F7360 Characterization of thin films and surfaces

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1. Chapter - Structure of Condensed Matter
spring semester 2014

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Outline

When the temperature of a melt is lowered to a certain point, the liquid will form either a **crystalline** or **amorphous** solid.

▶ Crystals are periodic arrays of long-range ordered atoms. A real crystal is never perfect – contains defects (vacancies, dislocations, impurities, and other imperfections).

▶ Amorphous materials posses only short-range ordering.

SiO_2 demonstrates the difference between crystalline and amorphous materials:

▶ Short-range ordering: silicon atoms are surrounded by three oxygen atoms.

▶ Long-range ordering in quartz: hexagonal structure.

Crystalline SiO_2 (Quartz)   Amorphous SiO_2 (Glass)

• Si • O
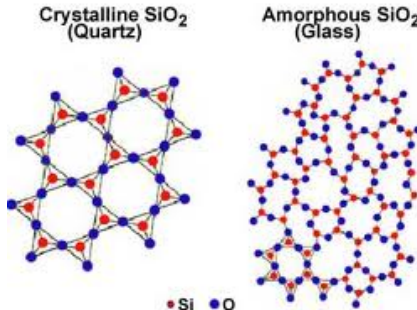
An ideal crystal is constructed by the infinite repetition of identical groups of atoms (a motif):

- ▶ A group is called the **basis**.
- ▶ The set of mathematical points to which the basis is attached is called the **lattice**.
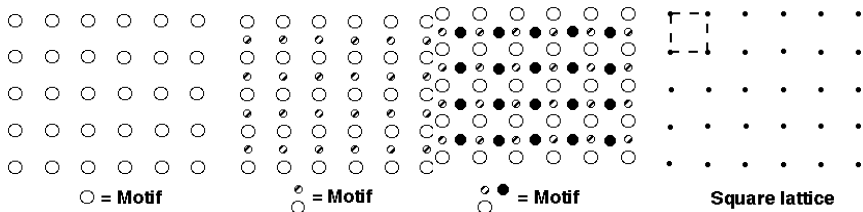
The lattice in 3D is defined by three **translation vectors** $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ - the arrangement of atoms in the crystal have to look the same when viewed from the points $\vec{r}$ and $\vec{r}'$

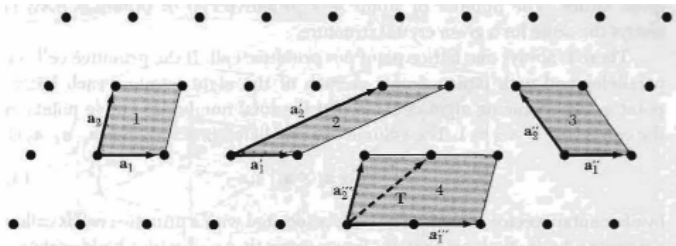$$\vec{r}' = \vec{r} + u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

where u_1, u_2 and u_3 are arbitrary integers.

The lattice is **primitive** if any two points from which the attomic arrangement looks the same always satisfy

$$\vec{r}' = \vec{r} + u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

with a suitable choice of the integers u_1, u_2 and u_3.

Then, the vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ are **primitive translation vectors**.
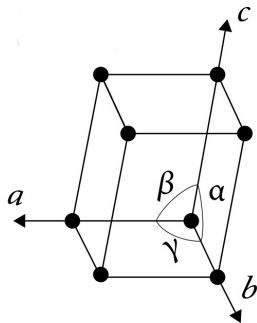

Lattice points in 2D -
all pairs of $\vec{a}_1$, $\vec{a}_2$ are translational vectors but $\vec{a}_1'''$, $\vec{a}_2'''$ are not primitive.

The parallelepiped defined by the primitive axes $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ is a **primitive cell**.
A primitive cell is type of unit cell (or just cell).
It is the smallest cell that can serve as a building block for the crystal structure. Its volume is
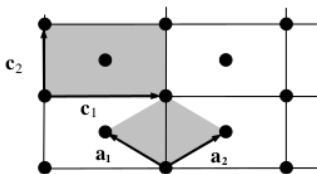
$$V = |\vec{a}_1 . \vec{a}_2 \times \vec{a}_3|$$

Primitive translation vectors $\vec{a}_i$ are often used to define the **crystal axes**
- three adjacent edges of the primitive parallelepiped.

Nonprimitive axes are used as crystal axes when they have a simple relation to the symmetry of the structure.

2D centered rectangular lattice with

- **primitive translation vectors** $\vec{a}_1$ and $\vec{a}_2$ and
- **nonprimitive translational vectors** $\vec{c}_1$ and $\vec{c}_2$.

In order to describe the crystal structure it is necessary to answeer three important questions:

1. **what lattice** we have (for a particular structure can be more than one),
2. **what translational vectors** $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ are we using to describe the lattice (more sets of translational vectors can be selected for a given lattice) and
3. **what is the basis** (which is choose after the lattice and translational vectors are selected).

Crystal lattice can be transformed into themselves by the lattice translation $\vec{T}$

$$\vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

and by various other symmetry point operations.

A typical **symmetry point operation** -
rotation about an axis that passes through a lattice point

Lattices can be found such that one-, two-, three-, four- and six-fold rotation axes carry the lattice into itself (corresponding rotations by 2π, $2\pi/2$, $2\pi/3$, $2\pi/4$ and $2\pi/6$ and their integral multiples).

Another symmetry operations are **mirror reflections about a plane through a lattice point**.

The collection of symmetry point operations which, applied about a lattice point, carry the latice into itself is called **lattice point group**.

Bravais lattices in two dimensions:

- general lattice known as oblique lattice - invariant only under rotation of π and 2π about any lattice point
- four special lattices (rectangular, centered rectangular or rhombic, hexagonal and square) - can be invariant under rotation $2\pi/3$, $2\pi/4$ and $2\pi/6$ or under mirror reflection
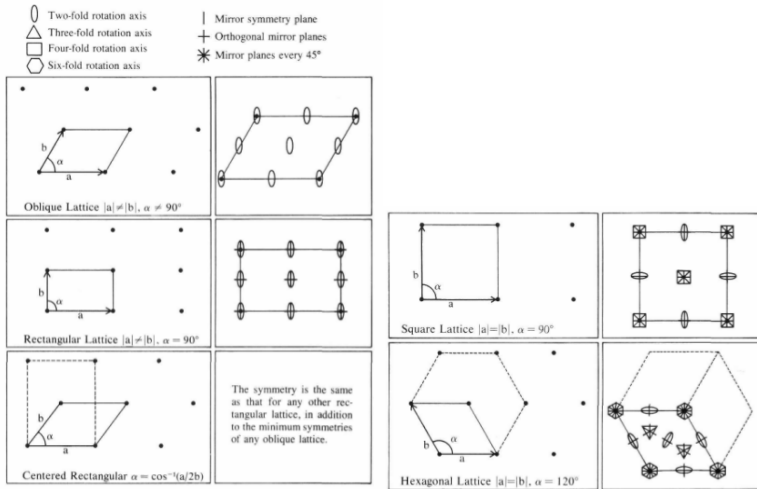
In 3D - 7 distinguishable point groups of unit cells (**7 crystal systems**) that can fill the space (triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal and cubic).

The **Bravais lattices** are obtained by combining one of the 7 lattice systems with one of the **lattice centerings**:

▶ simple - lattice points on the cell corners only.

▶ body-centered
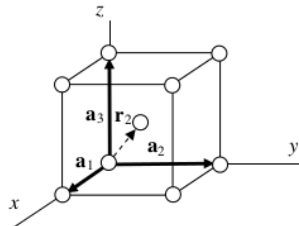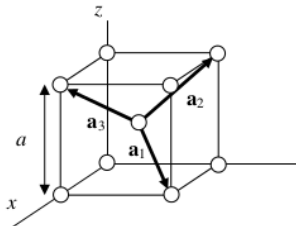
▶ face-centered

▶ base-centered

in total $7 \times 6 = 42$ combinations but from the full symmetries (point operations and translations) 14 different space groups (**14 Bravais lattices**) have been found.

Primitive translation vectors of the **body-centered cubic (bcc) lattice** (in units of lattice parameter *a*)

- $\vec{a}_1 = (1/2, 1/2, -1/2)$;
- $\vec{a}_2 = (-1/2, 1/2, 1/2)$;
- $\vec{a}_3 = (1/2, -1/2, 1/2)$

The **primitive cell** is the rhombohedron. The **packing ratio** is 0.68, defined as the maximum volume which can be filled by touching hard spheres in atomic positions. Each atom has 8 nearest neighbors.

The **conventional unit cell** is a cube based on vectors $\vec{a}_1 = (0,0,1)$; $\vec{a}_2 = (0,1,0)$; $\vec{a}_3 = (0,0,1)$. It is twice big compared to the primitive unit cell and has two atoms in it with coordinates $\vec{r}_1 = (0,0,0)$ and $\vec{r}_2 = (1/2, 1/2, 1/2)$.


The bcc lattice have alkali metals such as Na, Li, K, Rb, Cs, magnetic metals such as Cr and Fe, and and refractory metals such as Nb, W, Mo, Ta.

Primitive translation vectors of the **face-centered cubic (fcc)** lattice (in units of lattice parameter *a*)

- $\vec{a}_1 = (1/2, 1/2, 0)$;
- $\vec{a}_2 = (0, 1/2, 1/2)$;
- $\vec{a}_3 = (1/2, 0, 1/2)$.

The **primitive cell** is the rhombohedron. The **packing ratio** is 0.74. Each atom has 12 nearest neighbors.

The **conventional unit cell** is a cube based on vectors $\vec{a}_1 = (0, 0, 1)$; $\vec{a}_2 = (0, 1, 0)$; $\vec{a}_3 = (0, 0, 1)$. It is 4 times bigger than the primitive unit cell and has 4 atoms in it with coordinates $\vec{r}_1 = (0, 0, 0)$; $\vec{r}_2 = (1/2, 1/2, 0)$; $\vec{r}_3 = (0, 1/2, 1/2)$; $\vec{r}_4 = (1/2, 0, 1/2)$.
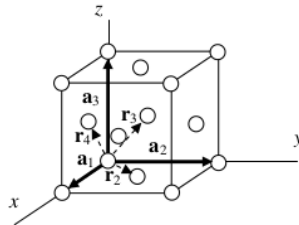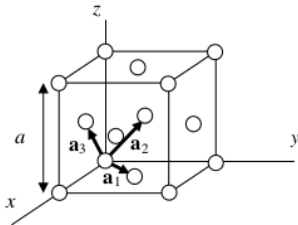
The fcc lattice have noble metals such as Cu, Ag, Au, common metals such as Al, Pb, Ni and inert gas solids such as Ne, Ar, Kr, Xe.

Crystal System	Centering	Axial Distances (edge lengths)	Axial Angles	Examples
Cubic	simple body-centred face-centred	a = b = c	$\alpha = \beta = \gamma = 90^o$	NaCl, Zinc Blende, Cu
Tetragonal	simple body-centered	a = b $\neq$ c	$\alpha = \beta = \gamma = 90^o$	White tin, SnO_2, TiO_2, $CaSO_4$
Orthorhombic	simple body-centered face-centered base-centered	a $\neq$ b $\neq$ c	$\alpha = \beta = \gamma = 90^o$	Allotropes of sulfur, KNO_3, $BaSO_4$
Hexagonal	simple	a = b $\neq$ c	$\alpha = \beta = 90^o, \gamma = 120^o$	Graphite, ZnO, CdS
Rhombohedral (trigonal)	simple	a = b = c	$\alpha = \beta = \gamma \neq 90^o$	$CaCO_3$, HgS
Monoclinic	simple base-centered	a $\neq$ b $\neq$ c	$\alpha = \gamma = 90^o, \beta \neq 90^o$	Monoclinic Sulp $Na_2SO_4 * 10H_2$
Triclinic	simple	a $\neq$ b $\neq$ c	$\alpha \neq \beta \neq \gamma \neq 90^o$	$K_2Cr_2O_7$, CuS$ * 5H_2O$, H_3BO_3

Index systems for crystal directions and planes (Miller indices)
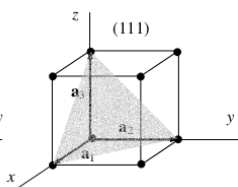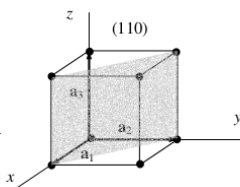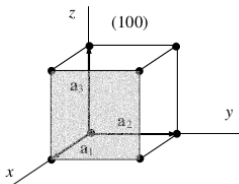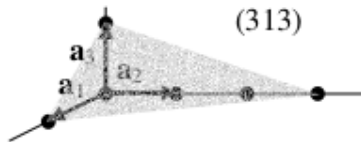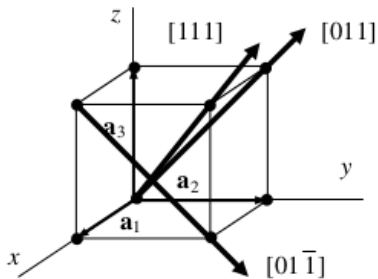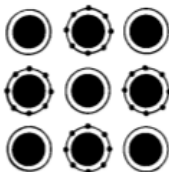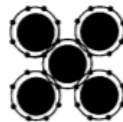
Interatomic bonds in solids are

- ionic (a)
- covalent (b)
- metalic (c)
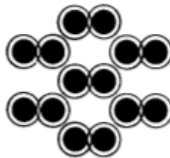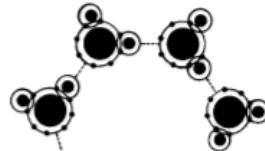- Van der Waals (d), (e)

bond energy:
1 kJ/mol = 0.010364 eV/atom

Ionic bonds - between particles which have a net electrical charge

- ▶ positive ions - **cations**,
  atoms with low **ionization energy** (lose electrons easily) - alkaline metals (only 1 s electron in outer shell)
- ▶ negative ions - **anions**,
  atoms with high **electron affinity** (easily accept electrons) - halogens (missing 1 p electron)

Interaction force - **Coulomb**. Repulsive forces of similarly charge ions and attractive forces of differently charged ions are equilibrated. **Pauli exclusion principle** does not allow ions to come too close.
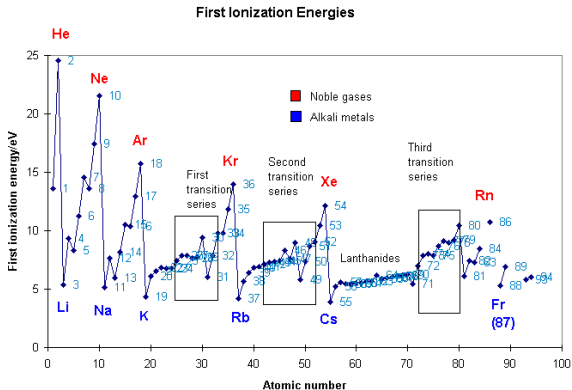

Periodic Table of the Elements

Ionization energy (energy necessary to release electron) is periodic function of atomic number, large atoms or molecules have lower ionization energy.

First Ionization Energies

Electron affinity (energy released if electron is added):

Fluorine	3.45 eV
Chlorine	3.61 eV
Bromine	3.36 eV
Iodine	3.06 eV

Directionality of ionic bond is low - electron configuration of ions resemble filled shells of inert gases, i. e. electron density is sherically symmetric.
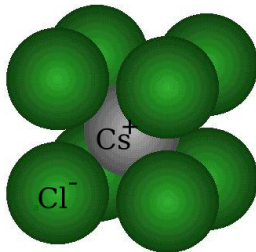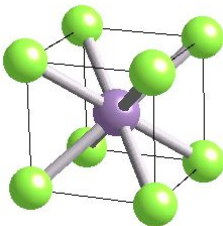
High coordination - cation (anion) is surrounded by as many anions (cations) as possible.

Relative size of cations and anions determines the lattice type. The most frequent types

- ▶ fcc - typical example NaCl (6 neighbors of different type)
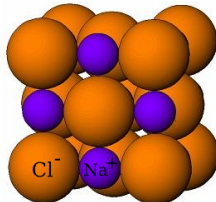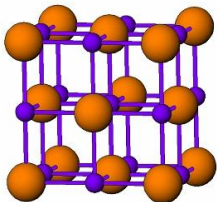
- ▶ bcc - typical example CsCl (8 neighbors of different type)

Cohesive energy of the crystal - energy released if ionic crystal is formed. The most important contribution - **Coulomb interactions** between ions, long range interaction

Consider Na^+ in NaCl. It is surrounded by six Cl^- at the distance r:

$$V_1 = -\frac{6e^2}{4\pi\varepsilon_0 r}$$

Another neighbors are 12 Na^+ each at the distance $\sqrt{2}r$:

$$V_2 = +\frac{12e^2}{4\pi\varepsilon_0\sqrt{2}r}.$$

Summed for the entire crystal:

$$
\begin{aligned}
V_{Coulomb} &= -\frac{e^2}{4\pi\varepsilon_0 r}\left(6 - \frac{12}{\sqrt{2}} + \dots\right) \\
&= -1.748\frac{e^2}{4\pi\varepsilon_0 r} \\
&= -\alpha\frac{e^2}{4\pi\varepsilon_0 r}.
\end{aligned}
\tag{1}
$$

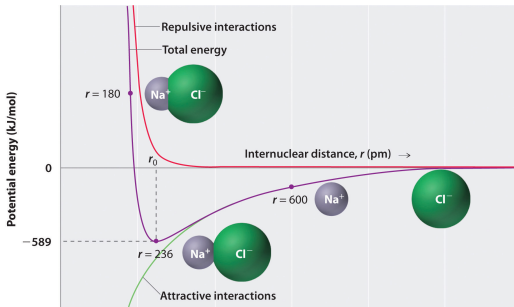The constant α is called **Madelung crystal constant**, values 1.6–1.8 for simple crystals.

The contribution of the **quantum-mechanical repulsive force** to the total potential energy can be written as:

$$V_{repulsive} = \frac{B}{r^n}.$$

Total potential energy in the crystal is:

$$V = V_{Coulomb} + V_{repulsive} = -\frac{\alpha e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n}$$

where n is about 9.

In the steady case the separation of ions at a distance r_0 must have minimum:

$$\left(\frac{dV}{dr}\right)_r = r_0 = 0,$$

so

$$B = \frac{\alpha e^2}{4\pi\varepsilon_0 n} r_0^{n-1}$$

Total potential energy:

$$V = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

Total potential energy (from previous slide):

$$V = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

In case of NaCl

- $r_0 = 2.81$, thus $V = -1.27 \times 10^{-18}$ J $= -7.97$ eV
- we have take into account energy for electron transfer between Na and Cl, i.e. the difference between the ionization energy 5.14 eV for Na and the electron affinity of -3.61 eV for Cl $\rightarrow$ 1.53 eV
- each atom is contributing with half of the value, so the overall cohesive energy per atom $E_{\text{cohesive}} = (-3.99 + 0.77)$ eV/atom $= -3.22$ eV/atom.
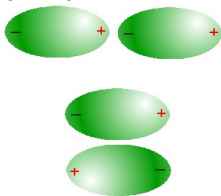
$\Rightarrow$ Ionic crystals are hard and they have high melting point.

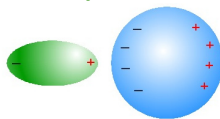They conduct electricity when molten or in solution, but not as a solid.

They tend to be soluble in water.

All atoms and molecules, even inert-gas atoms, exhibit weak, short-range attractions for one another (proportional to r^{-7}) due to **van der Waals forces** (0.01–0.1 eV/molecule).
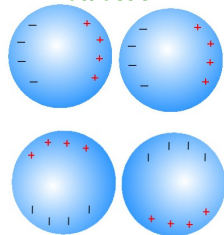
polar-polar attraction   **polar-nonpolar attraction**   **nonpolar-nonpolar attraction**

The different types of van der Waals forces were first explained by different people at different times $\Rightarrow$ different names

- **London dispersion forces** between **non-polar** atoms or molecules were described by Fritz London in 1930. He suggested that the motion of electrons within an atom or non-polar molecule can result in a transient dipole moment. Dispersion forces are the weakest of the van der Waals forces. They are stronger for larger atoms and molecules (higher polarizability).

- **dipole-dipole interactions** explained by Keesom in 1912 as interaction between permanent electrical dipole moments of molecules (depends on the value of electrical dipole).

Hydrogen bonds - a special type of attractive dipole-dipole interaction between an electronegative atom and a hydrogen atom bonded to another electronegative atom (e. g. for H-F, H-O or H-N).

▶ It is strong type of van der Waals forces (0.04–0.26 eV/molecule) because H atom has only 1 electron that is "donated" almost whole to the electronegative atom, leaving the small effective size of proton unshielded (electric forces vary as r^{-2}).

▶ Hydrogen bonds can occur between molecules or within parts of a single molecule.

Typical example of molecules with permanent electric dipole moments is H_2O:
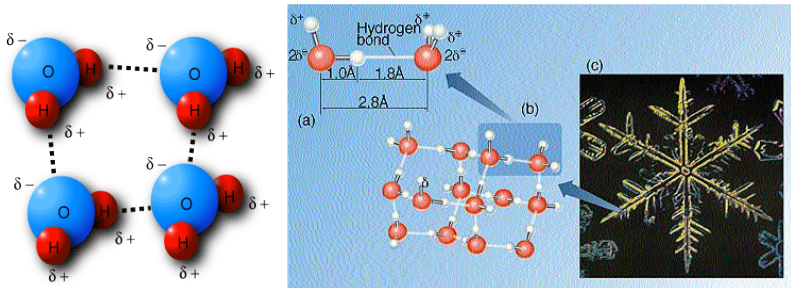
Characteristics of attractive force between **polar and nonpolar molecules**:

The electric field $\vec{E}$ at a distance r from a polar molecule having **dipole moment** $\vec{p}$

$$\vec{E} = \frac{1}{4\pi\varepsilon_0}[\frac{\vec{p}}{r^3} - \frac{3(\vec{p}\vec{r})}{r^5}\vec{r}]$$

$\vec{p}\vec{r} = pr\cos\theta$ (θ is angle between $\vec{p}$ and $\vec{r}$).

induced electric dipole moment $\vec{p}'$ in the other, normally nonpolar molecule,

$$\vec{p}' = \alpha\vec{E}$$

where α is a constant called **polarizability** of the molecule.

The energy of the induced dipole in the electrical field $\vec{E}$ is

$$\mathcal{E} = -\vec{p}'\vec{E} = -\frac{\alpha}{(4\pi\varepsilon_0)^2}(1 + \cos^2\theta)\frac{p^2}{r^6}$$

The mutual energy of the molecules that arises from their interaction is thus negative, signifying that the force between them is attractive, and is proportional to r^{-6}.

The **force** itself is equal to $d\mathcal{E}/dr$ and so **proportional to r^{-7}**, which means that it drops rapidly with increasing separation. Doubling the distance between two molecules reduces the attractive force between them to only 0.8 % of its original value.

http:
//chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/
Atomic_and_Molecular_Properties/Intermolecular_Forces/Intermolecular_Forces

Explanation of **covalent bonds** - quantum mechanics is necessary. Two theories

- ▶ **valence bond (VB) theory** or local electron model: chemical bonds are formed by overlapping of atomic orbitals. This overlap of orbitals causes localization of the electrons in the bond region.
- ▶ **molecular orbital (MO) theory**: construction of new orbitals called molecular orbitals, electrons are redistributed throughout the molecules.

VB theory provides an excellent agreement with observed molecular geometries (bond angles and bond lengths) but physical properies cannot be explained $\Rightarrow$ MO theory.

In discussing chemical bonds it is helpful to visualize the various atomic orbitals qualitatively resembling those of hydrogen:
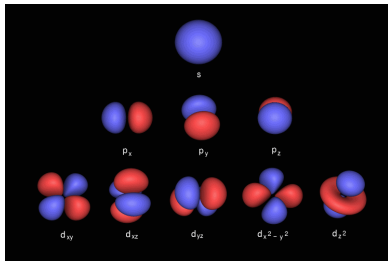
Schrödinger's equation for hydrogen atom:

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\vec{r}) \quad \text{and} \quad \hat{V} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

Solution for $\lim_{r\to\infty} \psi = 0$ is

$$\psi_{n,l,m}(\vec{r}) = R_{nl}(r)P_l^m(cos\theta)e^{im\phi}$$

$$E_n = -\frac{me^4}{2\hbar^2(4\pi\varepsilon_0)^2}\frac{1}{n^2}$$
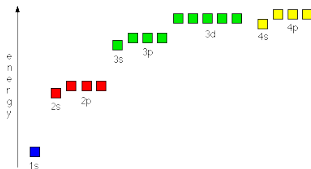
$n = 1, 2, 3, \ldots$ principal quantum number
$l = 0, 1, 2, \ldots n - 1$ orbital quantum number
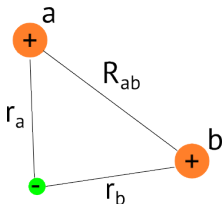$m = -l, \ldots, 0, \ldots, l$ magnetic quantum number

- ▶ Carbon, C - $1s^2 2s^2 2p^2$
- ▶ Nitrogen, N - $1s^2 2s^2 2p^3$
- ▶ Oxygen, O - $1s^2 2s^2 2p^4$
- ▶ Fluorine, F - $1s^2 2s^2 2p^5$
- ▶ Titanium, Ti - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

http://www.docbrown.info/page07/ASA2ptable2a.htm

Electron Configurations in the Perodic Table

by: Sarah Faizi

H_2^+ molecule - the easiest quantum mechanical calculation

For separated cores

$$\hat{H}_a \phi_a(r_a) = (-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a})\phi_a(r_a) = E_a^0 \phi_a(r_a)$$

and similarly for ϕ_b; $E_a^0 = E_b^0 = E^0$.

If the cores come closer electron from the core *a* will be influenced by the core *b*. Additionally, Coulomb repulsive force occurs (shifts energies by constant value up, i. e. omitted for now)

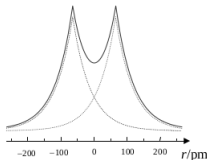$$(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a} - \frac{e^2}{4\pi\varepsilon_0 r_b})\psi = E\psi$$

Solution by **Linear Combination of Atomic Orbitals** (LCAO)

$$\psi = c_1 \phi_a + c_2 \phi_b$$

results in equation

$$(E^0 - E - \frac{e^2}{4\pi\varepsilon_0 r_b})c_1 \phi_a + (E^0 - E - \frac{e^2}{4\pi\varepsilon_0 r_a})c_2 \phi_b = 0$$

that will be multiplied by ϕ_a^* or ϕ_b^* (but ϕ_a, ϕ_b are real - ground state of H)

Wave functions are normalized $\int \phi_{a,b}\phi_{a,b}dV = 1$

Wave functions are not orthogonal $\Rightarrow$ **overlap integral**

$$S \equiv \int \phi_a\phi_b dV$$

Interaction of e^- with separated cores (charge density $-e\phi_a^2$ with core b or $-e\phi_b^2$ with core a)

$$C \equiv \int -e\phi_{a,b}^2 \frac{e^2}{4\pi\varepsilon_0 r_{b,a}} dV$$

Interaction of electron exchanged density $-e\phi_a\phi_b$ with core - **exchange integral**

$$D \equiv \int -e\phi_a\phi_b \frac{e^2}{4\pi\varepsilon_0 r_{a,b}} dV$$
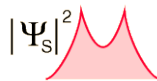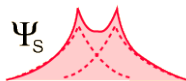
It gives algebraic set of equations

$$(\Delta E + C)c_1 + (\Delta E.S + D)c_2 = 0 \qquad (\Delta E.S + D)c_1 + (\Delta E + C)c_2 = 0$$

which determinant has to be equal to zero $\Rightarrow c \equiv c_2 = \pm c_1$ i.e.

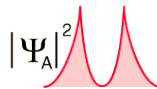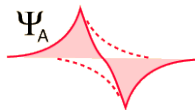**bonding state** (symmetric wave functions) $\psi_S = c(\phi_a + \phi_b)$

$$E_{\text{binding}} = \frac{C + D}{1 + S} + \frac{e^2}{4\pi\varepsilon_0 R_{ab}}$$

antibonding state (antisymmetric wave function) $\psi_A = c(\phi_a - \phi_b)$

$$E_{\text{binding}} = \frac{C - D}{1 - S} + \frac{e^2}{4\pi\varepsilon_0 R_{ab}}$$

Bonding

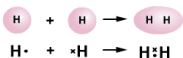Anti-bonding

Valence Bond Theory

Valence bond theory concentrates on direction of bonds given by the overlap of atomic orbitals (s, p) - pairing of unpaired electrons from vallence shell atomic orbitals.

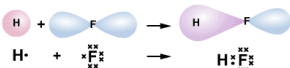In VB we name the bond according to its direction:

- σ bond - cylindrical symmetry, no nodal plane on the internuclear axis.
- π bond - a single nodal plane along the internuclear axis

Sigma bond head on overlap, can form between differently shaped orbitals:

Pi bonds form as a side on overlap when p-orbitals are parallel $\Rightarrow$ overlap in two places, below and above the line connecting the two atoms nuclei.
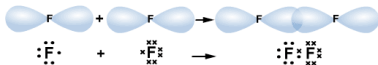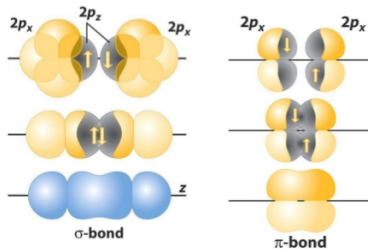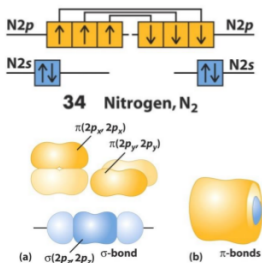
A. *s* orbital + *s* orbital

B. *s* orbital + *p* orbital

C. *p* orbital + *p* orbital ('head-on' overlap)

p orbital + *p* orbital ('side-on' overlap)
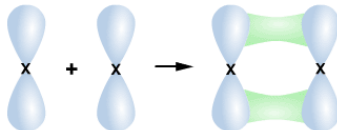
Pi bond only occurs in molecules with **double or triple bonds**:

► the first bond is always a sigma bond

► the second and the third bond are pi bonds.

However, this is oversimplified sketch because so called **hybridization of orbitals** takes place.

Hybrid orbitals - mixtures of atomic (s, p, d) orbitals. Hybrid orbitals do not exist in an isolated atom, even when it is in excited state but arise while the atom is interacting with others to form molecule.

Theory of hybridization is necessary to explain **bonding in CH_4**

- ▶ One 2s electron of carbon atom is **promoted** to higher state, i. e. 2p and
- ▶ 4 equivalent **sp^3 hybrid orbitals** are formed:
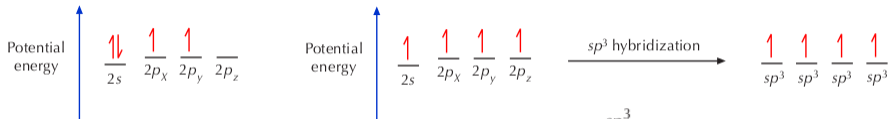
Four sp^3 hybrid orbitals may be considered as combination of 1/4s and 3/4p - tetrahedral bonding directions
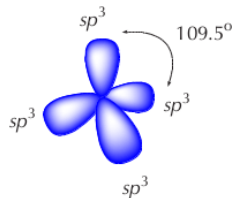
In CH_4, 4 sp^3 hybrid orbitals create 4 σ bonds in combination with 4 hydrogen atoms (1s orbitals)

Two other types of hybrid orbital can occur in C atoms:

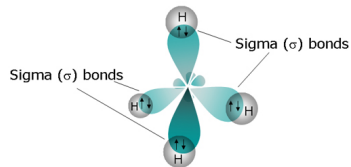- in **sp^2 hybridization**, one valence electron is in pure p state and the other three are in hybrid orbitals
- in **sp hybridization**, two valence electrons are in pure p state and the other two are in hybrid orbitals

Formation of 3 sp^2 hybrid orbitals: combination of 1/3s and 2/3p - trigonal planar bonding directions with angles of $120°$
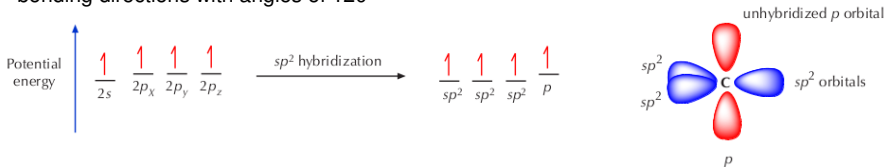
In ethylene, C_2H_4, two C atoms are joint by two bonds, 1 σ bond formed by sp^2 hybrid orbitals and 1 π bond created by p orbitals. Four H atoms create σ bonds with sp^2 hybrid orbitals of C atoms:
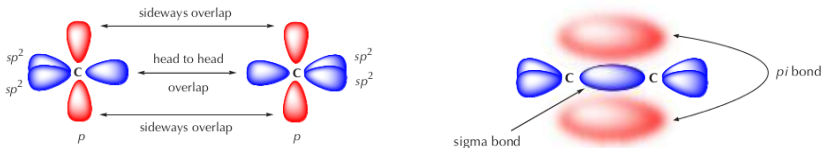
In benzene, C_6H_6, the six C atoms are arranged in a flat hexagonal ring, bond angle $120°$ $\Rightarrow$ sp^2 hybrid orbitals forming the σ bonds between C atoms and hydrogen.
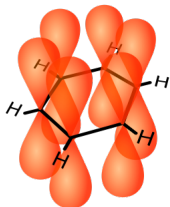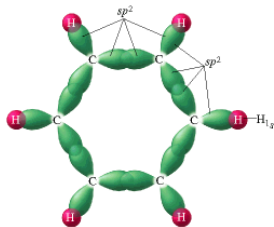
6 p-orbitals   delocalized

In acetylene, C_2H_2, two C atoms are joint by three bonds, 1 σ bond formed by sp^2 hybrid orbitals and 2 π bond created by p orbitals. Two H atoms create σ bonds with sp^2 hybrid orbitals of C atoms:
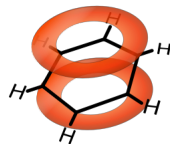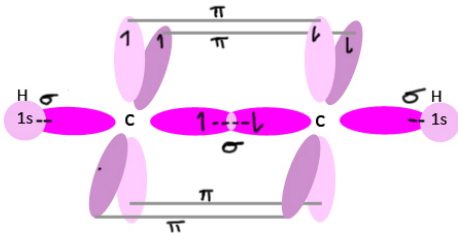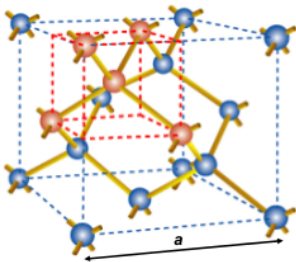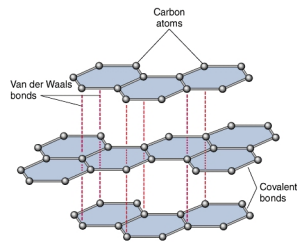
Natural solid carbon materials:

- **diamond**, sp^3 bonded C
- **graphite**, sp^2 bonded C
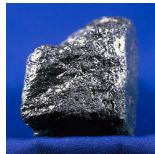
Classification of Carbon Films

Carbon thin films can be

- crystalline or amorphous
- pure, hydrogenated or modified with other elements
- part of (nano)composite structure

Necessity of carbon film classification:

- ternary phase diagram (sp^3C, sp^2C and H) for amorphous films (Jacob and Moller 1993, Robertson 2002)
- classification of a-C:H films into **four cathegories** by Cambridge University group (2005):
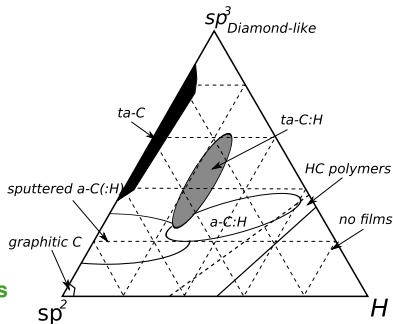
- **polymer-like a-C:H (PLCH)**: high H content (40–60 at. %); up to 70 % sp^3 but most sp^3C are H terminated $\Rightarrow$ soft, low density, optical band gap 2–4 eV
- **diamond-like a-C:H (DLCH)**: intermediate H content (20–40 at. %); lower overall sp^3 content but more C-C sp^3 bonds than PLCH $\Rightarrow$ better mechanical properties, optical gap 1–2 eV.
- **hydrogenated tetrahedral amorphous carbon films (ta-C:H)**: increased C-C sp^3 content whilst keeping a H content low (25–30 at. %) $\Rightarrow$ higher density (up to 2.4 g/cm^3) and Young's modulus (up to 300 GPa)
- **graphite-like a-C:H (GLCH)**: low H content ($<$ 20 at. %); high sp^2 content and sp^2 clustering $\Rightarrow$ gap under 1 eV

C. Casiraghi, A. C. Ferrari, and J. Robertson, Phys. Rev. B 72(8):1–14, 2005.

- classification of carbon films by Fraunhofer Institute for Surface Engineering and Thin Films (IST) 2009
- activities on international standardization, e.g. workshop at 12th International Conference on Plasma Surface Engineering (PSE) in 2010

|	Carbon films												
Designation	1 Plasma-polymer films	2 Amorphous carbon films (diamond-like-carbon films / DLC)							3 Crystalline carbon films				
									Diamond films				Graphite films
Thin film / thick film	Thin film	Thin film							Thin film		Thick film (free standing)		Thin film
Doping, additional elements		hydrogen-free			hydrogenated				undoped	doped	undoped	doped	undoped
			modified				modified						
			with metal				with metal	with non-metal					
Crystal size on the growth side	./.	(amorphous)							1 to 500 nm, nano-crystalline	0.5 to 10 μm, mikro-crystalline	0.1 to 5 μm	(5 μm to) 80 to 500 μm	80 to 500 μm
Predomina-ting C-C-bond type	sp² or sp³, linear bond	sp²	sp³	sp²	sp² or sp³	sp³	sp²	sp²	sp³	sp³	sp³	sp³	sp²
Film No.	1	2.1	2.2	2.3	2.4	2.5	2.6	2.7	3.1	3.2	3.3	3.4	3.5	3.6
Designation	Plasma-polymer film	Hydrogen-free amorphous carbon film	Tetrahedral hydrogen-free amorphous carbon film	Metal-containing hydrogen-free amorphous carbon film	Hydrogenated amorphous carbon film	Tetrahedral hydrogenated amorphous carbon film	Metal-containing hydrogenated amorphous carbon film	Modified hydrogenated amorphous carbon film	nano-crystalline CVD diamond film	micro-crystalline CVD diamond film	doped CVD diamond film	CVD diamond	doped CVD diamond	graphite film
Recom-mended abbreviation	./.	a-C	ta-C	a-C:Me	a-C:H	ta-C:H	a-C:H:Me (Me = W, Ti, ...)	a-C:H:X (X = Si, O, N, F, B, ...)	./.	./.	./.	./.	./.	./.

http://www.ist.fraunhofer.de/english/c-products/tab/complete.html
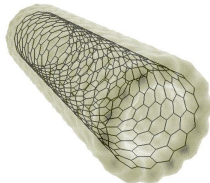
Carbon nanostructured materials - formed by sp^2 C

Fullerene - hollow sphere, ellipsoid *etc.*
Buckyballs - spherical fullerenes.
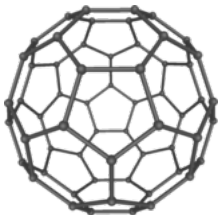
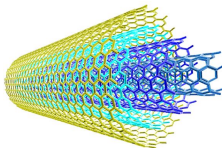C60 - Buckminsterfuleren

prepared in 1985 at Rice University
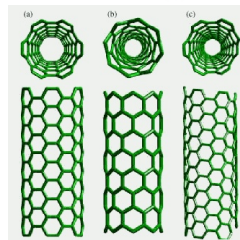
Single-walled carbon nanotube (SWCNT)

Multi-walled carbon nanotube (MWCNT)

- prepared 1991 by Iijima
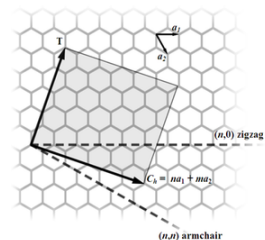
Different chirality of SWNT:

(a) armchair
(b) zigzag
(c) chiral (n,m)

Hybridization in nitrogen

$$\frac{\uparrow\downarrow}{2s} \quad \frac{\uparrow}{2p_x} \quad \frac{\uparrow}{2p_y} \quad \frac{\uparrow}{2p_z} \qquad \xrightarrow{sp^3 \text{ hybridization}} \qquad \frac{\uparrow\downarrow}{sp^3} \quad \frac{\uparrow}{sp^3} \quad \frac{\uparrow}{sp^3} \quad \frac{\uparrow}{sp^3}$$

Nitrogen: 5 valence electrons
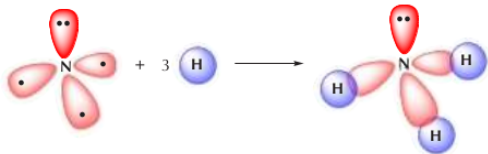
3-D representation of the ammonia molecule

Hybridization in oxygen

$$\frac{\uparrow\downarrow}{2s} \quad \frac{\uparrow\downarrow}{2p_x} \quad \frac{\uparrow}{2p_y} \quad \frac{\uparrow}{2p_z} \qquad \xrightarrow{sp^2 \text{ hybridization}} \qquad \frac{\uparrow\downarrow}{sp2} \quad \frac{\uparrow\downarrow}{sp2} \quad \frac{\uparrow}{sp2} \quad \frac{\uparrow}{p}$$
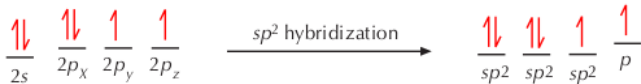
Oxygen: 6 valence electrons
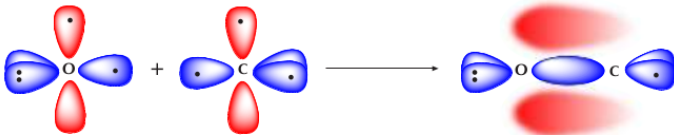
Molecular orbital theory

In **molecular orbital theory**, bonding atoms produce entirely new orbitals. Theory predict energies of bonding and anti-bonding states and shape of orbitals. It depends on

1. energies of orbitals interacting
2. shape/symmetry of orbitals interacting

formation of **bonding** and **anti-bonding** molecular orbitals
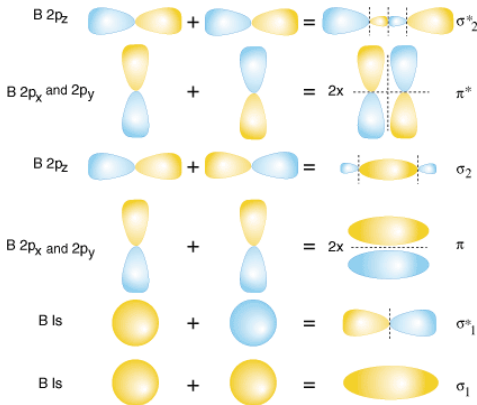
H$_2$ molecule
(homonuclear)
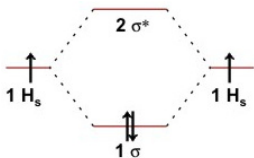
heteronuclear
molecule
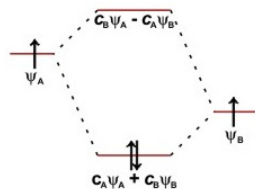
Li$_2$ to N$_2$ molecules
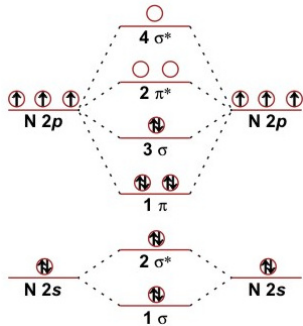
O$_2$ and F$_2$
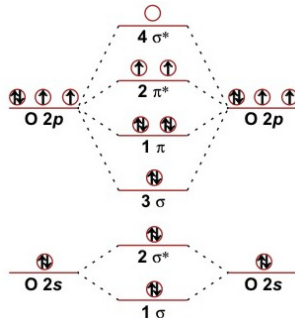
Molecules with more atoms, e. g. CH_4
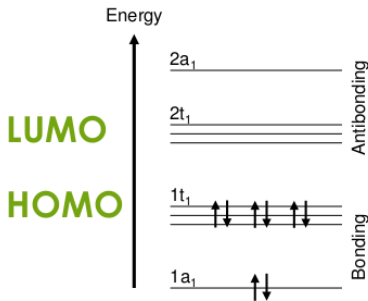
▸ **Highest Occupied Molecular Orbital** (HOMO):
The highest-energy molecular orbital in the energy ground state of a molecule occupied by at least one electron.

▸ **Lowest Unoccupied Molecular Orbital** (LUMO):
The lowest-energy molecular orbital that is unoccupied in the ground state.

H_2 molecule - two 1s electrons with opposite spins (maximum electrons in K shell)
⇒ **saturated covalent bonds**

Li_2 (6 unfilled 2p states with energy similar to 2s): $Li + Li_2 \rightarrow Li_3$ (without violating exclusion principle - all valence electrons remain in L shells)
⇒ **unsaturated covalent bonds**

▶ Li forms bcc crystals (8 nearest neighbors, i. e. each bond = 1/4 of electron instead 2 for covalent bond) - electrons participating in unsaturated bonds are **not localized**.

▶ Cloud of **free electrons** - atoms "lose" outermost, s or p, electrons while the positively charged ions are left over. In transition metals (partially filled d-shells under the outermost shell) further electrons may participate in metallic bonding.
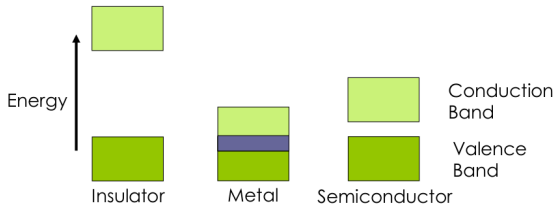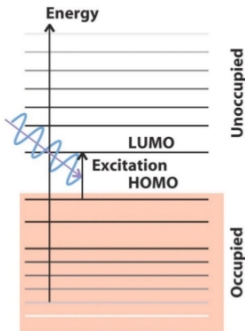
Electrons in metals

Quantum mechanically solved by the **one electron approximation** (precise only if electrons do not interact) and

- ▶ **approximation of free electrons** - can correctly explain many properties of metals, such as specific heat, thermal conductivity, electrical conductance.
- ▶ **approximation of weakly bound electrons** - explain other important phenomena such as the difference between metals, insulators and metalloid, the relationship between conductivity and valence electrons in the metal

System of electrons - **ideal gas of fermions** (max 1 particle in a given state).

distribution function $n(\epsilon)$

$$n(\epsilon)d\epsilon = f_{\mathrm{FD}}\ g(\epsilon)d\epsilon$$

Fermi-Dirac distribution function f_{FD}
(for $T = 0$ step-wise Heavyside function)

$$f_{\mathrm{FD}} = \frac{1}{exp(\frac{\epsilon - \mu}{kT}) + 1}$$
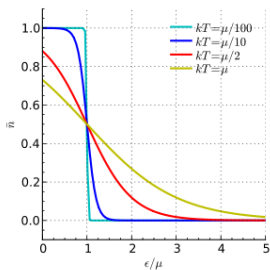
electrochemical potential

$\mu(T)$

Fermi energy

$\epsilon_{\mathrm{F}} = \mu(T = 0)$

energy distribution of states $g(\epsilon)$

$$g(\epsilon)d\epsilon = \frac{4\pi L^3}{h^3}(2m)^{3/2}\epsilon^{1/2}d\epsilon$$

Electrons in metals (contin.)

electrochemical potential is given by the normalization condition (*N* electrons)

For highly degenerated gas (low *T*) its temperature dependence can be approximated as

$$N = \int\limits_0^\infty f_{\mathrm{FD}} \; g(\epsilon) d\epsilon$$

$$\mu = \epsilon_{\mathrm{F}} \left(1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_{\mathrm{F}}} \right)^2 \ldots \right),$$

The solution for Schrödinger equation in electric field for periodic ionic crystals shows the existence of a separate area of the energy bands - forbidden band (**band gap**).

The position of **Fermi level (electrochemical potential)** with respect to band gap is important for behaviour of materials.

Property	Ionic	Covalent	Metallic	Van der Waals
	Non-directional; Structures of high coordination	Direcional; Structures of low coordination and low density	Non-directional; Structures of high coordination and high density	Analogous to metallic bonds
Mechanical	Strong, hard crystals	Strong, hard crystals	Variable crystals	Weak, soft crystals
Thermal	High melting point, low expansion coefficient	High melting point, low expansion coefficient	Range of melting points extended liquidus range	Low melting point large expansion coefficient
Electrical	Weak insulator, conduction by ion transport when liquid	Insulator in solid and liquid state	Conduction by electron transport	Insulator
Optical	Absorption and other properties mainly of the individual ions	High refractive index, absorption different in solid and gas	Opaque, with similar properties in liquid state	Properties of individual molecules

Classification of materials based on **nature** and **applications** by Bever (1986):

- ▶ by nature: ceramics, glasses, metals and alloys, other inorganic materials, polymers, elastomers, fibres, composite materials, wood, paper and paperboard, other biological materials
- ▶ by application: electrical materials, electronic materials, superconductors, magnetic materials, materials for nuclear applications, materials for other energetic applications, optical materials, biomaterials, building materials, materials for textile and packaging industry (*modified*)

M. B. Bever (ed.): Encyclopedia of Materials, Science and Engineering, 1986, sv. 1 ed. R. W. Cahn (Oxford: Pergamon)

other references - **material science conferences**

- ▶ Spring and Fall Meetings of Material Research Society (MRS) in U.S.
- ▶ Spring and Fall Meeting of European Material Research Society (EMRS)
- ▶ TechCon of Society of Vacuum Coaters (SVC)

Ceramic Materials

- A combination of **one or more metals** with a **non-metallic element** (usually oxygen but others include nitrogen, carbon . . .).
- May be crystalline or partially crystalline.
- The atoms are linked by ionic/covalent bonds - ionic bond character occurs especially for oxygen that effectively borrows two electrons from the neighbouring metal atoms

Types of ceramics

- traditional ceramic materials: natural stone, clay minerals such as kaolinite
- modern ceramic materials, classified as advanced ceramics: aluminium oxide (alumina), silicon carbide, tungsten carbide, . . .
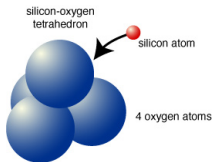

Ceramic Si_3N_4 bearing parts
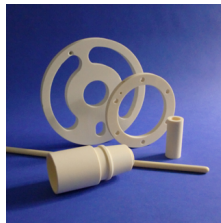
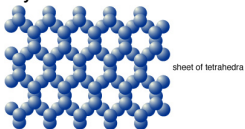
Fine ceramic components from alumina

Ceramic Materials (contin.)

Physical and mechanical properties are controlled by the crystal structure and chemical composition. It can be demonstrated for SiO_2

silicon-oxygen tetrahedron
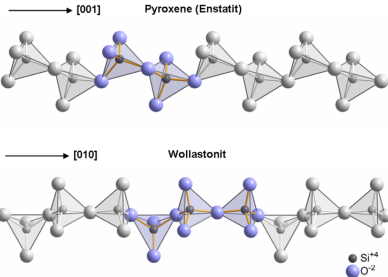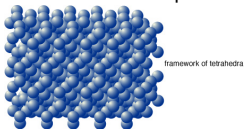
silicon atom

4 oxygen atoms

single chain of tetrahedra

fibrous asbestos

layered minerals as mica

sheet of tetrahedra

3D structure of quartz

framework of tetrahedra

[001]   Pyroxene (Enstatit)

[010]   Wollastonit

Si^{+4}
O^{-2}

Ceramic Materials (contin.)

Ceramic materials

- ▶ are brittle, hard, strong in compression, weak in shearing and tension.
- ▶ withstand, in many cases, erosion that occurs in an acidic or basic environment.
- ▶ withstand very high temperatures such as temperatures that range from 1000 °C to 1600 °C, exceptions include inorganic materials that do not have oxygen such as silicon carbide.

Crystal lattice imperfections (vacancies, dislocations) and **microstructural defects** (inclusions, pores, voids and distribution of irregular size grain) influence the properties

- ▶ mechanical failure occurs from pre-existing flaws - high mechanical stresses which exceed the local tensile strength effect crack propagation from flaws followed by rupture
- ▶ deffect is weak point for electrical load and aggressive environment

Glasses

▶ Class of materials that does not crystallise when cooled from the molten state, no long range periodicity

▶ The major constituents of glasses are in two separated regions of the periodic table

    ▶ Group VI (O, Si, Se and Te) plus some neighbouring elements (B) and

    ▶ Groups I and II that are used primarily as fluxes. The addition of fluxing atoms such as sodium reduces the number of bond cross links.
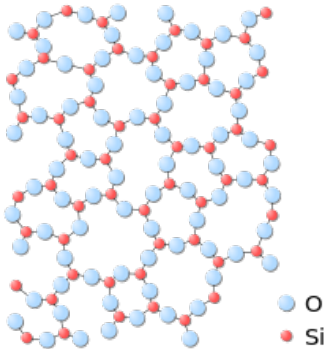
The structure of soda-lime-silica float glass

| O |
| Si |

| Calcium | Sodium | Oxygen | Silicon |
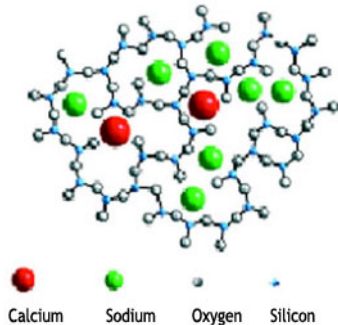
Metals and Alloys

Properties of metal and alloys are a consequence of the metallic bonds. They

- have good mechanical strength, high thermal and electrical conductivity,
- are opaque, lustrous and relatively heavy,
- are easily fabricated and shaped.

In general, they form one of the face centred cubic (fcc), body centred cubic (bcc) or hexagonal close packed (hcp) structures.

Changes in the strength of metallic bond cause differences in optical, electrical, thermal and mechanical properties.

The overall mechanical properties of metals and alloys are controlled by the crystal lattice defects, such as dislocations and vacancies. Mechanical and chemical properties can be modified by the addition of alloying elements in varying proportion.

Polymers

Polymers are by definition materials composed of long-chain molecules, typically 10 to 20 nm, that have been developed as a consequence of the linking of many smaller molecules, monomers.
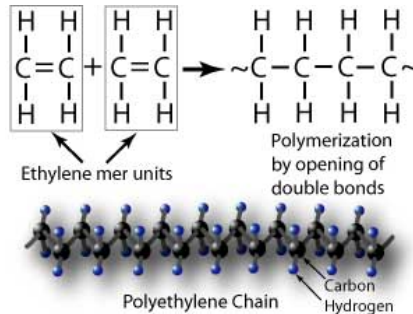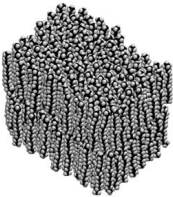

The combination of tensile strength and flexibility make these materials attractive.

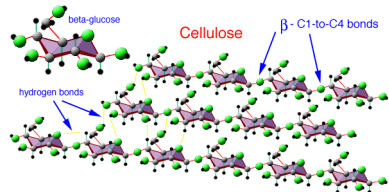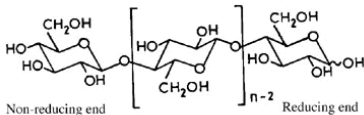

⇒ **polymer cross-linking**

Polymers (contin.)

If the molecular chains are packed side by side, the molecules form an array with a **crystalline structure**.

Natural polymers have complex microstructure comprising a mixture of crystalline and amorphous material.

The interatomic bonds between molecular chains are the weak van der Waals forces, but in the crystalline structures, the chains are closer ⇒ more rigid material.

To develop stronger, more rigid, polymers:

1. production of a crystalline structure (polyethylene, nylon),
2. formation of a strong covalent bond between the molecular chains by cross linking (vulcanising raw rubber by heating with the controlled addition of sulphur atoms).
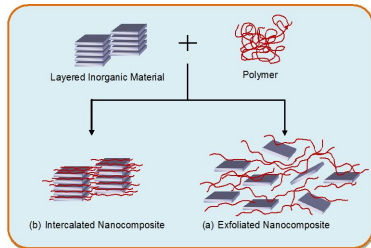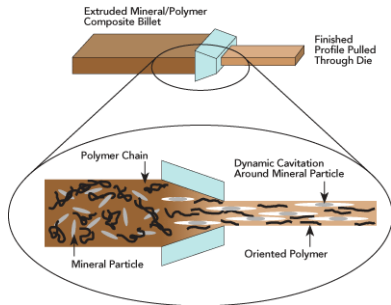
Composites

A composite material

- ▶ was originally considered to be a combination of two materials
- ▶ now it is regarded as any combination of various materials or their polymorphs.

Composites have particular physical, mechanical and other properties that are not found in their constituents:

- ▶ natural composites: wood - cellulose fibres provide tensile strength and flexibility and lignin provides the matrix for binding and adds the property of stiffness; bone - strong, but soft, protein collagen and the hard, brittle mineral apatite,
- ▶ synthetic composites: combining individual properties such as strong fibres of a material (for example carbon) in a soft matrix (such as an epoxy resin).
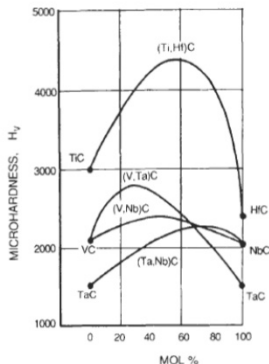
The concept of composite materials has led to the design and manufacture of a new range of structural materials that are generally lighter, stiffer and stronger than anything previously manufactured.
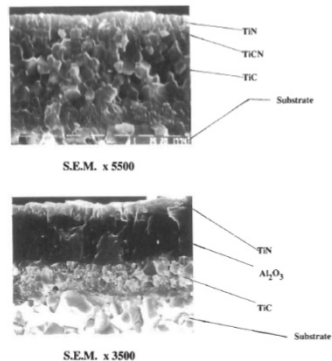
Composites (contin.)

Composites (contin.)

Alloys can have properties superior to each component

Figure 12-5. Microhardness of mixed carbides due to solid solution and precipitation hardening (From Ref. 3).

M. Ohring, The Materials Science of Thin Films

Multilayer structures can combine properties of different compounds

Figure 12-6. SEM images of CVD multilayer coatings for cutting tool inserts. (a) Carbide substrate/TiC/TiCN/TiN (5500 ×). (b) Carbide substrate–TiC–Al$_2$O$_3$–TiN (3500 ×). (Courtesy of S. Wertheimer, ISCAR Ltd.)

Composites (contin.)

- ▶ improves CNTs dispersion in matrix $\implies$ shorter preparation time, better uniformity
- ▶ strengthens fiber-matrix interface $\implies$ high composite stiffness and strength together with high toughness (thanks to nanotubes flexibility)
- ▶ adds additional functional groups $\implies$ sensors
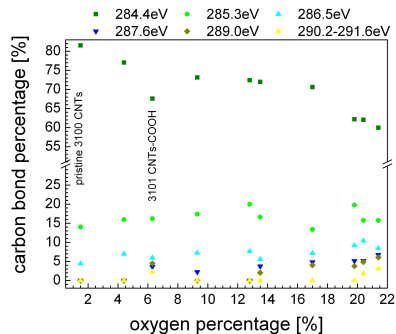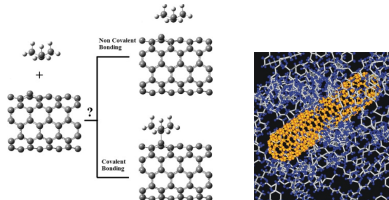
Changes of carbon bonding (by XPS) after plasma funct. in low pressure RF discharges

$\implies$ **significantly improved hardness and elastic modulus of polyurethane/CNTs composites** for optimum plasma conditions (Ar/H_2O, O_2/C_2H_6O)

L. Zajíčková et al. Plasma Process. Polym. 6 (2009) S864–S869
L. Zajíčková et al. Thin Solid Films 538 (2013) 7-15