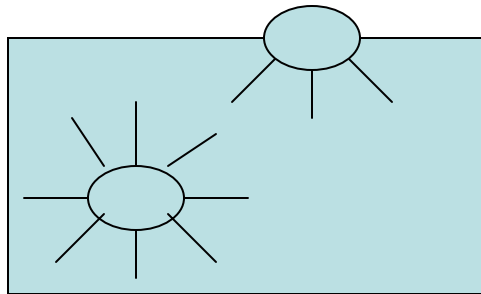# Chem 728
Introduction to Solid Surfaces

•**Solids**: hard; fracture; not compressible; molecules close to each other.
•**Liquids**: molecules mobile, but quite close to each other.
•**Gases**: molecules very mobile; compressible.

Properties of a Surface Differ from the bulk because of in equivalency of bonding.

Properties affected by surface:

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  • *Liquid-gas*: vapor pressure; surface tension, electric double layer
  • *Liquid- solid*: capillarity, liquid adsorption
  • *Solid-solid*: phase equilibria, mixing.
  • *Solid-gas*: monolayer adsorption; chemisorption; physisorption; geometry of adsorbed layer.

Interface Importance

- *Corrosion*: occurs when adsorbing molecule adsorbed by the solid to form an oxidized layer; passivation layer reduces rate of this.
- *Adhesion*: Interfacial reactions make it possible for two substances to form strong bonds so that they won't fall apart (airplane composites, deposition of layered structures to make computer chipes).
- Catalysis: Interaction of metals/ metal oxides with an adsorbate increases rate of reaction (e.g. catalytic converters).
- *Wear processes*: Placement of a molecule on the surface of two solids, which move against each other can reduce the friction.

Crystallography

Solids form crystals and amorphous structures:

- Amorphous material – no order; (glass, butter)
- Crystalline material – molecules or atoms in a solid distributed in a regular array (salt, sugar).
- Diffraction used to determine properties of an ordered (crystalline) structure.
- Crystallography – study of crystalline materials.
- X – ray directed at a surface can be either
  - Absorbed: X-ray photoelectron spectroscopy
  - Reflected: X-ray crystallography;
- Reflected X-rays come off at angles related to the spacing between atoms.
- X-rays travel different distances to exit out of the sample at the same angle.
- Constructive interference occurs, when waves are in phase.

Destructive Interference

Intensity vs Angle chart showing Series 1, Series 2, Series 3.

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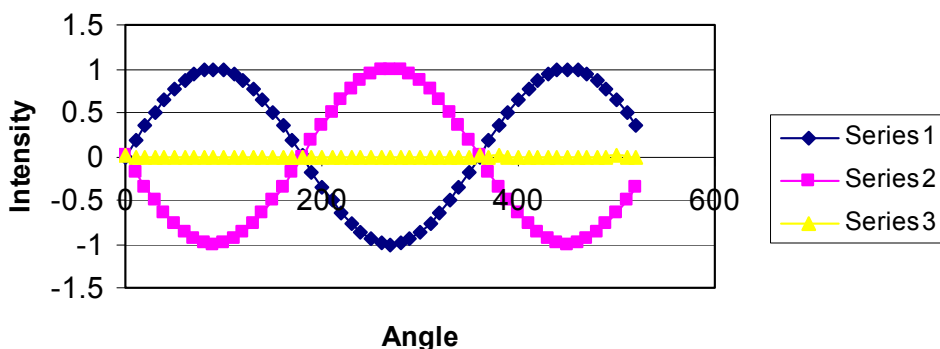
Bragg Equation

- Second layer must travel an additional distance of AP + PC to make it out of the crystal.
- This distance must equal a multiple of the wavelength, λ.

$$AP + PC = n\,\lambda$$
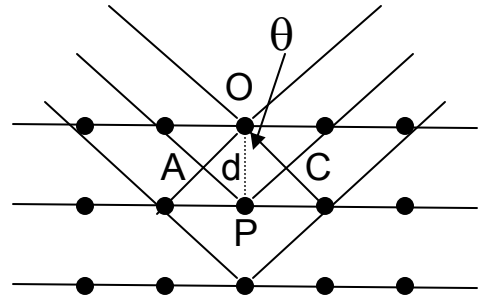
But $d \sin\theta = AP = PC$
So that: $n\,\lambda = 2d \sin\theta$

- Instrumentation
  - <u>X-ray Tube</u>: Rapid deceleration of energetic electrons at a metal surface produces x-rays. Only about 1% of power converted to useful photons. Characteristic and Bremstrahlung produced. Typical metals (W, Cu, Mo, Rh, Ag, Fe, Co).
  - <u>Filters</u>: Cutoff filters (e.g. Al, Be) removes most of Bremstrahlung radiation.
  - Monochromators: use a crystal to diffract radiation of desired wavelength.

Symmetry

- Degree of Symmetry determines the three dimensional shape of the solid.
- *Rotation* can produce equivalent structure:
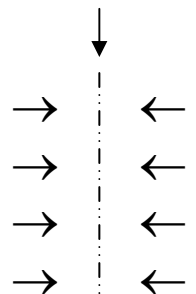 - Sphere: infinite number of rational directions.
  - Two dimensional structures:

| C_∞ | C_4 | C_3 | C_2 | C_1 |
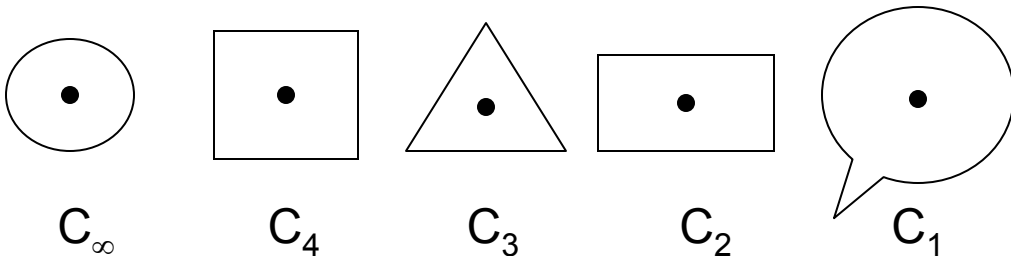
- H_2O has 2 fold axis of symmetry, C_2
- NH_3 has 3 fold axis, C_3
- Cube: has 3 C_4 axes; 4 C_3, and 6 C_2

•<u>Other symmetry operations</u>
- *Reflection* through a mirror plane:
  - H_2O has mirror plane perpendicular to the hydrogens and another going through them.
 - NH_3 has three mirror planes through one H and between other two.
- *Inversion* through a center of symmetry to an equal distance on the other side leads to an identical structure. Eg. Cube, benzene; sphere; not H_2O, NH_3 or tetrahedral structure.

Mirror plane

$\rightarrow \quad \leftarrow$
$\rightarrow \quad \leftarrow$
$\rightarrow \quad \leftarrow$
$\rightarrow \quad \leftarrow$

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Symmetry(cont.)

- *Rotatory-reflection*: S_n, a combination of rotation and reflection to produce an indistinguishable structure. E.g. Ch_4 has an S_4 plane of symmetry.

- *Translation*: same structure produced at another place by simple linear movement; such as in a crystal lattice.
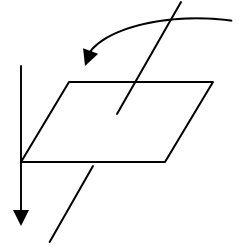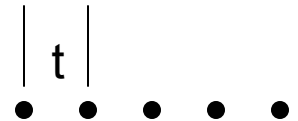
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Lattices

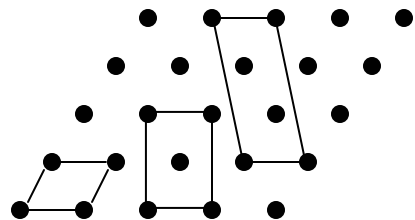Symmetrical array of structurless points. Usually, visualized as a three dimensional array of ions, atoms or molecules.

•Simplest lattice: row of equally spaced dots separated by a translation vector, t.

•Two dimensional lattice-planar array: all points reached by translations in two dimensions with t_1, t_2.

- •P = primitive

- •DP =doubly primitive

- •TP = triply primitive

Bravais Lattices
(Space lattices)

- 14 known lattice structures describe most of the known structures. Symmetry of the lattice is reduced when dealing with more than one element.

- Lattice is described in terms of a, b, c (translation vectors) and α, β, γ which are the angles between atoms.

- Symmetry elements for main structures:

Cubic	4 axes of three fold symmetry
Tetragonal	1 axis of four fold symmetry.
Trigonal and Hexagonl	Single axis of 3 fold or 6 fold symmetry
Orthorhombic	3 mutually perpendicular 2 fold axes
Monoclinic	One 2 fold axis
Triclinic	No axis of symmetry

- *Miller Indices*: Planes of lattice points form arrays that cause diffraction; we use Miller indices to describe the planes.

- Consider two dimensional array of points. A line pq is defined by the coordinates: At_1 and Bt_2.

Miller Indices

- Three dimensional array: a plane can be defined in terms of where it intersects the axes.
- Intersection on each of axes given by the coordinates: At_1, Bt_2, Ct_3.
- A line parallel to the x-direction would be: ∞t_1, Bt_2
- Usually, it is more convenient to describe coordinates in terms of the inverse of the number in front of the translation vector. I.e. the above would become: (0, 1/B).
- Similar treatment of three dimensional structures leads to: (110), 112), (111), (200), (0$\bar{1}$0),
- Bar over number indicates number is in the negative direction.
- Some of the possible planes are equivalent. E.g.

$$(\bar{1}00), (100), (001), (010), (0\,\bar{1}\,0), (00\,\bar{1})$$

Crystalline Structure of Metals

- 70 Elements are metallic; others become metallic with moderate amounts of pressure.

- Metals have silvery sheen; high electrical and thermal conductivity.

- These properties are due to the presence a band of low energy antibonding orbitals. Electrons can be easily promoted to one of the antibonding orbitals and then can move to an orbital of similar energy on a neighboring metal atom.

- Bonding not directional indicating that the metal atoms develop a highly symmetric structure.

- Most metals form: BCC, FCC, or HCP structure.

- Ions and atoms having no tendency toward covalent bonding have no preferred direction of bonding.

- Greatest stability achieved by maximizing co-ordination number.

Body Centered Cubic Structure

- Three forms of cubic structure: Primitive (simple), Body centered cubic (BCC) and Face centered cubic (FCC).
- Po only one in primitive structure.
- Most refractory metals have BCC, when close to melting pt.
- Unit cell has one atom in center of cube in the unit cell and atoms at each of the corners of the cube.

$$r = a_O \sqrt{3} / 4$$

- The distance to the nearest neighbor is $r = a_O \sqrt{3} / 2$
- The extended lattice is constructed by "squeezing" several cells together.
- Each atom has eight nearest neighbors and 6 others at a distance of a_o.
- Two neighbors differ by a distance of only 13%.
- Small atoms such as C, O, N, H often occupy interstitial positions between lattice atoms. E.g. carbon migrates in steel to an interstitial position.
  - <u>Tetrehedral site</u> = position between center atom in two cubes as well as two atoms in the corners of the shared edge. Coordinates: ½, 0, ¾ and ½, 0, ¼
  - Octohedral site = interstitial atom in the center of a face (as in FCC). Two center atoms and atoms at face make up the atoms of the cube. Coordinates: ½, ½ ,1

Closest Packed Structures

- Structure resulting from the maximum packing density possible for the atoms in the crystal.
- Formed from the stacking of two dimensional layers.
- Stacking determines if it is hexagonal closest packed or face centered cubic.
- HCP: stacking order is ABAB
- FCC: stacking order is ABCABCABC…
- Similarities in structure sometimes gives a mix of two: ABABABCABCABAB.
- Face Centered Cubic:
    - Nearest neighbor (from diagonal of face is a distance of $d = a_o \sqrt{2}/2$
    - Coordination number of 12
    - 6 next nearest neighbors at a distance of a_o.
    - Interstitial cavity at the center of the cube (½, ½, ½); octahedral; max radius of atom = 0.41r.
    - Interstitial cavity with eight tetrahedral sites at (¼, ¼, ¼).