Mankind has studied surface and interface phenomena since antiquity.

- In old Babylon a form of divination, called lecanomancy, involved an examination of the properties of oil poured into a boul of water.
- Pliny noticed that choppy waves could be calmed by pouring oil into the sea.

In the 18th century the humanist Benjamin Franklin noticed that “a tea spoon full of oil is sufficient to make a space of perhaps half an acre as smooth as a looking-glass”. Unfortunately he did not perform the simple calculation that would have told him that the film thickness was of the order of the nanometer!

→ first observation of ultrathin films
In July 1823 Wolfgang Doeberiner reported to his minister, J.W. Goethe, “that finely divided platinum powder causes hydrogen gas to react with oxygen gas by mere contact to water whereby the platinum itself was not altered”. → birth of surface chemistry

This phenomenon was further investigated some 10 years later by Michael Faraday and finally by Jöns Jacob Berzelius who coined the term *Catalysis* (from Greek “wholly loosening”)
The term catalysis remained heavily debated for the rest of the century until Wilhelm Ostwald proposed a definition in term of the concept of chemical kinetics: “a catalyst is a substance which affects the rate of a reaction without being part of its end products“
World population and ammonia production

\[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3 \]

Haber & LeRossignol, 1909

Fritz Haber
1868 - 1934
Nobel Prize 1918

Carl Bosch
1874 - 1940
Nobel Prize 1931
Main advancements:

discovery of photoemission by Albert Einstein Nobel Prize in 1921

Electron Diffraction: Davisson and Germer firstly observed a surface structure by electron diffraction Nobel Prize in physics in 1937
Surface Science

Surface Science becomes a discipline with a pivotal paper of Irving Langmuir of 1922

“Most finely divided catalysts must have structures of great complexity. In order to simplify our theoretical consideration of reactions at surfaces, let us confine our attention to reactions on plane surfaces. If the principles in this case are well understood, it should then be possible to extend the theory to the case of porous bodies. In general, we should look upon the surface as consisting of a checkerboard ...”


Irving Langmuir
1881 – 1957
Nobel Prize 1932
Surface Science

Despite progress, surfaces remained tough to handle

The surfaces of bodies are the field of very powerful forces of whose action we know little

(Lord Rayleigh)

The surface was invented by the Devil

(Wolfgang Pauli)

... until surface cleanliness could be controlled thanks to the development of ultra high vacuum
Ultra High Vacuum allowed to finally investigate reproducibly well defined surfaces

From the kinetic theory of gases, the flux $F$ of molecules striking the surface of unit area at a given pressure $P$ is

$$F = \frac{N_A P}{\sqrt{2\pi MRT}}$$

$$F(\text{atoms/cm}^2/\text{sec}) = 3.51 \times 10^{22} \frac{P(\text{Torr})}{\sqrt{M(\text{g/mole})T(K)}}$$

If $P = 3 \times 10^{-6}$ Torr, $M = 28$ g/mole (say, CO), $T = 300$K, we obtain $10^{15}$ molecules/cm$^2$/s.

If each incident molecule sticks on the surface (or sticking coefficient is unity), then the surface is covered with one monolayer of molecules.

If we achieve UHV ($1.0 \times 10^{-10}$ Torr), it may take three hours before a surface is covered completely.
Towards the Transistor

Surface states are studied in the 1930s by Igor Tamm and by William Shockley.

This knowledge allowed J. Bardeen and Walter H. Brattain to construct the point contact transistor prompting the interest towards semiconductor surfaces (Nobel Prize in Physics 1956).
Towards understanding nanoscience

Heinrich Rohrer and Gert Binning develop the STM (Nobel Prize in Physics 1986): Surface states can now be directly imaged

Scattering of Surface State Electrons at Large Organic Molecules

Leo Gross, Francesca Moresco, Letizia Savio, André Gourdon, Christian Joachim, and Karl-Heinz Rieder
Breakthroughs in understanding surface chemistry

Kai Siegbahn discovers ESCA (Electron Spectroscopy for Chemical Analysis or XPS)
Nobel Prize in Chemistry 1981

John Polanji studies the dynamics of chemical reactions (Nobel Prize in Chemistry in 1986)

Walter Kohn goes beyond the Thomas Fermi approximation for the theoretical description of the electronic ground state developing the Density Functional Theory approach (Nobel Prize in Chemistry 1998)
Towards knowledge based design of catalysts

At the surface the coordination of the atoms as well as the dimensionality of the system are different than in the bulk. This implies different physical as well chemical properties. This information allows for a knowledge based optimisation of electronic devices (by controlling crystal growth and electronic properties) and for the design of efficient and selective of catalysts working in the heterogeneous phase.

Nobel Prize in Chemistry of 2007 awarded to Gerhard Ertl for his contribution to the understanding of catalysis.

Prof. Ertl will be in Genoa on Nov. 3rd 2010. Talks at DIFI at 16.00 and in Palazzo Ducale Salone del Maggior Consiglio at 18.30
Application of Surface Science

Catalysis
Microelectronic semiconductor
Tribology
Electrochemistry
Renewable energy conversion
Corrosion
Environmental chemistry
Biointerface
Outline of the Course

1. Introduction
2. Surface Thermodynamics and crystal shape
3. Crystallographic and electronic structure of Surfaces
4. Electronic excitations and Surface Plasmons
5. Surface Magnetism
6. Vibrational excitations and Surface Phonons
7. Growth phenomena

8. Adsorption and chemical reactions (Catalysis Course)
9. Surface Analytical Techniques (Cat Course)
1. Introduction

2. Surface Thermodynamics and crystal shape
   2.1 Surface tension
   2.2 Gibbs Duhem and adsorption equations
   2.3 Wulff construction and crystal shape
   2.4 Roughening transition

3. Structure of surfaces
   3.1 Crystal planes and surface modifications
      3.1.1 Relaxation
      3.1.2 Reconstruction
      3.1.3 Defects at surfaces and stepped surfaces
      3.1.4 Adsorbates and Overlayer structures
      3.1. Surfaces in an electrochemical environment
   3.2 Surface electronic structure
      3.2.1 The free electron and the jellium model
      3.2.2 Work function
      3.2.3 Electron Affinity and Ionization Potential
      3.2.4 Surface electronic states
      3.2.5 Quantum size effects
Outline

4. Surface electronic excitations
   4.1 Screening of electromagnetic fields
   4.2 Surface plasmons
   4.3 Acoustic surface plasmons
5. Surface Magnetism
   5.1 magnetic anisotropy in thin films
   5.2 domain walls at surfaces and thin films
   5.3 giant magnetoresistance
   5.4 surface magnons
6. Surface phonons
   6.1 Volume, surface and adsorbate modes
   6.2 Anharmonicity
   6.3 Phonon softening and surface relaxation
   6.4 Electron-phonon interaction and the Kohn anomaly
Parallel Course on Catalysis: outline

7. Adsorption and chemical reactions
   7.1 How do molecules bond to surfaces?
      7.1.1 Physisorption
      7.1.2 Chemisorption
   7.2 Dynamics of adsorption
      7.2.1 Sticking coefficient
      7.2.2 Effect of internal degrees of freedom of incoming molecules
   7.3 Adsorption isotherms
      7.3.1 Langmuir adsorption isotherm
      7.3.2 BET adsorption isotherm
   7.4 The desorption process
   7.5 Adsorbate diffusion
   7.6 Simple chemical reactions: ammoniac synthesis, three way automotive catalyst, ethene epoxidation

8. Surface Analytical Techniques
Definition of a Surface and Surface Science

We live in the physical world. We all know about three-dimensional objects. They have insides and outsides. We know what is part of an object and what is not part of an object. The surface is the boundary between a given object and what is outside of it. The mathematical definition of surface is the locus of points in space that are that boundary. Of course, mathematical points have no physical size; and a mathematical surface has no thickness.

It turns out that physics in the two dimensional realm of surfaces can be very different than that well-known to us in three dimensions. Within the solid, the atoms are constrained by neighbouring bonds, but at the surface, the atoms are not constrained in the same manner. They are said to be relaxed. Any dangling bonds of the surface atoms are then available for chemical reactions with other entities outside the crystalline solid. This forms the basis for the branch of chemistry known as surface chemistry.
Types of interfaces

Surface Chemistry and Catalysis
G. A. Somorjai (1994)
What is Surface?
- surface versus bulk
Surface property versus bulk property

Surface property:
- Adsorption, catalysis, oxidation
- Friction, adhesion, lubrication

Bulk property:
- Electrical conductance,
- Thermal conductance,
- Melting temperature,
- Heat capacity,
- Modulus, hardness
Types of surfaces

External Surfaces
Single Crystal Surfaces

Internal Surfaces

Nanoparticle Surfaces

Zeolite (Silicalite)
- Pore size < 2 nm
- Pores are ordered with interconnections

Nanoparticles in Mesoporous Silica (SBA-15)
- Pores of 2 – 50 nm with narrow size distribution
- Pores are ordered

Transmission Electron Microscopy image of Platinum Nanoparticle Synthesized by Wet Chemistry
Size: 7.2 nm
The role of surface is more important as the size of object gets small

\[
D \text{ (dispersion)} = \frac{\text{Number of surface atoms}}{\text{Total number of atoms}}
\]

Surface Chemistry and Catalysis
G. A. Somorjai (1994)
Dependence of shape of particles on dispersion

- cube
- Truncated cube

Graph showing the number of surface atoms (×10^6) against the number of total atoms (×10^6).
External Surfaces-Thin film technology

Rh monolayer is used for catalysis such as NO/CO

Diamond coating

Magnetic disk – lubricant layer
External Surfaces
-Miniaturization of microelectronic devices
External Surfaces
-Biointerfaces

Figure 1-4 The intricate folds of the human brain expose the large interface area of this remarkable organ. The brain may be viewed as a device with enormous solid-liquid interface area.
Bonding nature of peptide revealed with SFG (Sum Frequency Generation) Vibration Spectroscopy

(a) Hydrophobic side
(b) 1.4 nm
2.1 nm

L = Leucine
K = Lysine

Ac(LKLLKLLKLLKLLKL)NH₂

- C-H ν
- O-H ν

SFG Intensity (a.u.)
Wavenumber (cm⁻¹)

- N-H ν₅

SFG Intensity (a.u.)
Wavenumber (cm⁻¹)

Deuterated Polystyrene
Fused Silica
nanoparticle systems – Two or three dimensional systems

(a) TEM image of two-dimensional (2D) TTAB coated platinum nanoparticle arrays and (b) TEM image of three-dimensional (3D) platinum nanoparticle encapsulated in mesoporous silica (SBA-15).
nanoparticle systems – surface characterization

AFM image of amine Capped PtNP (10nm)

SEM image of thiol Capped PtNP (10nm)

XPS spectrum of PVP capped PtNP

- O1s
- Pt 4d₃/₂
- Pt 4d₅/₂
- N1s
- C1s
- Pt 4f₅/₂
- Pt 4f₇/₂
- Si2p
- Si2s
nanoparticle systems – 3D characterization – TEM and XRD

TEM image of Pt-Rh Nanoparticles

XRD patterns of PtRh nanoparticles

Rh_{0.2}Pt_{0.8}  
Rh_{0.4}Pt_{0.6}  
Rh_{0.6}Pt_{0.4}  
Rh
Bridging Materials Gap

Metal single crystal surface

SEM images of Pt nanowires fabricated with lithography

SEM images of nanoparticle monolayer on silicon substrate

TEM images of colloid nanoparticles in mesoporous oxide support

Commercial catalyst
Evolution of Model Catalyst Systems

Pt single crystal surface

- Colloid synthesis
- Lithography

Nanoparticle array (>25nm, ordered)
3D nanoparticle array
Nanowire array

Semiconductor (TiO$_2$, GaN)

Metal-oxide Catalytic nanodiode
# Surface science techniques

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