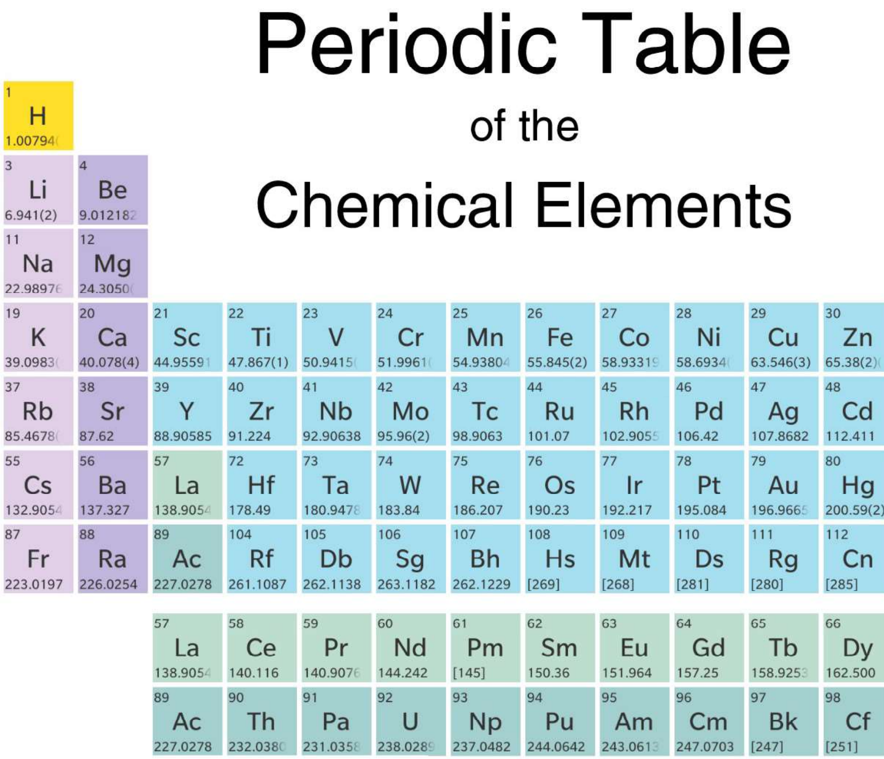
Smart Material Properties

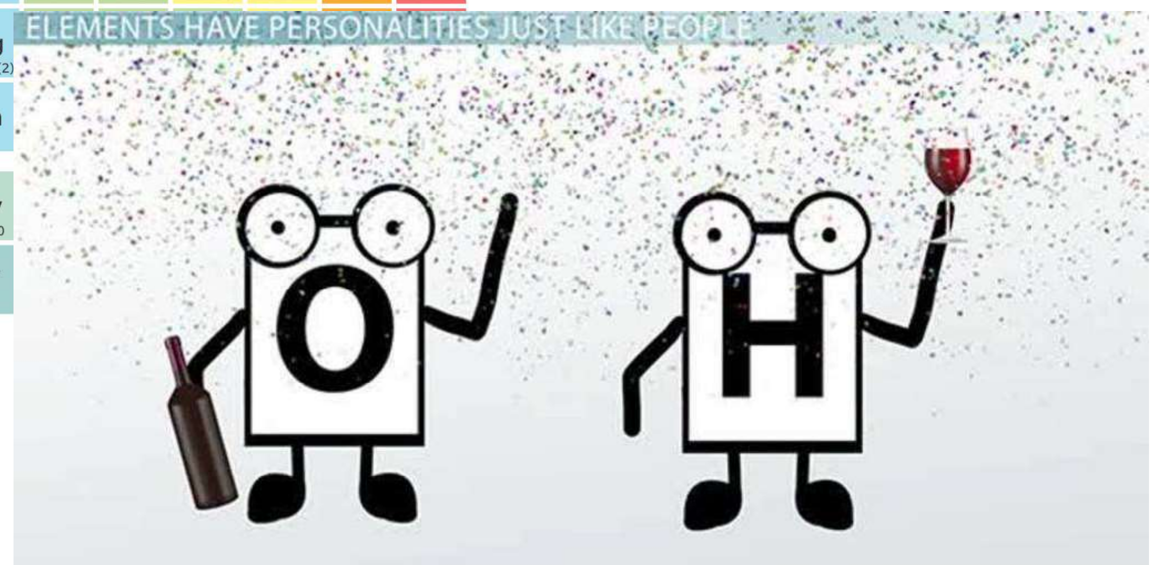
Sensor materials are generally compared in terms of a range of extrinsic properties related to the sensitivity of material, the linearity of response, and the resolution.

As an example, we will see that piezoelectric materials are often used as sensors that convert displacement or force to an electrical signal. The **sensitivity** of the sensor is defined as the *electrical output per unit force or displacement*, and the **resolution** of the sensor is the *smallest variation of force or displacement that can be measured*.

An important metric for sensing applications is the **signal-to-noise ratio** of a device. *Noise* consists of random fluctuations in the output signal that are not correlated with the physical variable that is being measured (e.g., force or displacement). Excellent sensors may exhibit a signal-to-noise ratio on the order of 10 000:1 or 1000:1, whereas poor sensors may exhibit a signal-to-noise ratio of 10:1 or even as low as 2:1.

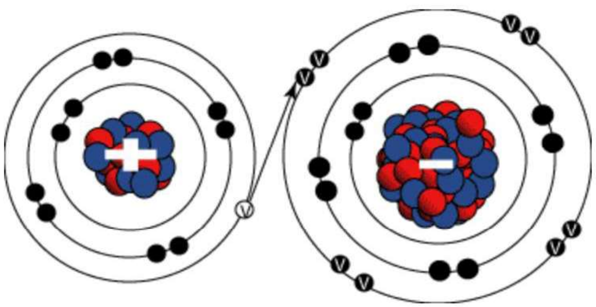
One of the **difficulties in direct comparison of sensors** is that figures of merit such as resolution and signal-to-noise ratio are functions of several *parameters that are not related to the properties of the material*. For example, piezoelectric sensors for measuring force or displacement require *electronics to convert a signal from the material to an electrical output.*



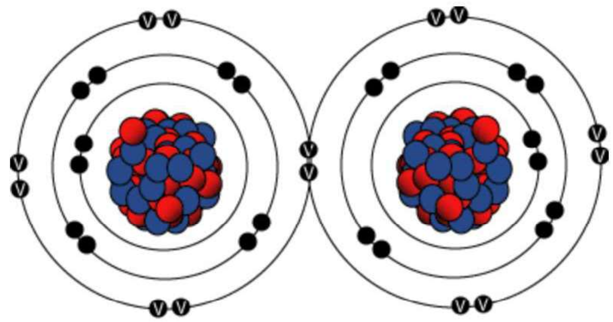


The atomic structure primarily affects the chemical, physical, thermal, electrical, magnetic, and optical properties.

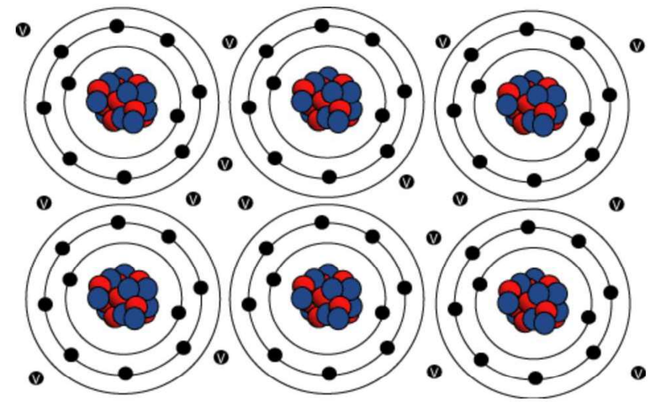
Atomic Bonding



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.

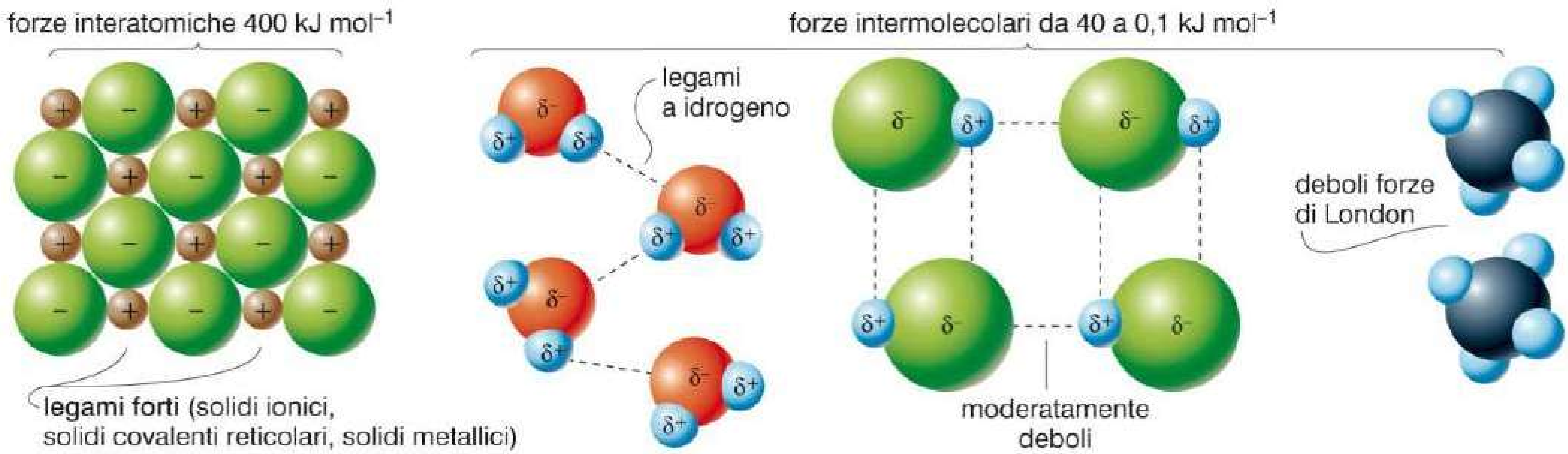


A **covalent bond** is formed by atoms sharing two or more electrons. Consequently, both atoms are held near each other since both atoms have a share in the electrons.



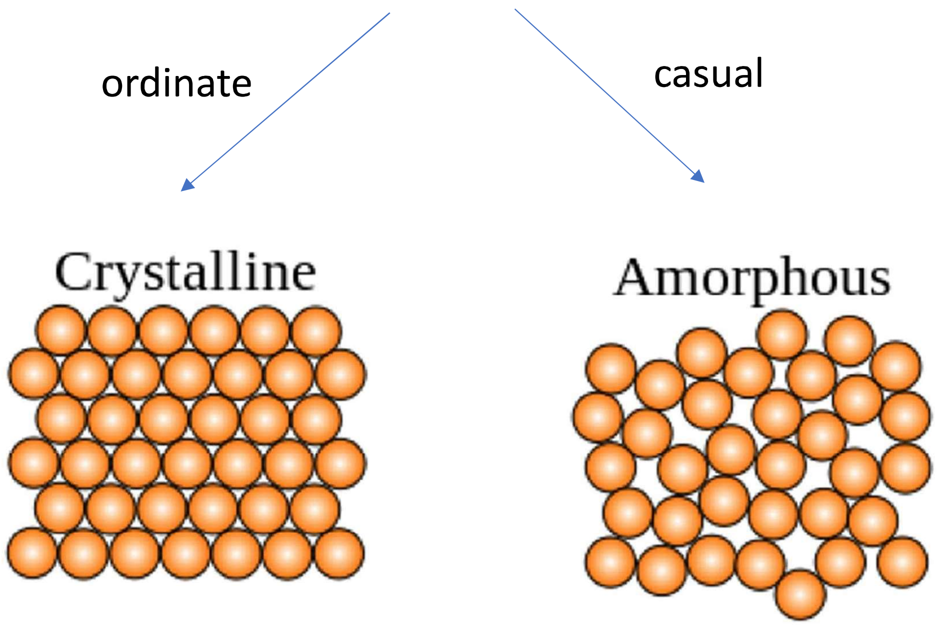
Metallic Bond is formed between metallic elements, which contains only 1 to 3 electrons in the outer shell. The bond between these electrons and the nucleus is relatively weak. So, the outer electrons leave individual atoms to become part of common “electron cloud.”

Forze interatomiche vs. intermolecolari



Solid state matter

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



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

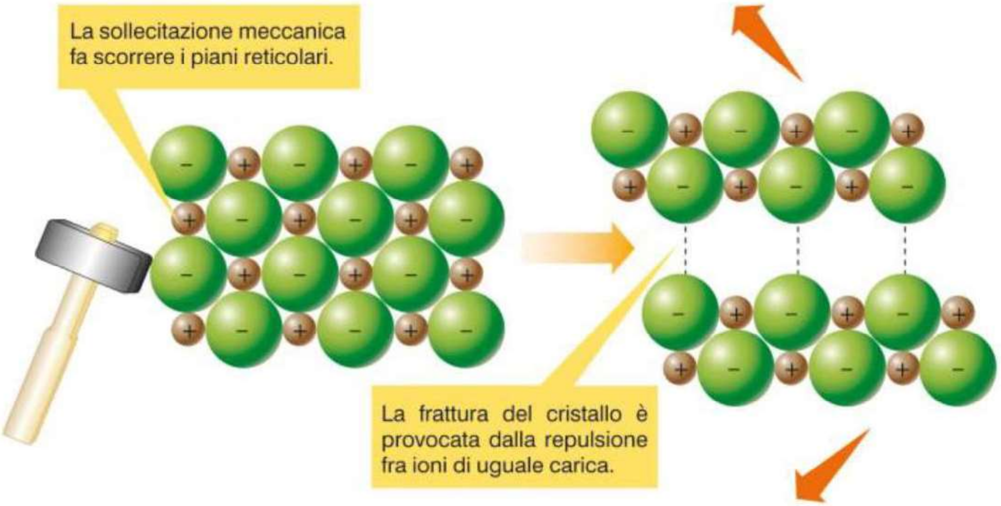
Tipo di cristallo	Unità strutturali	Legame tra le unità strutturali	Esempi	Punto di fusione	Proprietà meccaniche ed elettriche
ionico	ioni positivi e negativi	ionico	NaCl (cloruro di sodio), KNO_3 (nitrato di potassio)	elevato	Duro e fragile. Se solubile in acqua, dà soluzioni conduttrici di elettricità.
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 inter-$^{+}$ molecolari	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 inter-$^{-}$ molecolari	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.

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:

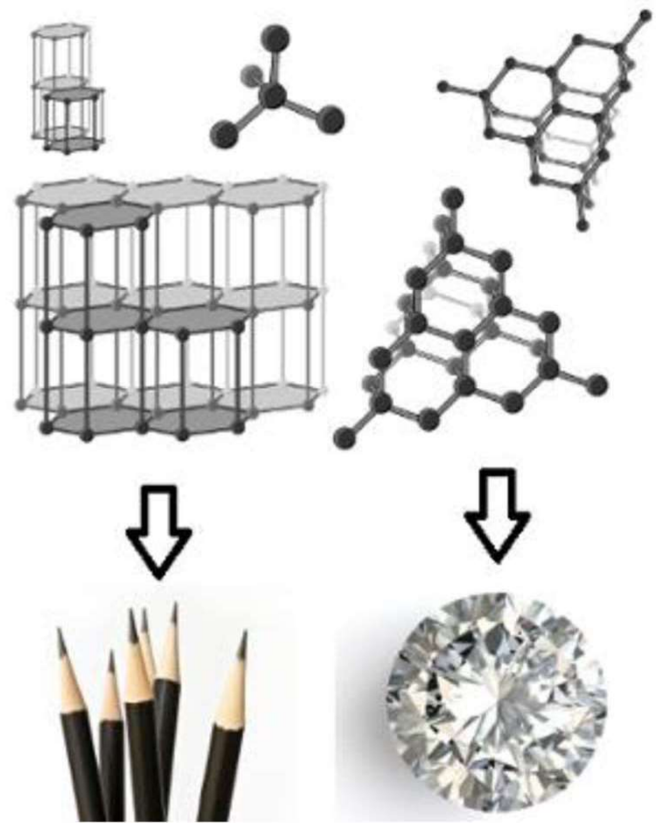
- **alti punti di fusione**
- **elevata durezza**
- **fragilità** (superfici di frattura molto nette disposte secondo piani in cui il vincolo tra gli ioni è minore)
- **scarsa conduzione** allo stato solido (gli ioni sono vincolati nelle posizioni fisse e non possono muoversi), ma sono buoni conduttori 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)



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*.

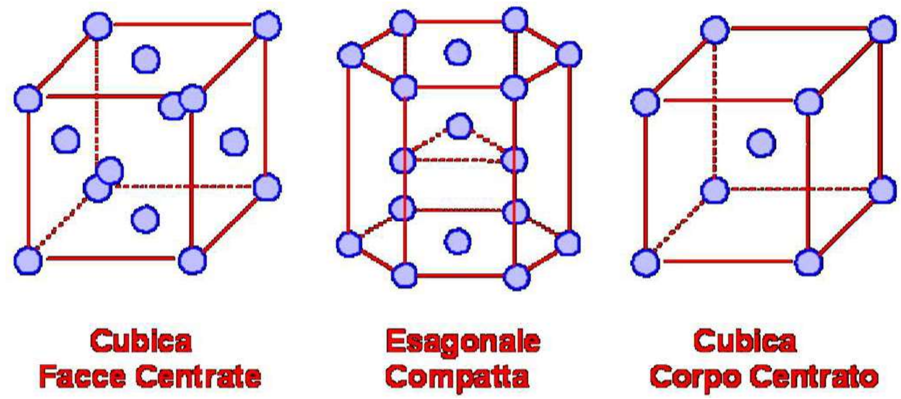


Solidi Metallici

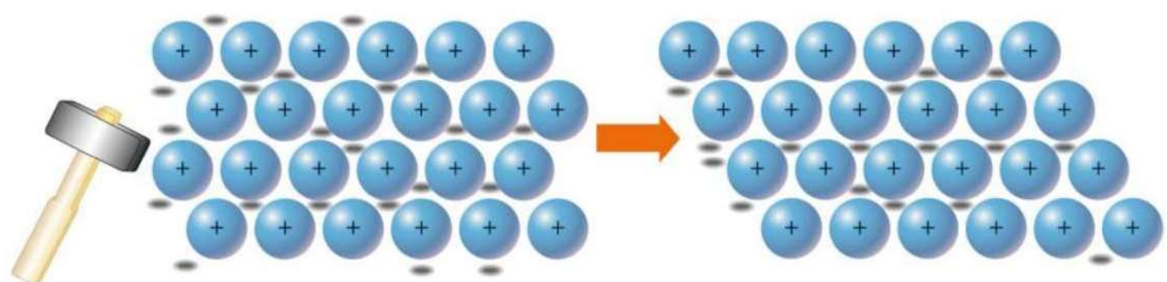
In questi solidi gli elettroni messi in comune dagli atomi permeano come un "gas" gli spazi tra gli ioni positivi che si sono formati. Gli atomi presenti hanno le stesse dimensioni e si dispongono in modo da occupare il minor spazio possibile in reticoli.

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*



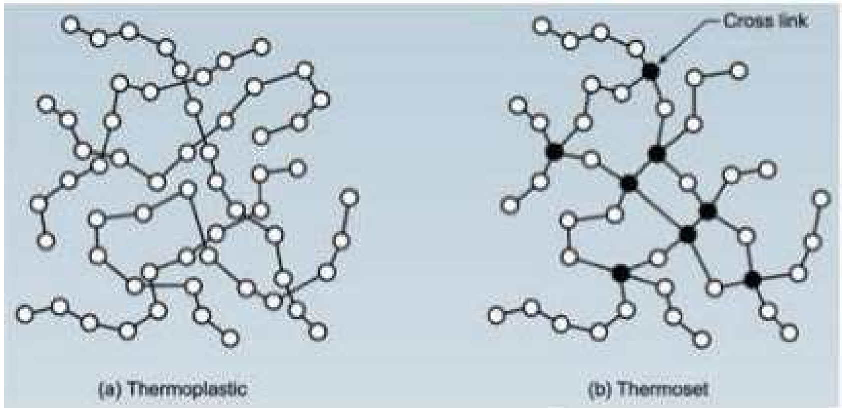
Solidi Molecolari

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.



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

Mechanical Properties

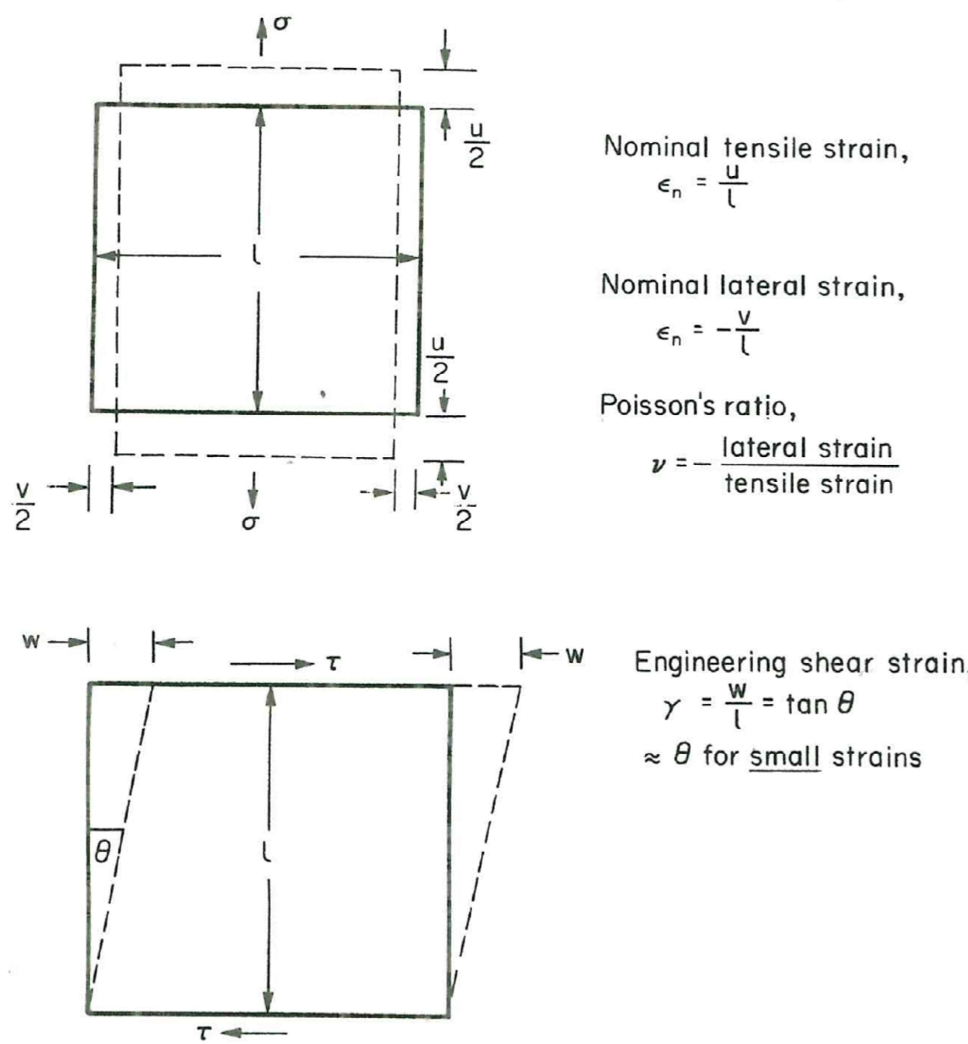
- The **elastic modulus** (E) represents the resistance of a material to deformation (**stiffness**).

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

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

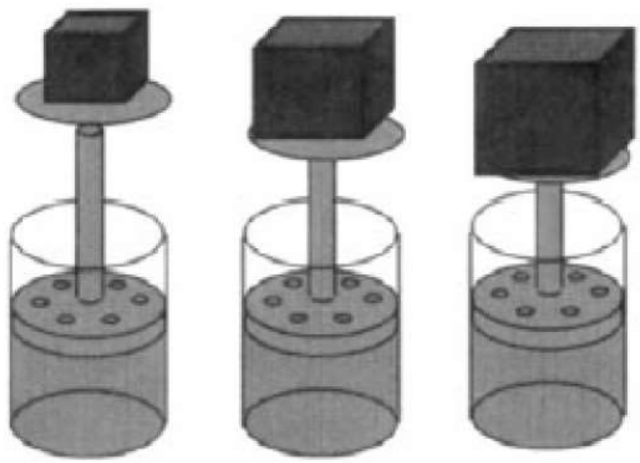
Elastic modulus *Shear modulus*

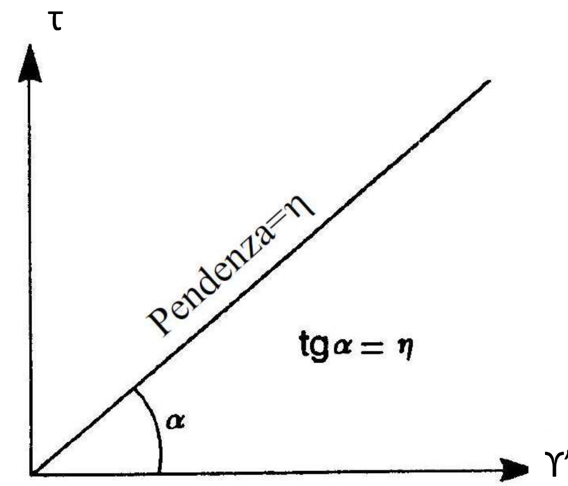
G = τ /γ



Mechanical Properties

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

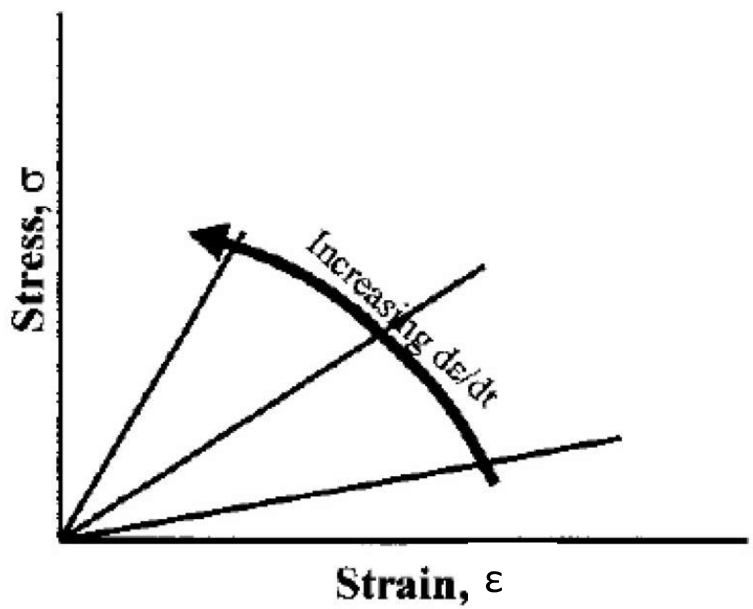




$$\tau = \eta \, \gamma'$$

Mechanical Properties

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



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

Universal Testing Machine

Bulk Properties

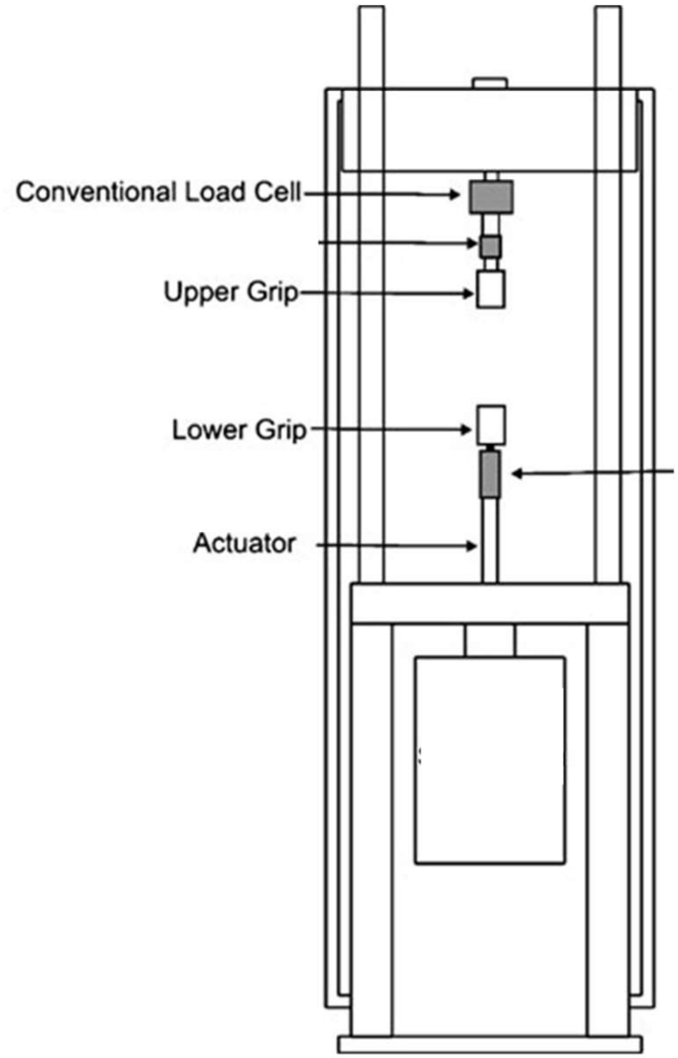
Universal testing machines (UTM):

Compression and tensile tests

Strain or stress-controlled

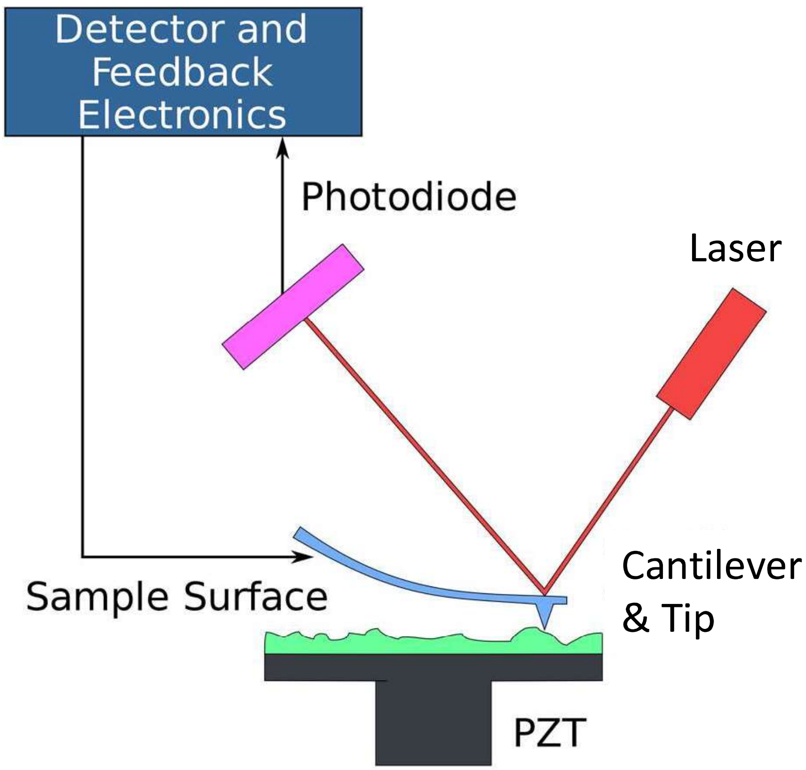
Main components:

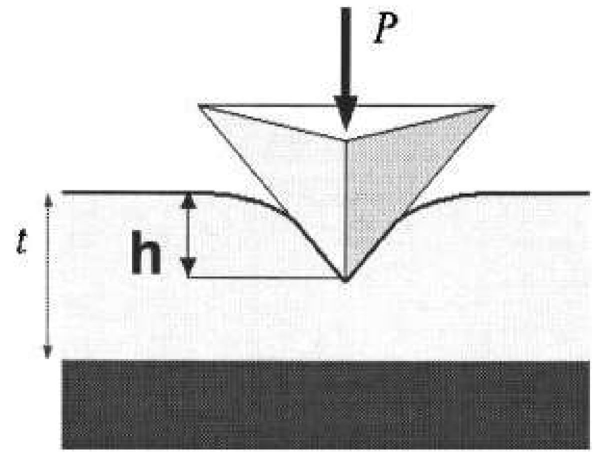
- **Load cell** (different maximum loads)
- **Actuator**
- **Control system**
- Sample holding system

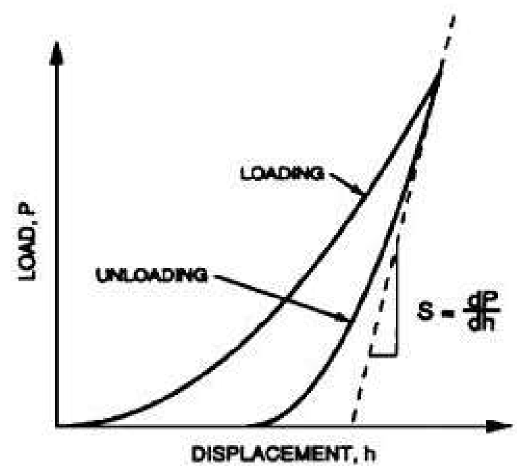


AFM & Nanoidentation

Surface Properties



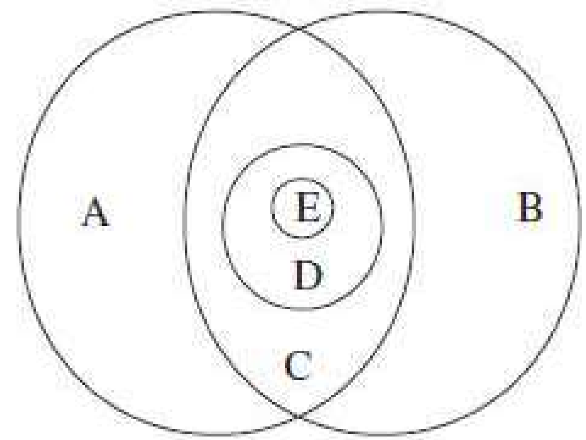




(Smart) Structures

Adaptive Structures *(A)*: have *distributed actuators* to alter characteristics in a prescribed manner.
Sensory Structures *(B)*: have *distributed sensors* to monitor the characteristics of the structure (health monitoring).
Controlled Structures *(C)*: overlap both adaptive and sensory structures. These constitute actuators, sensors, and a *feedback control system to actively control the characteristics of the structure*.

- **Active Structures** *(D)*: are a subset of controlled structures. Integrated actuators and sensors have *load carrying capability* (structural functionality).
- **Smart Structures** *(E)*: are a subset of active structures. Additionally, they have *highly integrated control logic and power electronics*.



A smart structure involves distributed **actuators and sensors**, and one or more **microprocessors** that analyze the responses from the sensors and use integrated control theory to command the actuators.

For smart material applications, **distributed control** functionality is a key ingredient. Levels of control strategies -> **local control**: single input and single output, related by a transfer function; **global control**: centralized controller in which the output from all sensors are processed by a centralized processor.

Attività

Individuare delle applicazioni biomediche per l'eff. Joule (idee, paper, applicazioni commerciali, etc)

Wireless Joule nanoheaters

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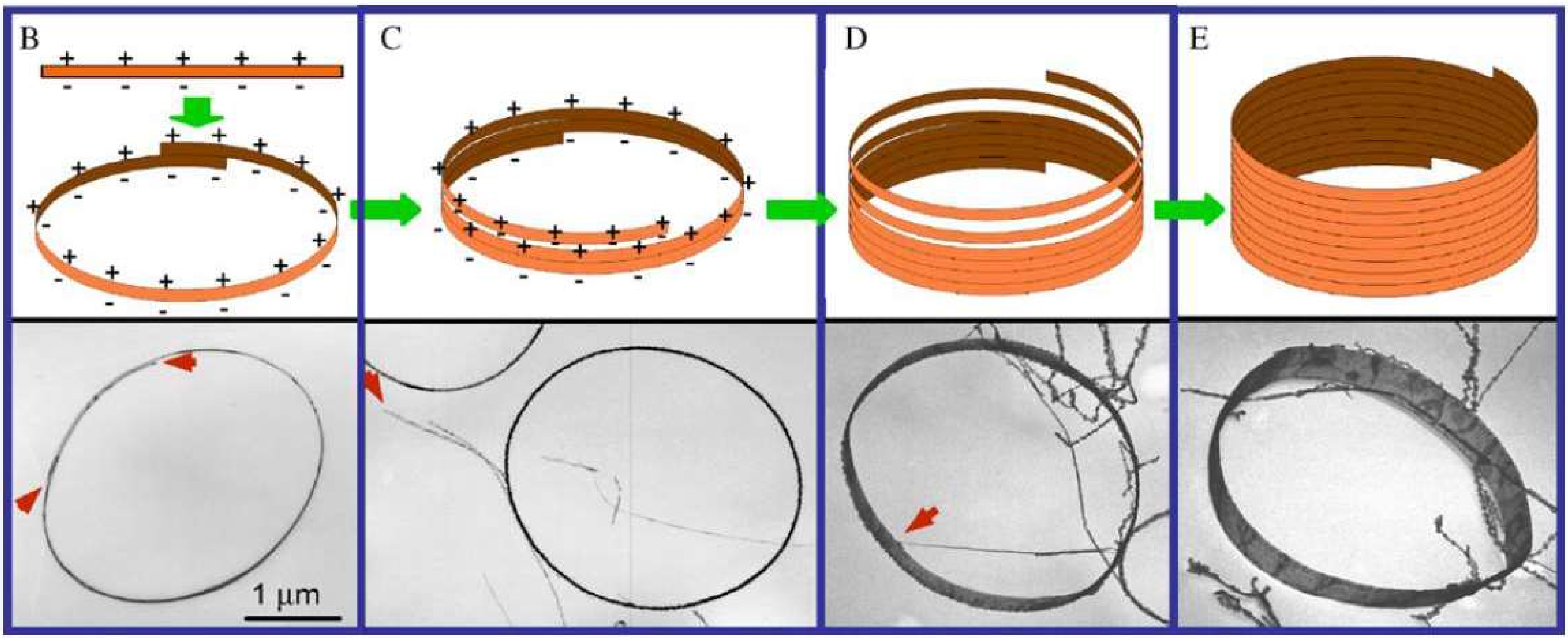
Abstract

In principle, biocompatible, wireless nanotransducers might be useful for many *in vivo* biomedical applications such as hyperthermia, thermal ablation, targeted drug delivery, and *in vivo* monitoring of physiological parameters. In this article, we theoretically study the possibility of applying ring-shaped wireless Joule nanoheaters as possible nanovectors for targeted drug delivery, hyperthermia, and thermal ablation. This examination may offer an approach for guiding practical experiments.

Keywords: Wireless nanotransducers; Wireless Joule nanoheaters; Targeted drug delivery; Nanorings; Zinc oxide nanostructures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