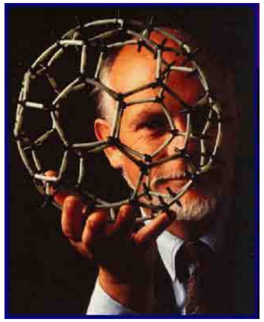
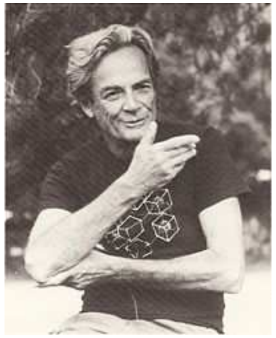
www.mscnano.eu

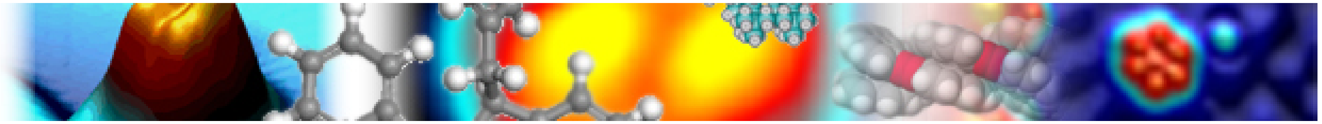




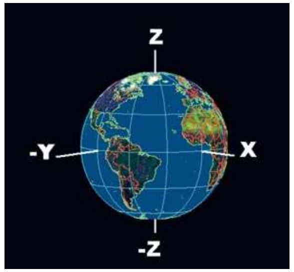
Nanoscience: A historical perspective

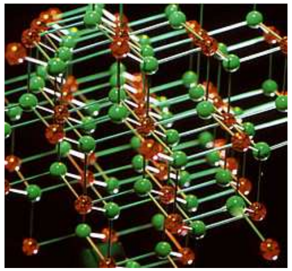
R. Díez Muiño and P. M. Echenique

Lecture Notes
Fall 2007

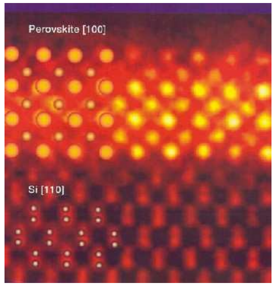


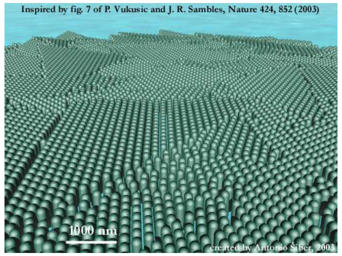
Nanoscience and reduced dimensionality



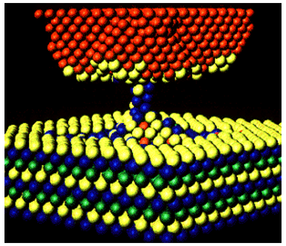


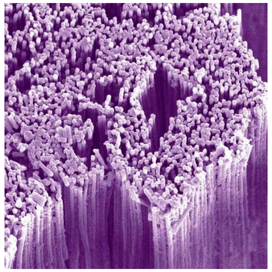
ours is a three-dimensional (3D) world



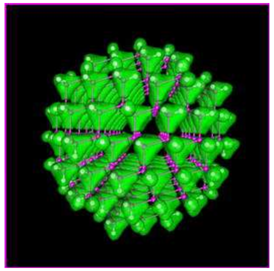


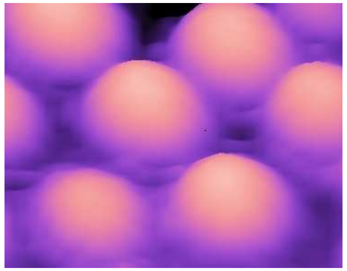
thin films and surfaces can be 2D





nanowires are, in practice, 1D



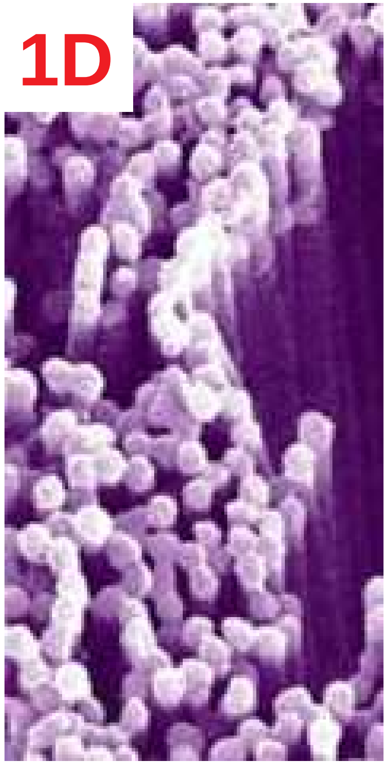


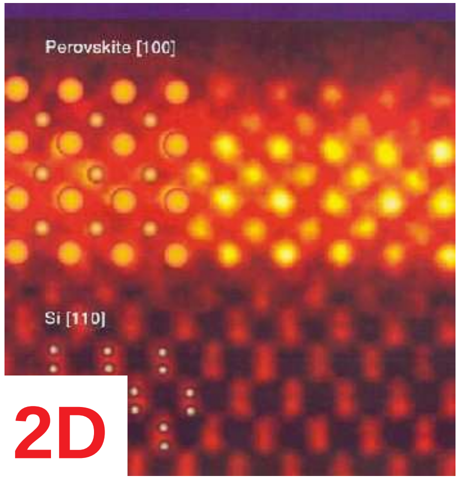
nanoscience reduces dimensionality
to objects that can be considered 0D

Nanoscience: from 3D à 0D CONFINEMENT!!

~nm

1D

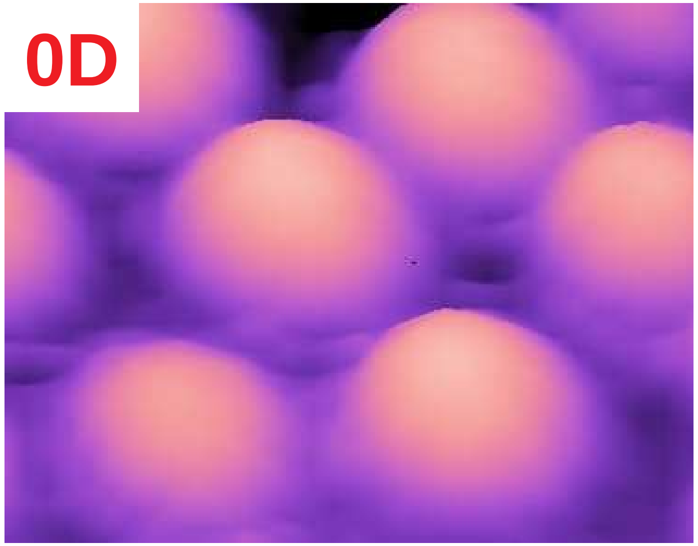




2D

~nm

0D



~nm

four reasons to study surfaces in a ‘nanoscience’ course:

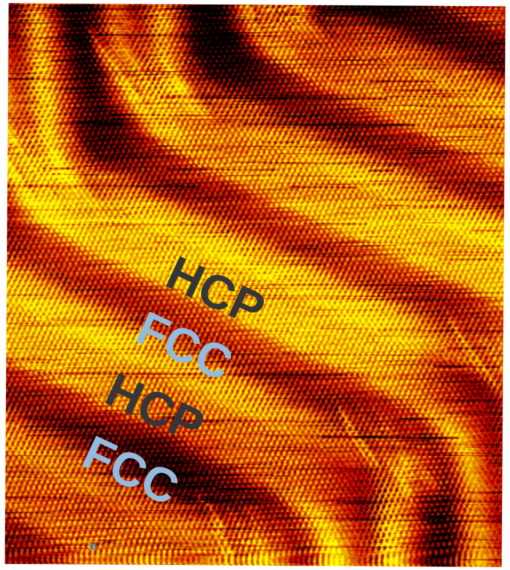
- because they can be nanosystems themselves (thin films, overlayers, self-assembled monolayers, etc.)

- because they can serve as support for nanosystems

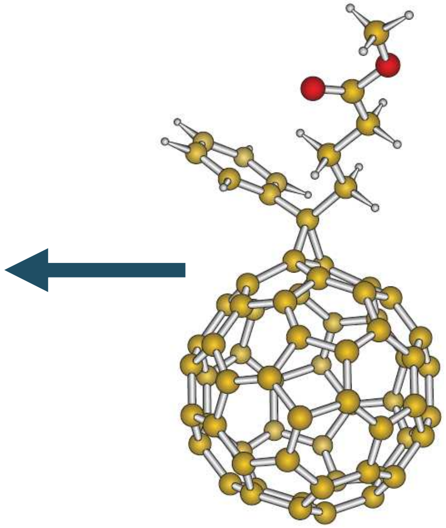
- because the surface of a nanosystem determines its properties in many cases

- because, historically, research on surface science has been very much linked to research in nanoscience (MBE, STM, etc.)

1.- because they can be nanosystems themselves (thin films, overlayers, self-assembled monolayers, etc.)



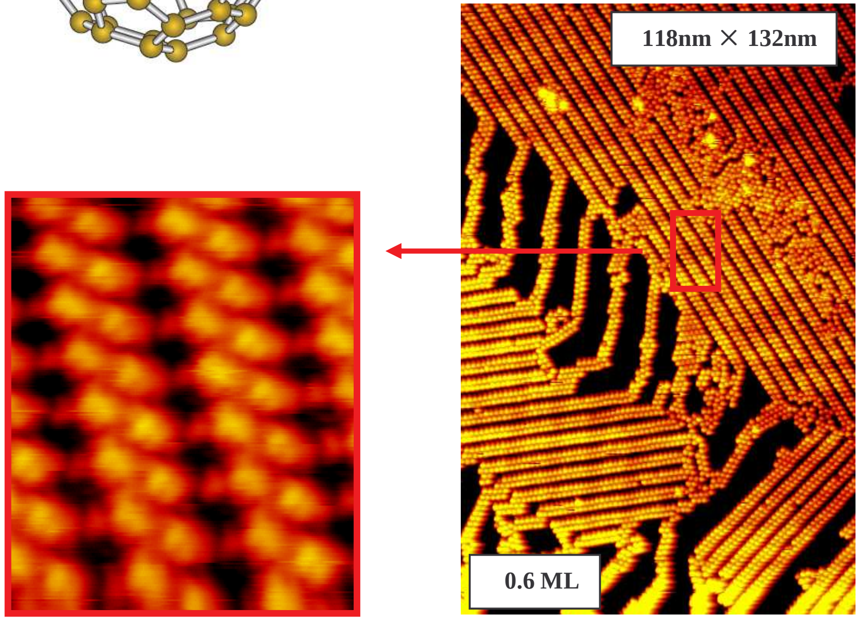
herringbone reconstruction
of Au(111) surface



PCBM on Au(111)

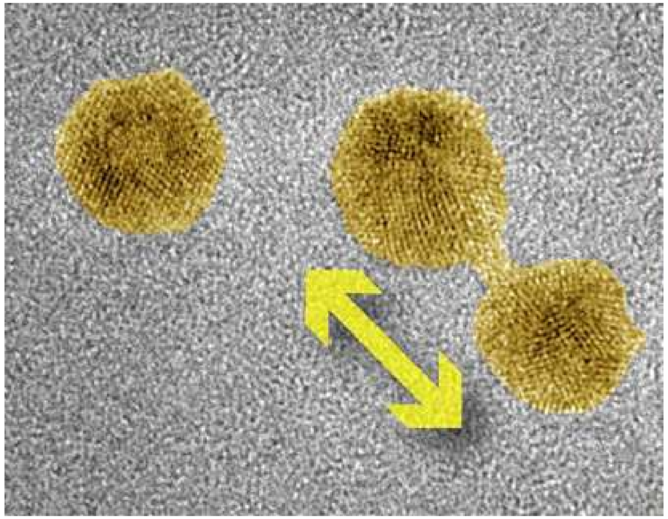
PCBM=
Phenyl-C_{61}-Butyric acid
Methyl ester

parallel twin chains are connected
laterally to form a well-ordered
2D arrangement

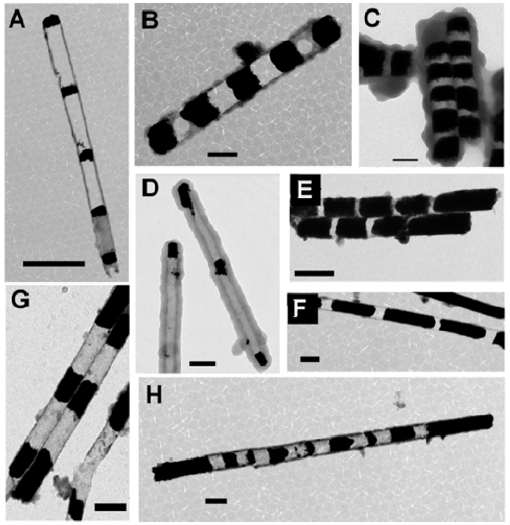


LASUAM, UAM, R. Miranda group

2.- because they can serve as support for nanosystems



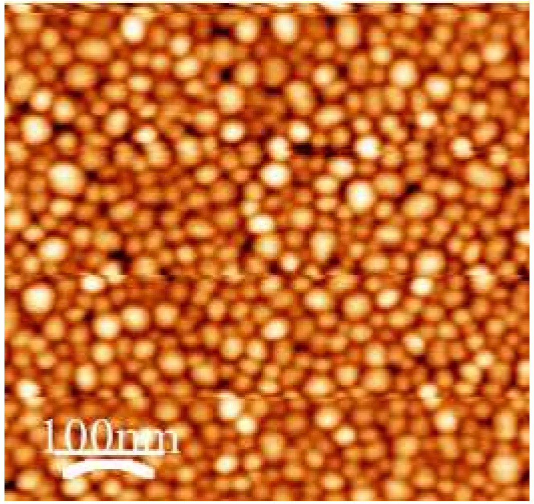
TEM images of Au nanoparticles
supported on C
Sutter *et al.*,
Nano Lett. **5**, 2092 (2005)

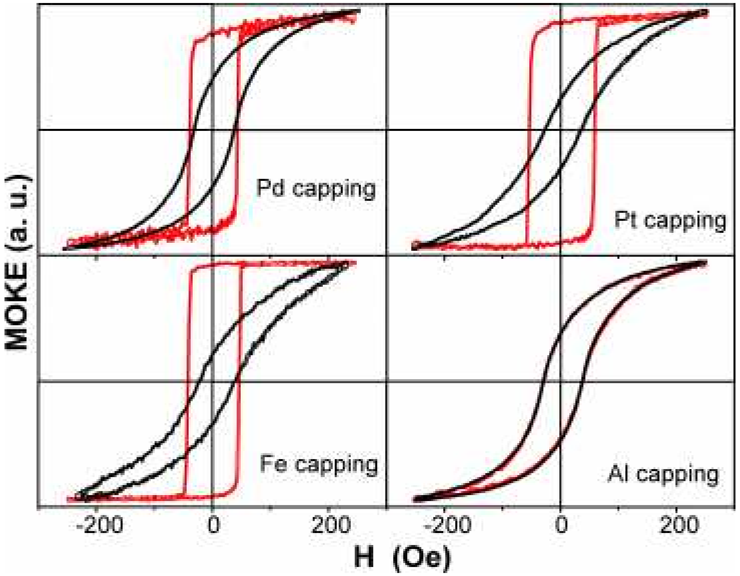


TEM images of representative
Au and Ag nanoparticle chains
Sioss and Keating,
Nano Lett. **5**, 1779 (2005)

3.- because the surface of a nanosystem determines its properties in many cases

In nanostructures, the number of surface atoms constitutes a large fraction of the total.This leads to **surface-dominated** effects.

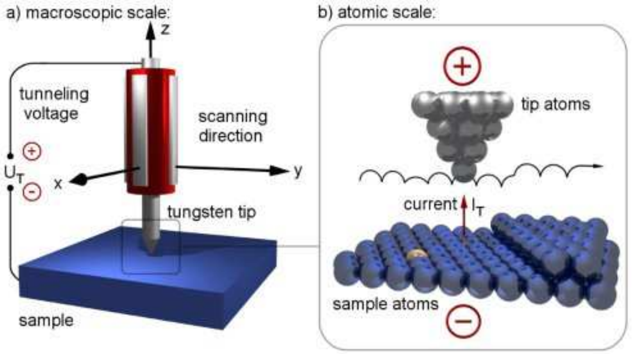


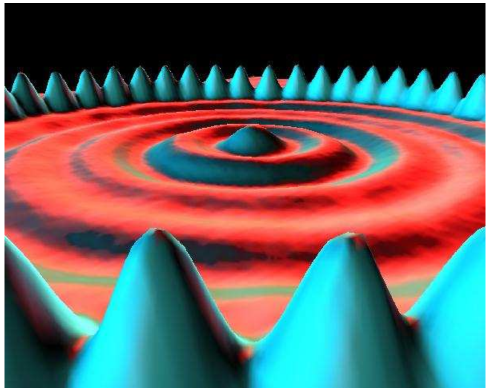


Kerr hysteresis loops for Fe nanoparticles before and after capping them with different metal layers. The magnetic behavior of the assembly of Fe nanoparticles changes considerably depending on the capping layer. Such phenomenon has been interpreted as being due to the magnetic connection of the islands through the capping layer that is magnetically polarized in its first 0.7 nm at the interface with the Fe nanoislands.
Navarro *et al*., APL **84**, 2139 (2004).

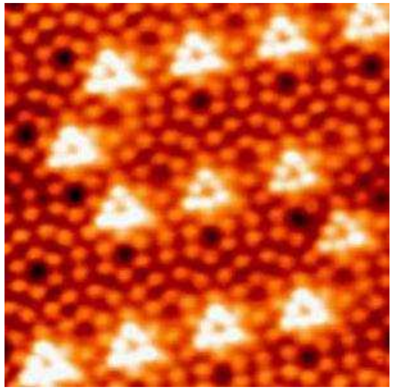
4.- because, historically, research on surface science has been very much linked to research in nanoscience

a good example is STM:

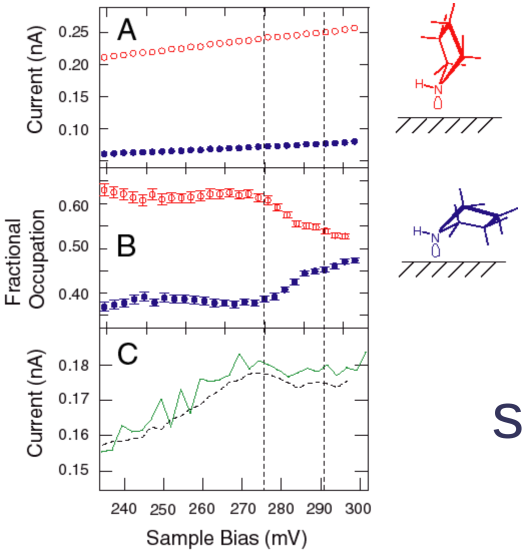




manipulation



topography

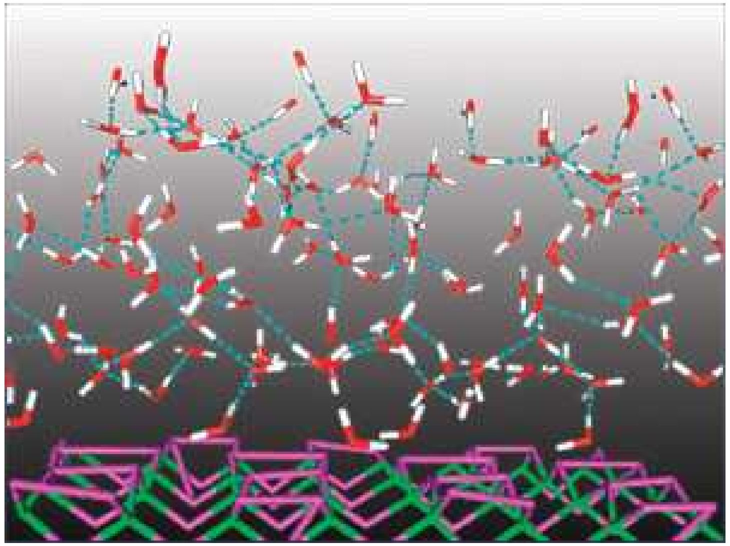


spectroscopy

Gaudioso *et al.*,
PRL 2000

surfaces and interfaces

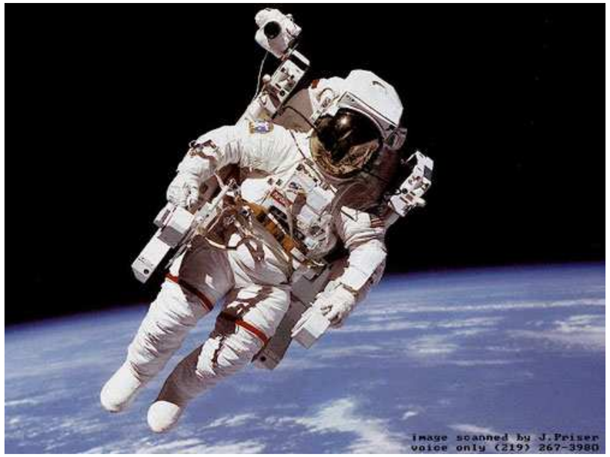
surface science is the study of physical and chemical phenomena that occur at the **interface** of two phases (one of them being a condensed phase, solid or liquid)



Liquid H_20 / solid SiC

interfaces

solid/
vacuum

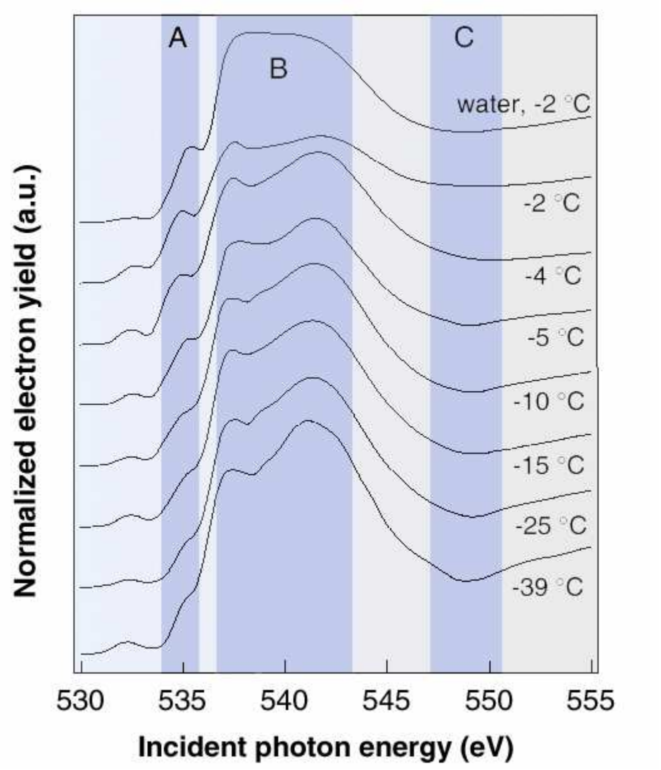


solid/
gas

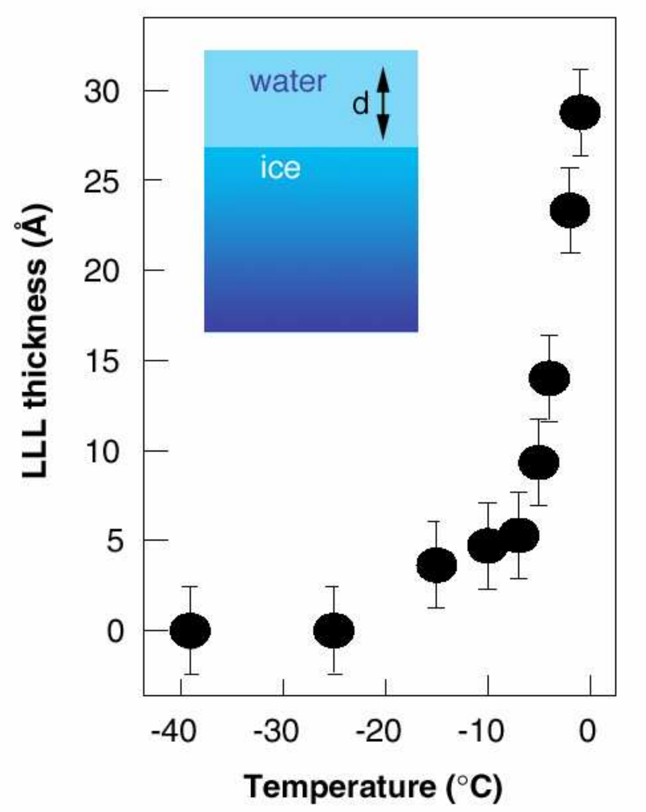
solid/
liquid

solid/
solid

Ice is wet: water shown to cover its surface



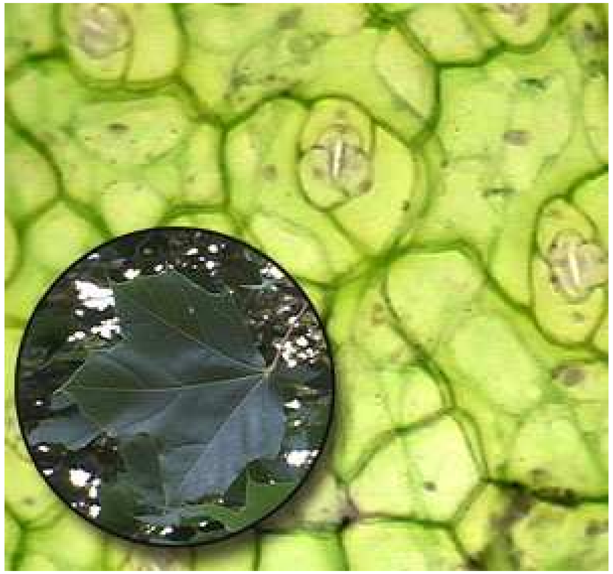
•Near-edge x-ray absorption fine-structure (NEXAFS) spectra obtained from the surface of ice. The spectrum of liquid water chilled to –2 ºC is shown for comparison (top). The increase in the peak in area A and the suppression of the dips in areas B and C are all assigned to the increasing presence of liquid water as the temperature is increased. (The thickness of water is assumed to be zero at –40 ºC since the signal does not change as the temperature is decreased below that point).



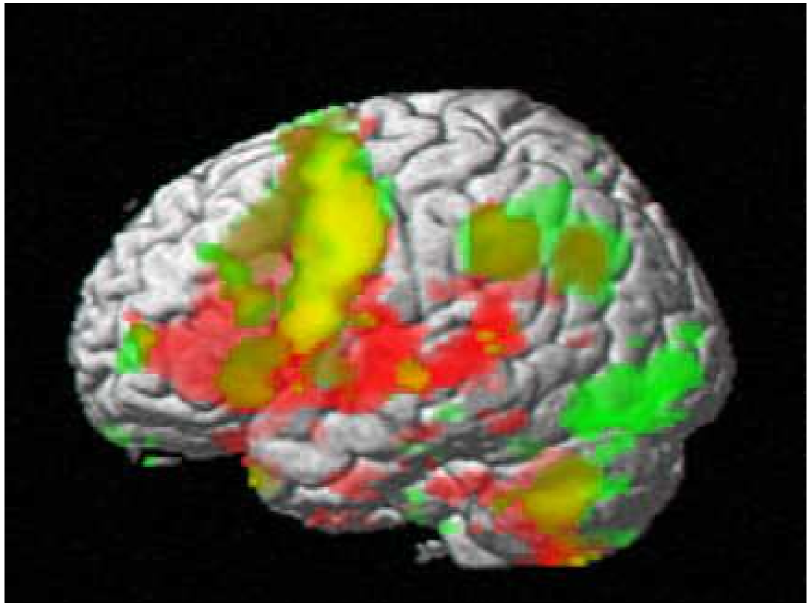
Quantitative analysis of the NEXAFS spectra using the relative intensity of the “water” peak in area A is used to measure the water thickness as a function of temperature. In pure ice, water begins to appear at –20 ºC and reaches a thickness of greater than 20 Å at –2 ºC.

Miquel Salmeron, LBNL, Berkeley USA

surface - complexity - functionality



green leaf (primary site
of photosynthesis in plants)

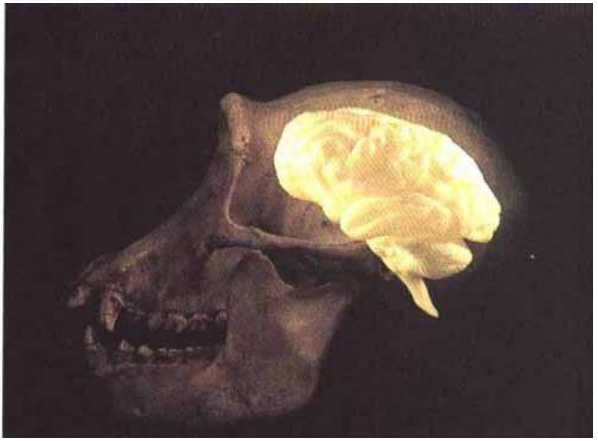


human brain

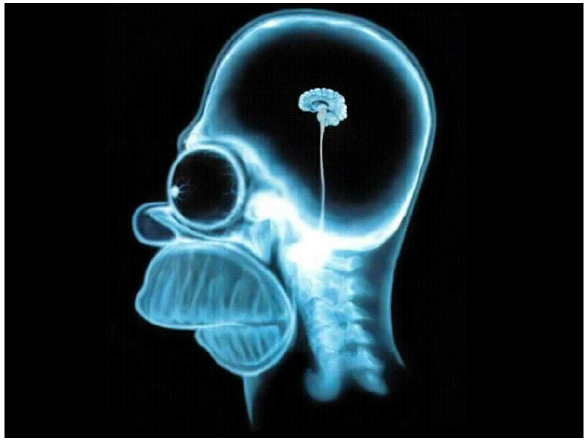
Surfaces and interfaces are the favorite media of evolution. Both photosyntetic and biological systems evolve and improve by ever increasing their interface area or their interface/volume ratio.

The brain may be viewed as a device with enormous solid-liquid interface area. The size and surface/volume ratio of the brain is thus as sign of evolution

human brain



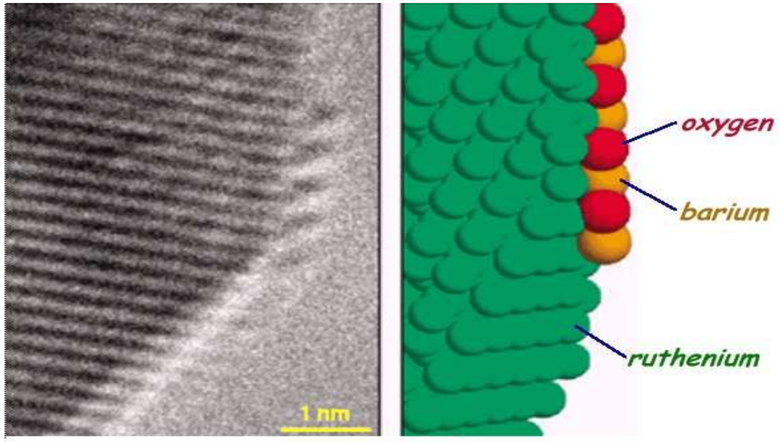
chimpanzee brain



Homer´s brain

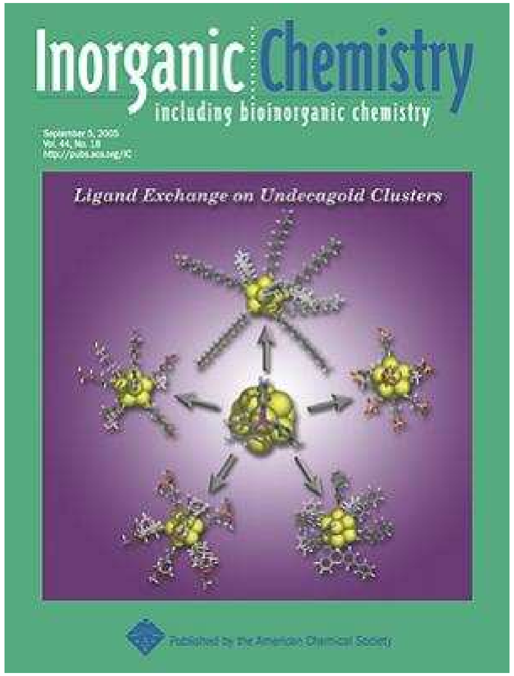
surface - complexity - functionality

... because surface = interaction



Magnified image of the surface of the ruthenium catalyst with barium promoter

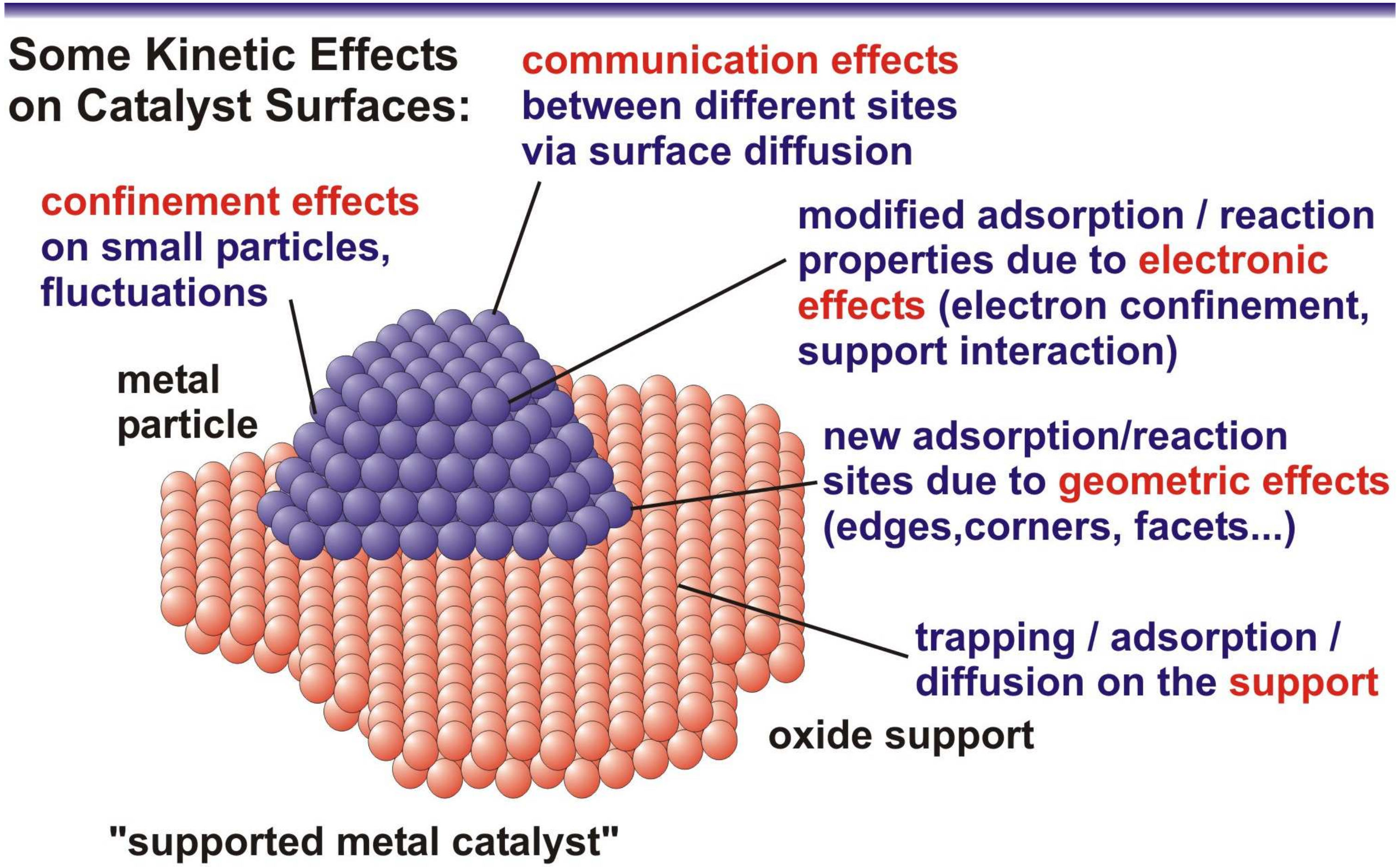
Heterogeneous catalysis:
only the surface region plays any role



Au nanoparticles functionalized
with thiol-containing ligands

surface - complexity - functionality

... because surface = versatility



Some Kinetic Effects on Catalyst Surfaces:

communication effects between different sites via surface diffusion

confinement effects on small particles, fluctuations

modified adsorption / reaction properties due to electronic effects (electron confinement, support interaction)

metal particle

new adsorption/reaction sites due to geometric effects (edges,corners, facets...)

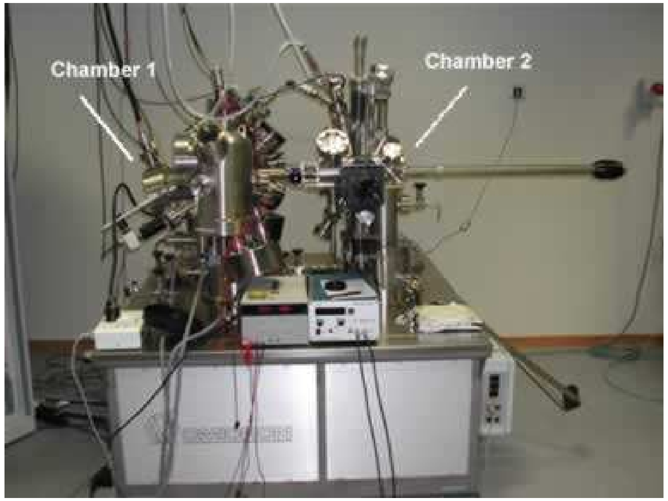
trapping / adsorption / diffusion on the support

oxide support

"supported metal catalyst"

experimental techniques
In surface science

- diffraction techniques (LEED, XRD, RHEED)
- electron spectroscopies (UPS, XPS, AES)
- ion-beam techniques (HAS, LEIS, SIMS)
- desorption spectroscopies (TPD)
- tunneling microscopies (STM, STS, AFM)
- molecular beams
- etc.



experimental techniques in surface science

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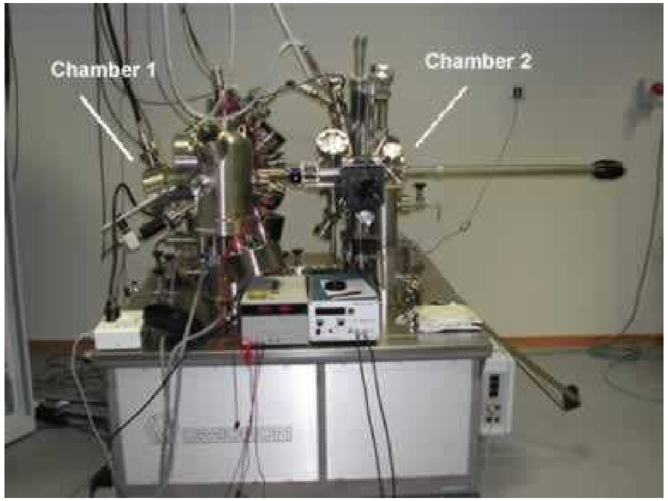
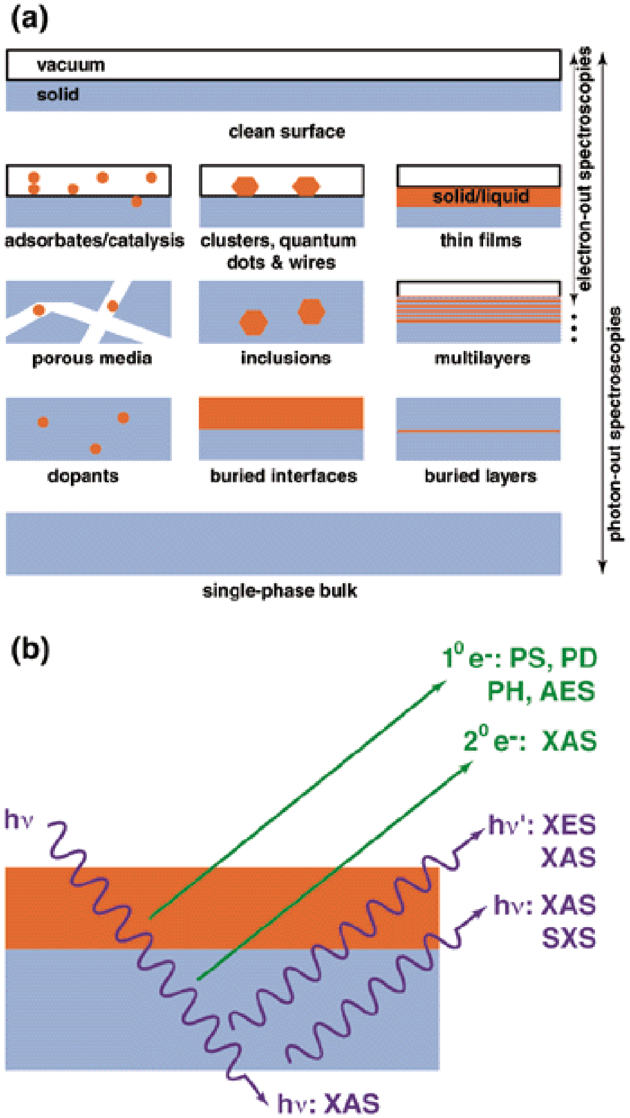


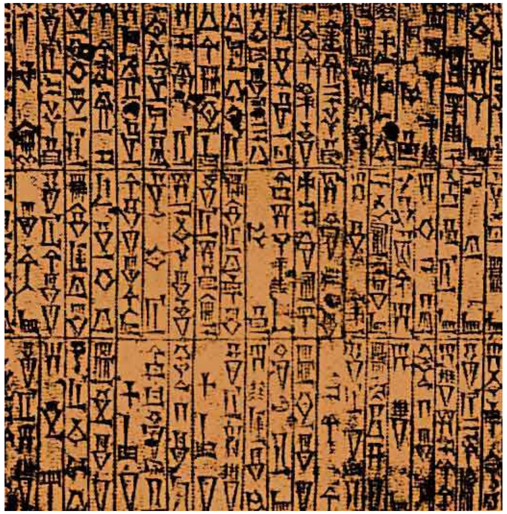
photoemission – related experimental techniques in the study of surfaces

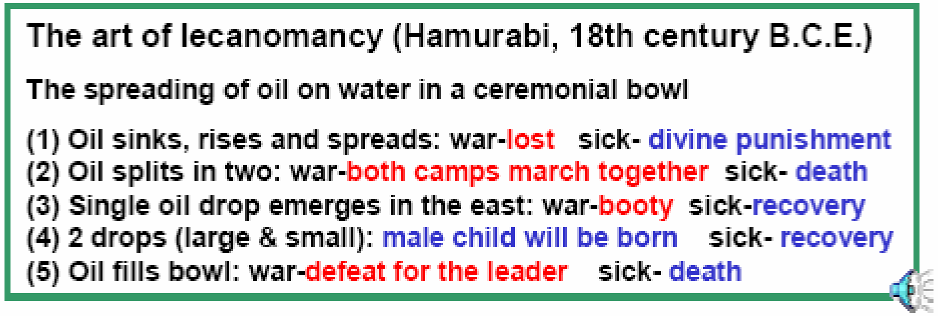


an historical account of surface science and some surface scientists

1st account of surface science: lecanomancy

The earliest known documented record of observations of surface physical phenomena are the inscriptions of the Babylonian cuneiform dating back to the time of Hammurabi (1758 B.C). They explain a certain practice called Babylonian Lecanomancy, in which a diviner (called the ‘baru’) made his prophesies based on the way oil spreads on water.





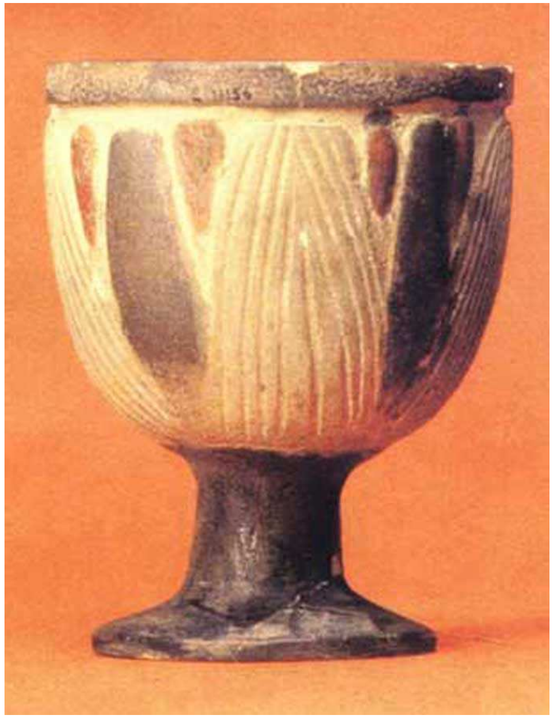
The art of lecanomancy (Hamurabi, 18th century B.C.E.)

The spreading of oil on water in a ceremonial bowl

(1) Oil sinks, rises and spreads: war-lost sick- divine punishment
(2) Oil splits in two: war-both camps march together sick- death
(3) Single oil drop emerges in the east: war-booty sick-recovery
(4) 2 drops (large & small): male child will be born sick- recovery
(5) Oil fills bowl: war-defeat for the leader sick- death

lecanomancy

"Is it not from this that my lord drinks?
Does he not indeed use it for divination?“
(Gen. 44:5)
Standard scholar interpretation is that Joseph’s cup was used for divination



Before that date, egyptians already used oils and unguents to modify the properties of (body) surfaces, XXth century BC

A lady wiping her face.
Relief of unknown provenance;
11th Dynasty ~2000BC
(British Museum, 1658)

Unguent vases as found
in the tomb of Tutankhamun
at Thebes (XIV B.C.)
(Egyptian Museum, Cairo)

Pliny the Elder, 1st century AD: oil on water

C. PLINII SECUNDI
NATURALIS
HISTORIÆ,
TOMUS PRIMUS.
Cum Commentariis & adnotationibus HERMOLAI
BARBARI, PINTIANI, RHENANI, GELENII,
DALECHAMPII, SCALIGERI, SALMASII,
IS. VOSSII, & Variorum.

Apud HACKIOS, A°. 1669.

Caius Plinius Secundus, also known as Pliny the Elder, Roman Officer and Encyclopedist AD 23-79, had first mentioned in his encyclopedic work, *Naturalis Historia* (37 books) his observations about how oil smoothed the rough sea waters

Bartholomew of England, 13th century

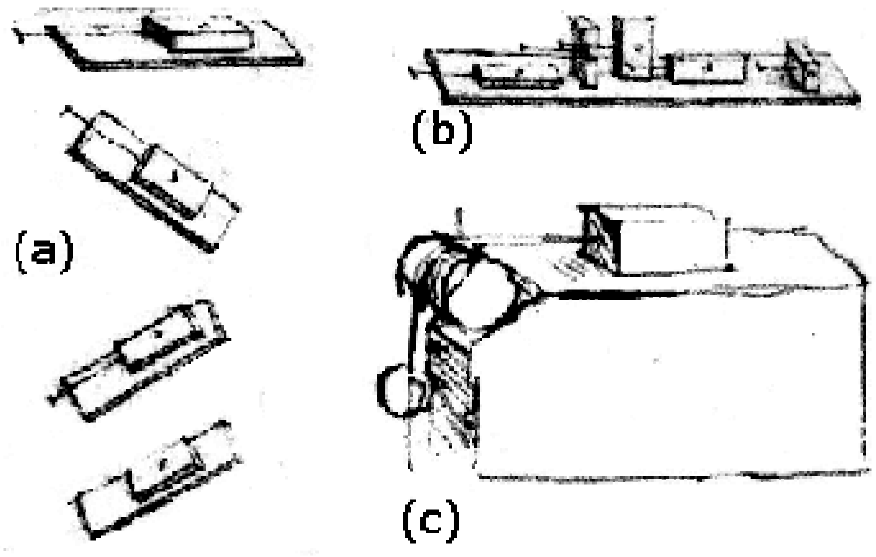
Bartholomeus Anglicus (Bartholomew of England) (born before 1203 - died 1272) was an early 13th century scholastic scholar of Paris, a member of the Franciscan order. He was the author of *De proprietatibus rerum* (On the Properties of Things), 19 books, dated at 1240. It is the first important encyclopedia of the Middle Ages and the first in which the works of Greek, Arabian, and Jewish naturalists and medical writers, which had been translated into Latin shortly before, were laid under contribution. Bartholomaeus's work went through eight editions in French, two in Belgian, one in English and one in Spanish prior to 1500.

He outlined the importance of surfaces by describing surface preparation techniques to achieve metal-metal bonding.

Leonardo da Vinci, 15th century

Leonardo da Vinci has the credit to be the first who made quantitative studies on the problem of friction. With his methods he was only able to measure static friction and most probably he wasn't aware of the difference between static and kinetic friction.

Leonardo defined a friction coefficient as the ratio of the friction divided by the mass of the slider. Experimentally, he found a universal friction coefficient of 0.25 independent of the material. Many other friction scientists after Leonardo believed in the existence of a universal material independent friction coefficient. However, most of them found another value but all in the range 0.1 - 0.6.



original sketches from Leonardo to study the problem of friction

Leonardo da Vinci, 15th century

In the normal course of events many men and women are born with remarkable talents; but occasionally, in a way that transcends nature, a single person is marvellously endowed by Heaven with beauty, grace and talent in such abundance that he leaves other men far behind, all his actions seem inspired and indeed everything he does clearly comes from God rather than from human skill. Everyone acknowledged that this was true of Leonardo da Vinci, an artist of outstanding physical beauty, who displayed infinite grace in everything that he did and who cultivated his genius so brilliantly that all problems he studied he solved with ease.

Giorgio Vasari, ‘*Lives of the artists*’, 1568

Benjamin Franklin, 18th century: oil on water… again

Benjamin Franklin (1706-1790), one of the founding fathers of the United States, as well as writer, civil activist, and scientist. During one of his visits to London, Franklin observed the effect of pouring oil on water. He used a simple bamboo cane with a hollow top for storing oil as his experimental apparatus.

One of Franklin´s letters explaining his observations:

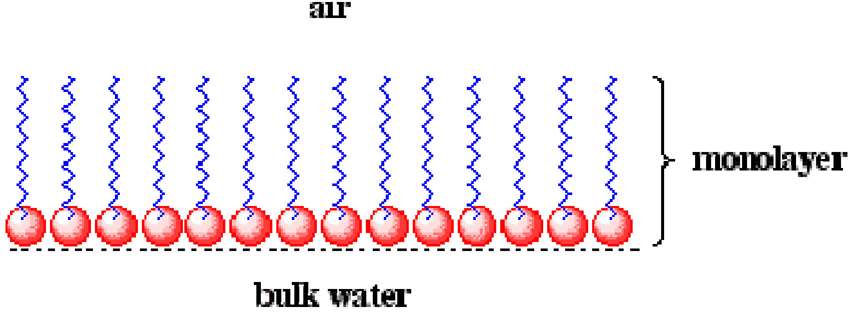
At length being at Clapham, where there is on the common a large pond which I observed one day to be very rough with the wind, I fetched out a cruet of oil and dropped a little of it on the water. I saw it spread itself with surprising swiftness upon the surface; but the effect of smoothing the waves was not produced; for I had applied it first on the leeward side of the pond where the waves were greatest; and the wind drove my oil back upon the shore. I then went to the windward side where they began to form; and there the oil, though not more than a **teaspoonful**, produced an instant calm over a space several yards square which spread amazingly and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps **half an acre**, as smooth as a looking glass.

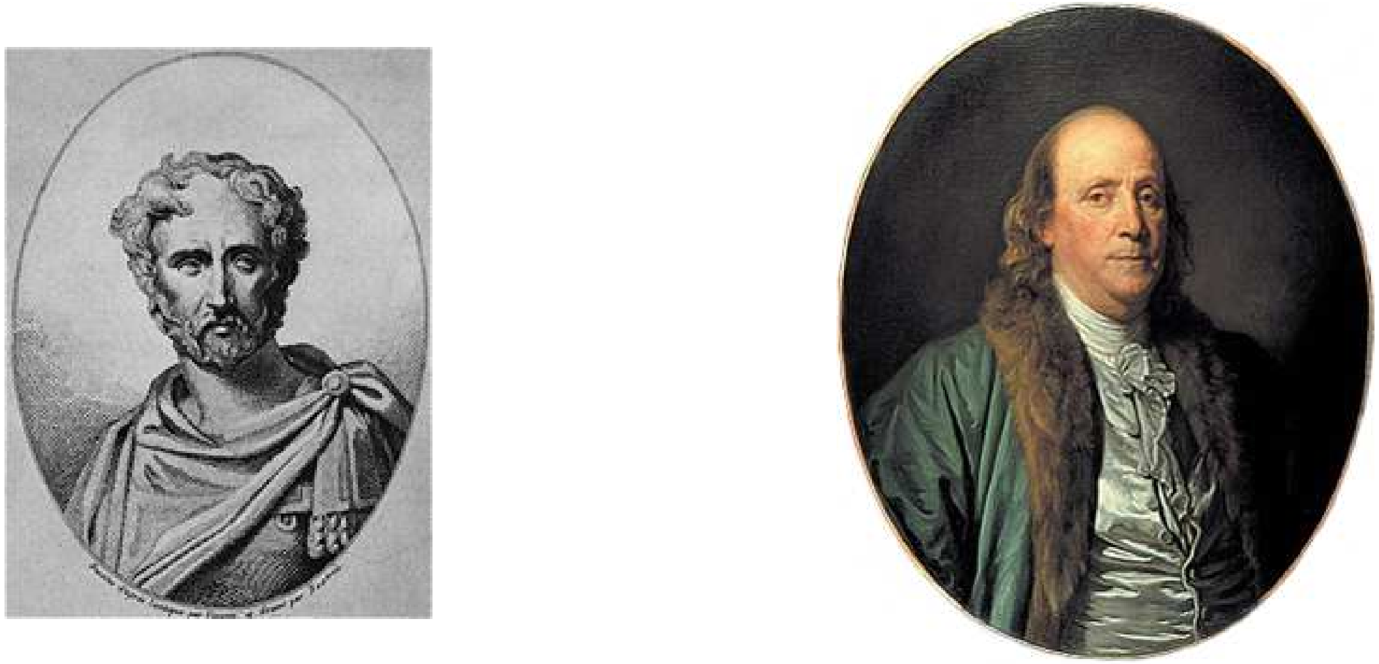
½ acre ~ 2000 $m^2 = 2 \times 10^{21}$ nm^2

Teaspoonful ~ 2 $cm^3 \sim 2 \times 10^{21}$ nm^3

↓

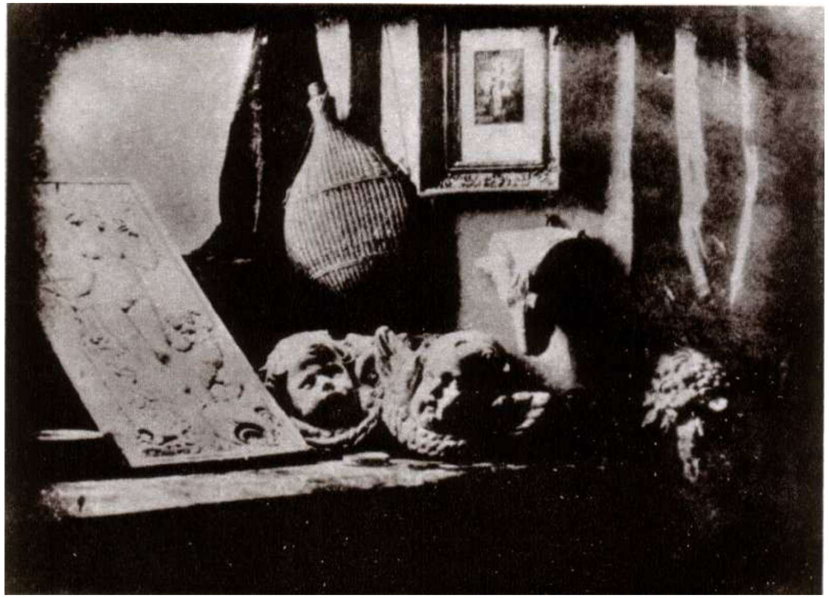
The oil layer was 1 nm width!!





He aptly credited Pliny for his discovery thus starting the respectful tradition of giving credit to people for their original research.

Louis Daguerre and the daguerreotypes (1839)



L'Atelier de l'artiste : un daguerréotype de 1837, réalisé par l'inventeur de ce procédé photographique, Louis Jacques Mandé Daguerre (1787-1851).

The image is exposed directly onto a mirror-polished surface of silver bearing a coating of photo-sensitive silver halide particles deposited by iodine vapor. Exposure to a scene or image through a focusing lens forms a latent image. The latent image is made visible, or "developed", by placing the exposed plate over a slightly heated (about 75C) cup of mercury. The mercury vapour condenses on those places where the exposure light was most intense, in proportion with the areas of highest density in the image.

XIXth century: the three phases of Auguste Comte (1798-1857)

Society has gone through three phases:
Theological, Metaphysical, and Scientific.
To the last of these he also gave the name
"Positive," because of the polysemous
connotations of that word.

scientific progress à social (and economical) progress

Fin de siècle and Modernism

Modernism is a series of reforming cultural movements in art and architecture, music, literature and the applied arts which emerged in the three decades before 1914. It is a trend of thought that affirms the power of human beings to create, improve, and reshape their environment, with the aid of scientific knowledge, technology and practical experimentation.

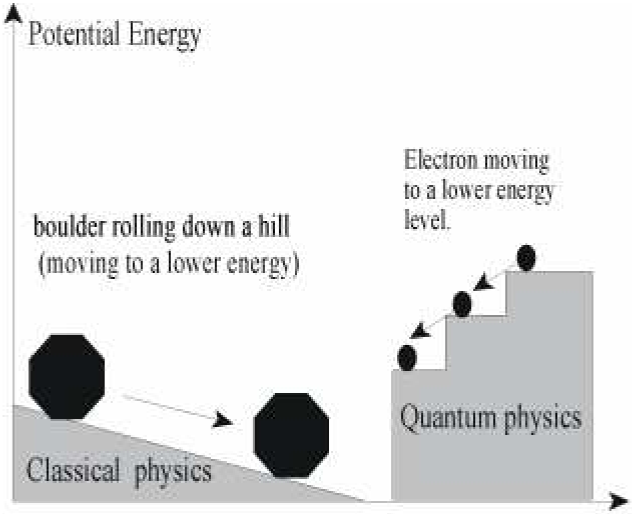
But also…

In a broader sense the expression fin de siècle is used to characterise anything that has an ominous mixture of opulence and/or decadence, combined with a shared prospect of unavoidable radical change or some approaching "end."

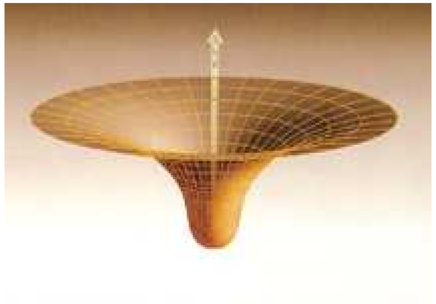
(From Wikipedia)

In science: the turn of the century is also the advent of quantum physics

The fundamentals of physics were apparently well established:
"There is nothing new to be discovered in physics now.
All that remains is more and more precise measurement.“
(Lord Kelvin)



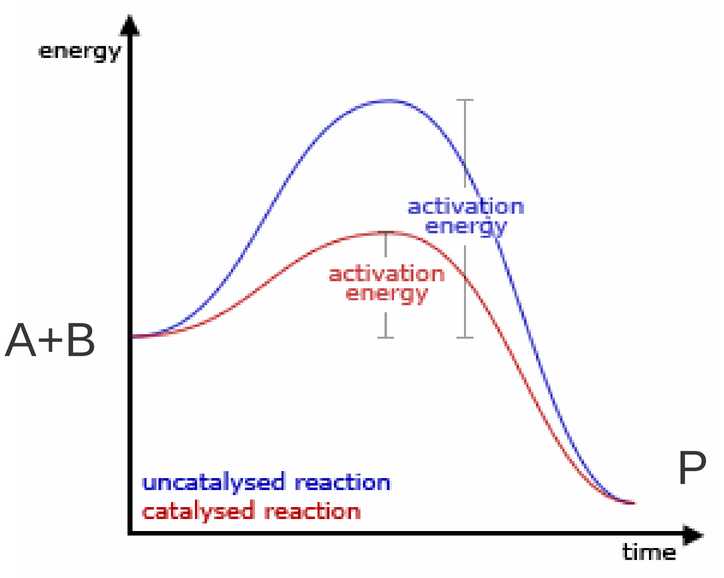
1900: quantum hypothesis by Max Planck that any energy is radiated and absorbed in quantities divisible by discrete ‘energy elements’ ε



1905: Relativity by Einstein

Surface chemistry and heterogeneous catalysis

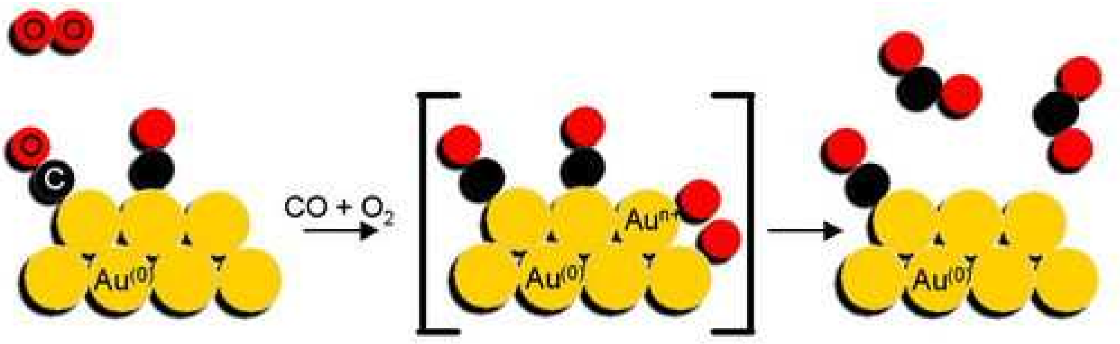
CATALYSIS:
The effect produced in facilitating a chemical reaction, by the presence of a substance, which itself undergoes no permanent change.
(Oxford english dictionary)



A+B à P	direct reaction
A+B+C à P+C	catalyzed reaction

A and B are reactants
C is the catalyst
P is the reaction product

Heterogeneous catalysis: role of surfaces



$2CO+O_2+Au$ à $2CO_2+Au$

Catalysts (surfaces) bring reactants together
in a way that makes reaction more likely.

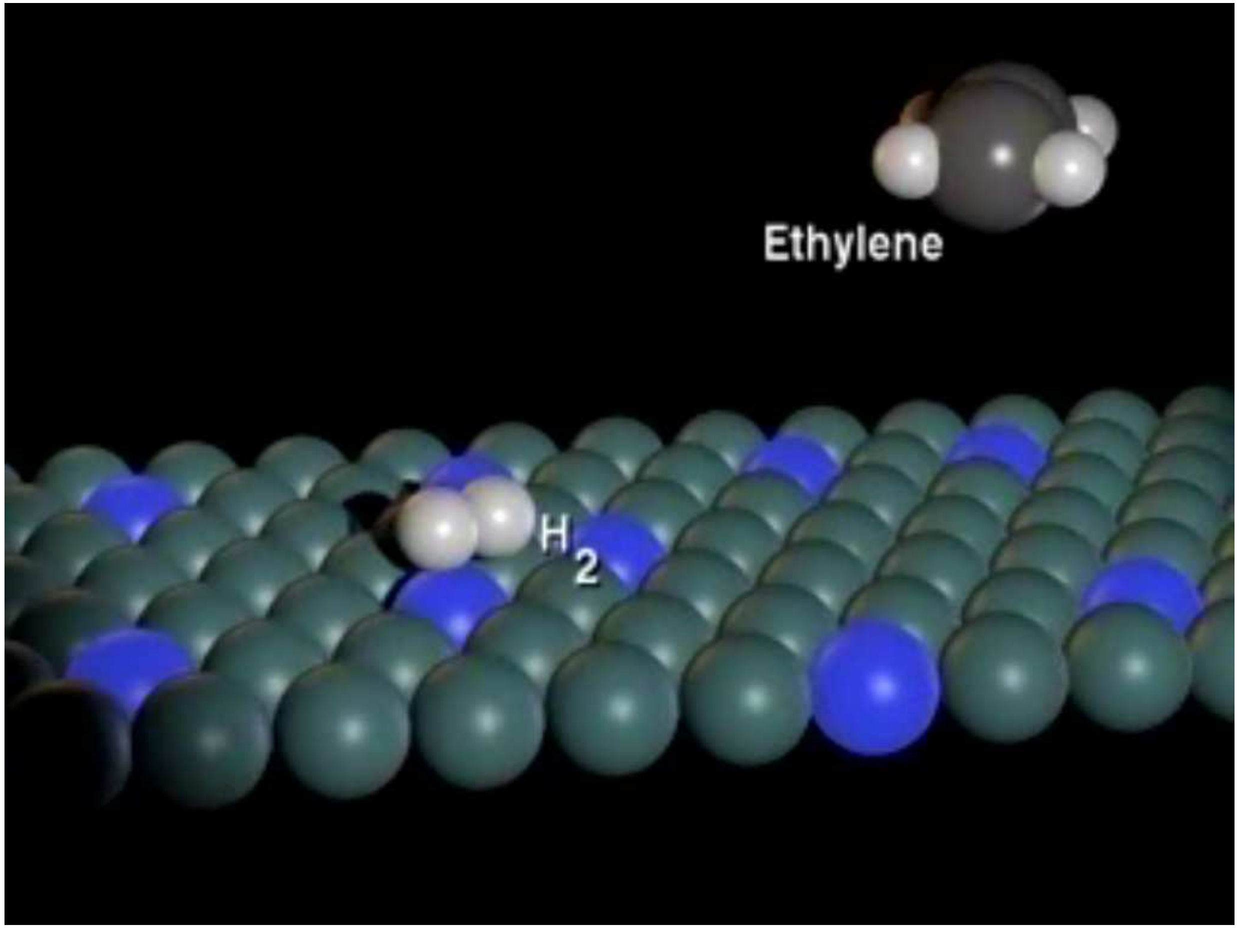
*The word "catalysis" was coined by Berzelius in **1836**.*

觸媒

The chinese symbol for catalyst is the same as the one for marriage broker (matchmaker)

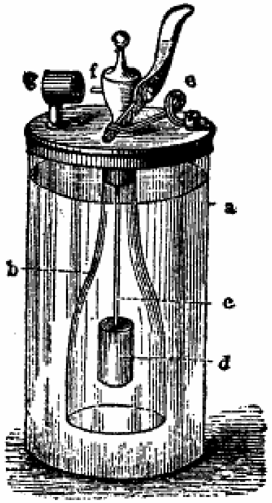
Heterogeneous catalysis: role of surfaces 觸媒

Hydrogenation of Ethylene to form Methane

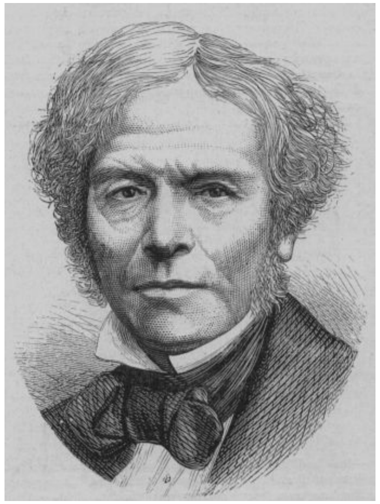


Surface chemistry and heterogeneous catalysis

Johann Wolfgang Döbereiner (1780 - 1849), a German chemist, friend of Goethe. He invented the Döbereiner-lighter in **1823**. He observed that if a stream of hydrogen was directed at Pt from a distance of 4 cm, so that it was premixed with air, the Pt became red-hot, then white-hot and the jet ignited spontaneously. Within five years of its discovery 20,000 lamps were in use in Germany and England.



Michael Faraday (1791-1867)



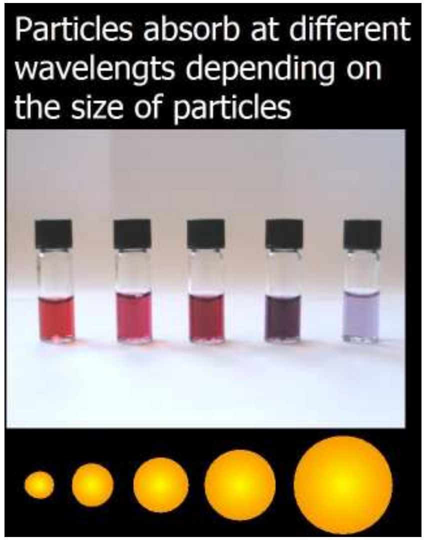
Although Faraday received little formal education and knew little of higher mathematics, such as calculus, he was one of the most influential scientists in history. Some historians of science refer to him as the best experimentalist in the history of science.

In addition to his contributions to the field of electromagnetism, let us mention two other scientific achievements:

- Heterogeneous catalysis: building on the work of Döbereiner, he studied how Pt could induce the reaction of H and O well below their combustion temperature. He proposed a qualitative theory of catalytic action (1833).
- Faraday was the first to report what later came to be called **metallic nanoparticles**. In 1847 he discovered that the optical properties of gold colloids differed from those of the corresponding bulk metal. This was probably the first reported observation of the effects of quantum size, and might be considered to be the birth of **nanoscience**.

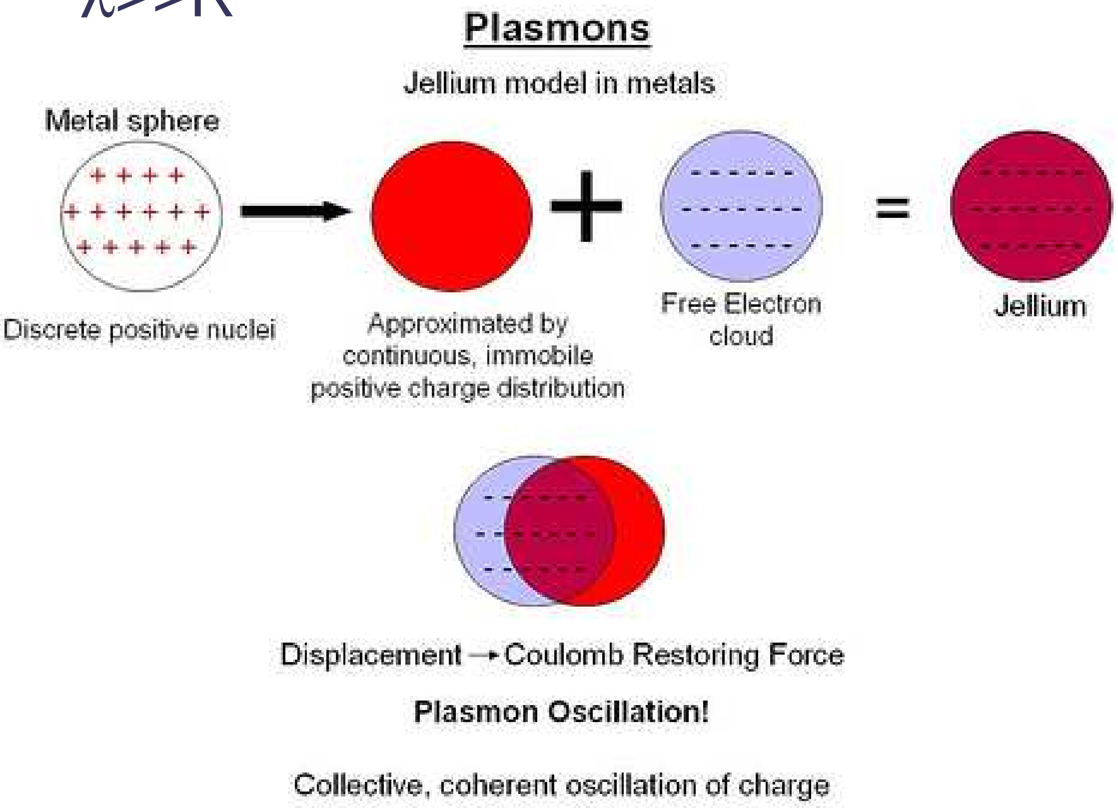
Mie plasmon

Gold nanoparticles absorb light at different wavelenghts depending on their diameter due to their size-dependent plasmon resonance frequency. This fact is responsible for the beautiful colors gold nanoparticles show when exposed to light.



Particles absorb at different wavelengts depending on the size of particles

$\lambda >> R$



Plasmons

Jellium model in metals

Metal sphere

Discrete positive nuclei

Approximated by continuous, immobile positive charge distribution

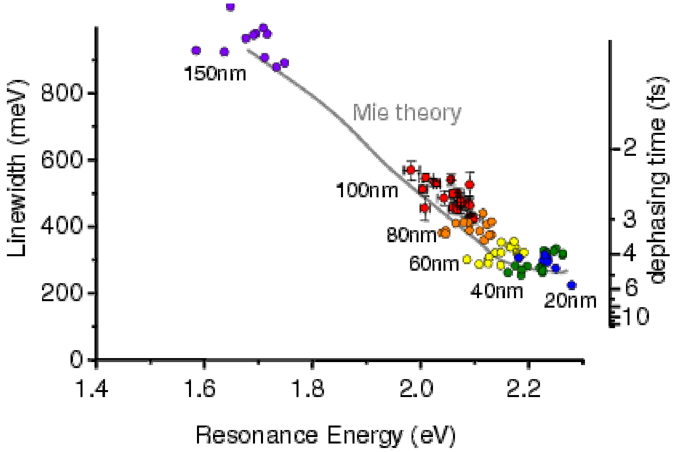
Free Electron cloud

Jellium

Displacement → Coulomb Restoring Force

Plasmon Oscillation!

Collective, coherent oscillation of charge



Faraday and size-dependent properties

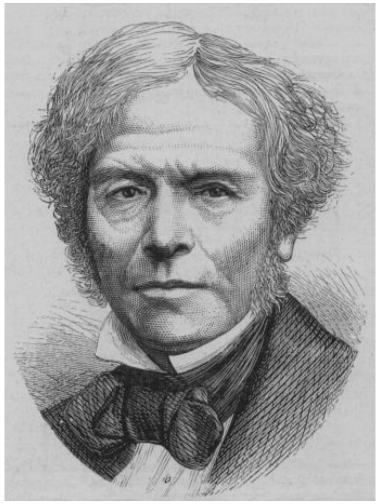
Faraday was famous for his captivating lectures featuring superbly choreographed demonstrations, and would have used a projecting microscope to show the slide.

The preparations of gold ‘sols’ (colloids) that Faraday studied were ruby-red in colour. He discovered that he could turn the preparation blue by adding certain salts.

Faraday made some attempt to explain what was causing the vivid colouration in his gold mixtures, saying that *"known phenomena seemed to indicate that a mere variation in the size of [gold] particles gave rise to a variety of resultant colours."*

Slide that Faraday used in his lecture on gold sols, in 1858.

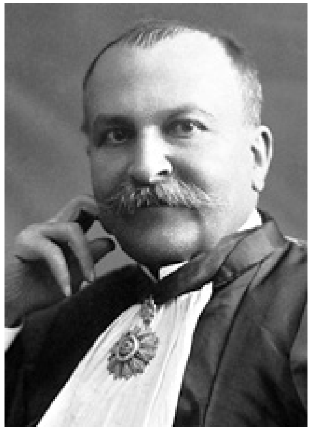
Michael Faraday (1791-1867)



Faraday refused to participate in the production of chemical weapons for the Crimean War citing ethical reasons.

"Work. Finish. Publish.“
his well-known advice to the young William Crookes

Surface chemistry and heterogeneous catalysis



In 1897, Sabatier discovered that the introduction of a trace of nickel as a catalyst facilitated the addition of hydrogen to molecules of carbon compounds.

Sabatier process:

$$CO_2 + 4H_2 + Ni \rightarrow CH_4 + 2H_2O + Ni$$

Paul Sabatier (1854-1941)

NASA is currently investigating the use of the Sabatier reaction to **recover water** from exhaled carbon dioxide, for use on the International Space Station and future missions. Currently, as astronauts consume oxygen, carbon dioxide is produced which must then be removed from the air and discarded as well. This approach requires copious amounts of water to be regularly transported to the space station for oxygen generation:

$2H_2O \rightarrow O_2 + 2H_2 \rightarrow$ (respiration) $\rightarrow CO_2 + 2H_2$ (discarded)

Ignoring other results of respiration, the new cycle would look like:

$2H_2O \rightarrow O_2 + 2H_2 \rightarrow$ (respiration) $\rightarrow CO_2 + 2H_2 + 2H_2$ (added) $\rightarrow 2H_2O + CH_4$ (discarded)

The loop could be completely closed if the waste methane was simply pyrolyzed into its component parts:

$CH_4 + \text{heat} \rightarrow C + 2H_2$

Surface chemistry and heterogeneous catalysis

In 1909, after considerable effort worldwide, Fritz Haber managed to fix nitrogen from the air, by reacting it with hydrogen. The secret was in the catalyst used and Haber and Carl Bosch systematically tested some **20,000 catalysts**, before succeeding with some iron ore from Kiruna in Sweden. By chance, this ore contained trace amounts of alkali metal compounds and the catalyst used today in the Haber- Bosch process, iron oxide with potassium hydroxide promoter, is not so very different to that discovered by Haber and Bosch.

Fritz Haber (1868-1934)

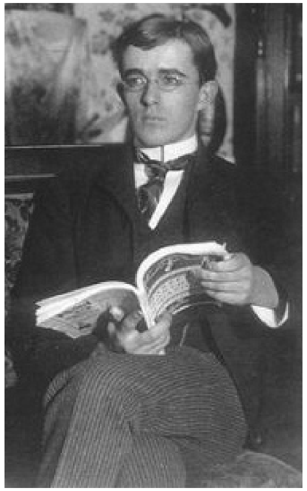
Haber process:

$3H_2(g) + N_2\ (g) \leftrightarrow 2NH_3(g)$ - catalyzed by Fe oxides

World War I

Haber played a major role in the development of chemical warfare in World War I.

Irving Langmuir (1881-1957)



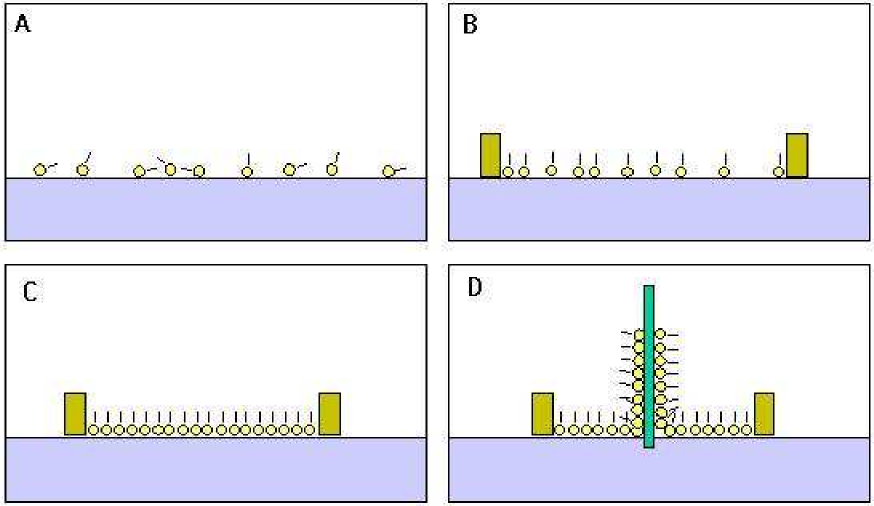
Langmuir was an American chemist and physicist. He was the first industrial chemist to become a Nobel laureate. He was awarded the 1932 Nobel Prize for Chemistry for his work in surface chemistry.

Katharine B. Blodgett (1898-1979)

Blodgett was the first woman to get her Ph.D. in Physics from University of Cambridge in 1926. She was the first female scientist to work at the General Electric Laboratory in Schenectady, New York, in 1920.

Katharine Blodgett and Langmuir worked on monomolecular coatings designed to cover surfaces of water, metal, or glass.

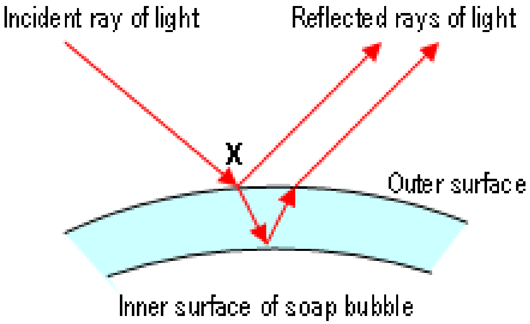
Langmuir and Blodgett studied thin films and surface absorption. They introduced the concept of a **monolayer** (a layer of material one molecule thick) and the **two-dimensional physics** which describe such a surface.

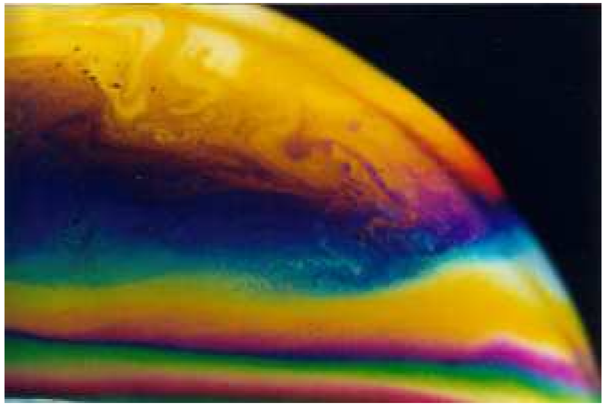


A Langmuir-Blodgett film contains one or more monolayers of an organic material, deposited from the surface of a liquid onto a solid by immersing (or emersing) the solid substrate into (or from) the liquid. A monolayer is added with each immersion or emersion step, thus films with very accurate thickness can be formed. Traditional compounds used to prepare these films are **amphiphilic** materials that possess a hydrophilic headgroup and a hydrophobic tail.

Color of soap bubbles and the thickness of thin films

The iridescent colors of soap bubbles are caused by interfering light waves and are determined by the thickness of the film. As light impinges on the film, some of it is reflected off the outer surface while some of it enters the film and reemerges after being reflected back and forth between the two surfaces. The total reflection observed is determined by the interference of all these reflections.

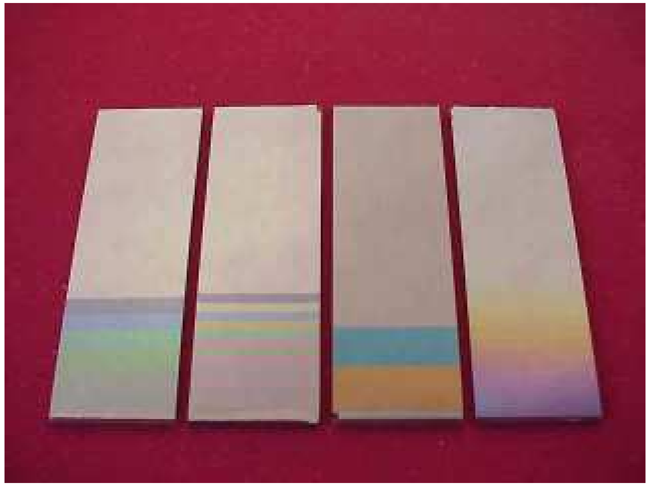


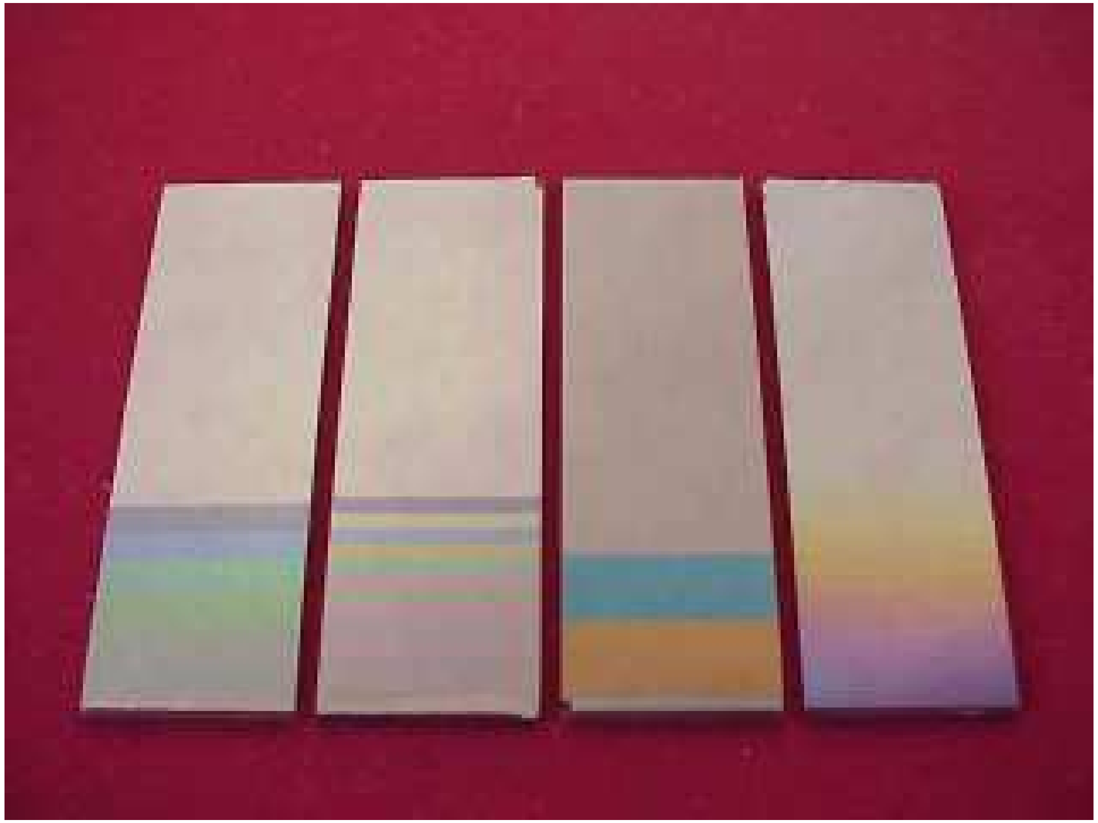


Thin film interference in a soap bubble. Notice the golden yellow color near the top where the film is thin and a few even thinner black spots.

Blodgett continued working with what has come to be known as the Langmuir-Blodgett film and in 1938 created non-reflecting glass by applying a thin layer of it to transparent glass. The light reflected by the film canceled out the light reflected by the glass itself, thus rendering the glass invisible. This "invisible glass" has been used in many consumer products from picture frames to camera lenses.

K. B. Blodgett defined the **‘color gauge’**: 'Anyone who wishes to measure the thickness of a film which is only a few millionths of an inch thick,' she said, 'can compare the color of his film with the series of colors in the gauge. The step on the gauge that matches his film in color will give him a measure of its thickness.'





**The thickness of these LB films are in the nanoscale. Their optical properties are size dependent. And they can be controlled.
This is nanoscience. In the late 1930's.**

Science and gender (a brief parentheses)

- In the 17th, 18th, and 19th centuries most women did not have access to higher learning and laboratories.
- This exclusion effectively prevented women from contributing to progress in science in these centuries.
- Only in the 20th century have reasonable opportunities for doing science begun to be available to women.

In 1692, Daniel Defoe wrote:

"one of the most barbarous customs in the world, considering us as a civilised and a Christian country, is that we deny the advantages of learning to women. ... Their youth is spent to teach them to stitch and sew, or make baubles. They are taught to read, indeed, and perhaps to write their names, or so; and that is the height of a woman's education. ... What is a man (a gentleman, I mean) good for, that is taught no more?"

Real Academia de Ciencias
Exactas • Físicas • Naturales

BERLIN-BRANDENBURGISCHE AKADEMIE DER WISSENSCHAFTEN

In red: Year of admission of the first woman in several European Research and Academic Institutions.

In black: Year in which the Institution was founded.

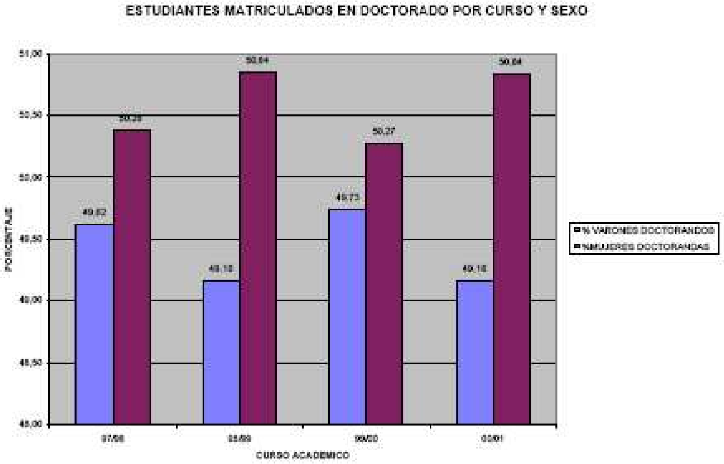
- Royal Society (Londres 1662) 1945
- Academie des Sciences (París 1666) 1979
- Akademie der Wissenschaften (Berlín 1700) 1964
- Real Academia de Ciencias (Madrid 1847) 1988

INSTITUT DE FRANCE
Académie des sciences

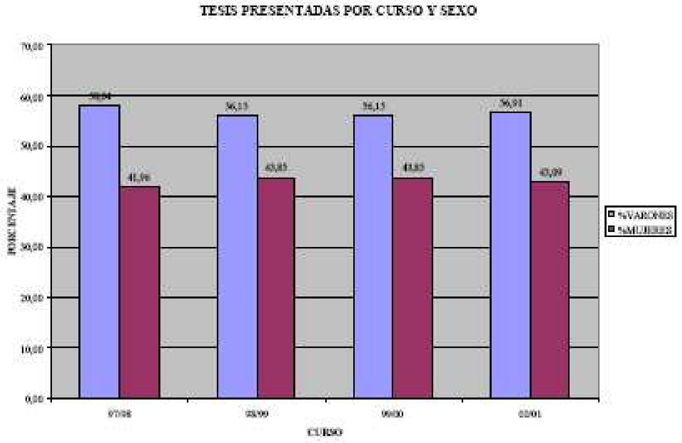
THE ROYAL SOCIETY

Women= 3,4%

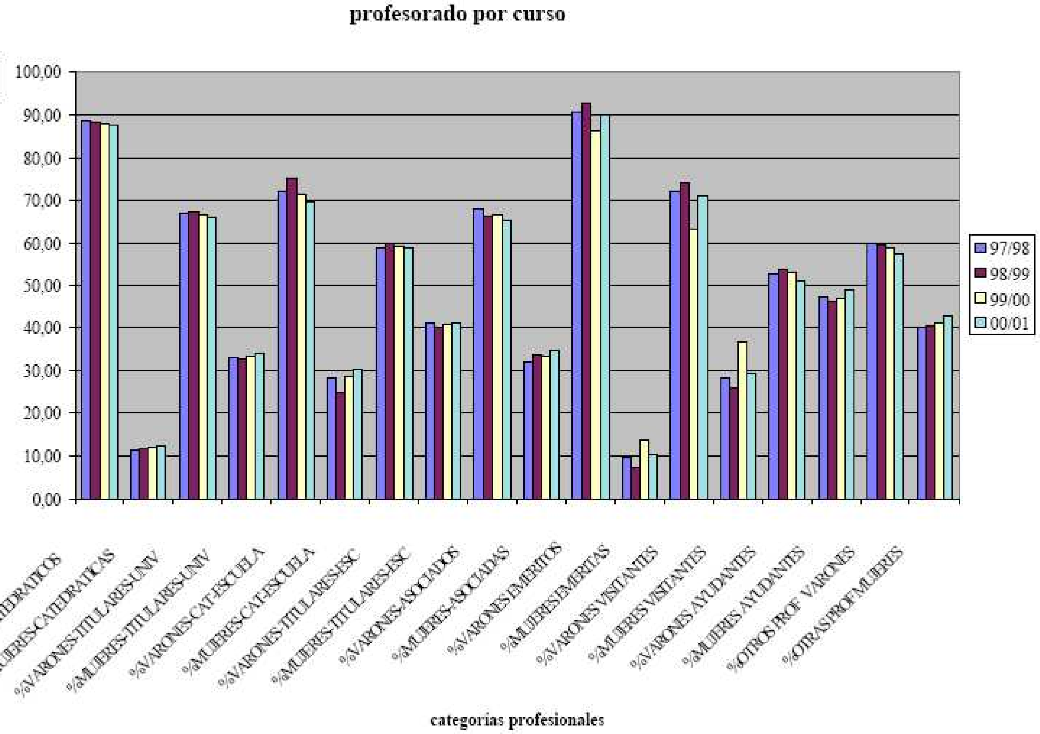
Brussels, 1927



post-graduate students,
by gender

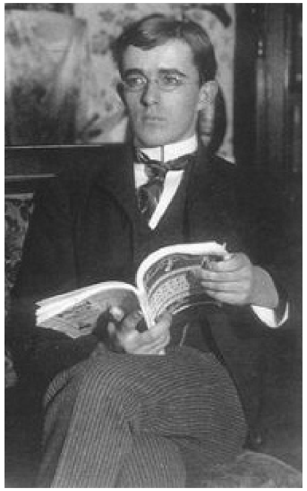


students obtaining a PhD degree,
by gender



professional categories at Spanish Universities,
by gender

Solvay Conference, 1927

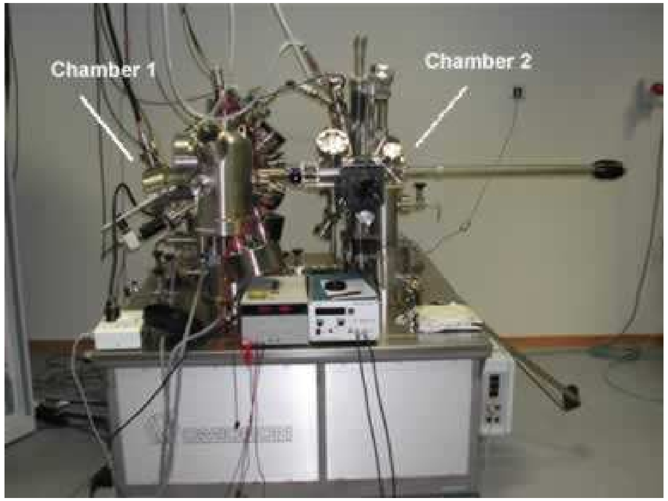


Irving Langmuir

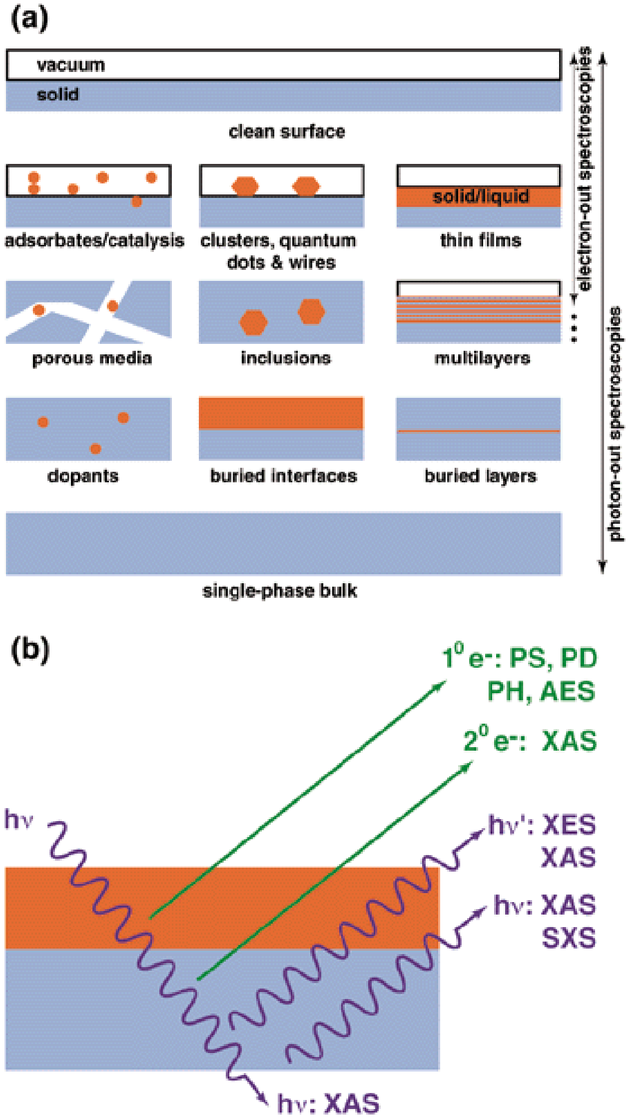
… and a home-made movie, shot at the meeting by Langmuir.

experimental techniques in surface science

- diffraction techniques (**LEED**, XRD, RHEED)
- electron spectroscopies (**UPS**, **XPS**, AES)
- ion-beam techniques (HAS, LEIS, SIMS)
- desorption spectroscopies (TPD)
- tunneling microscopies (STM, STS, AFM)
- molecular beams
- etc.



photoemission – related experimental techniques in the study of surfaces



Low energy electron diffraction (LEED)

In **1927** at Bell Labs, Clinton **Davisson** and Lester **Germer** fired slow moving electrons at a crystalline nickel target. The angular dependence of the reflected electron intensity was measured, and was determined to have the same diffraction pattern as those predicted by Bragg for X-rays.

The Davisson–Germer experiment provided a critically important confirmation of the de Broglie hypothesis that particles, such as electrons, could behave as waves. More generally, it helped cement the acceptance of quantum mechanics and of Schrödinger's wave equation.

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Davisson and Germer published notes of their electron diffraction experiment result in *Nature* and in *Physical Review* in 1927. Just one month after Davisson and Germer's work appeared on *Nature*, Thompson and Reid published their electron diffraction work with higher kinetic energy (thousand times higher than the energy used by Davisson and Germer) in the same journal.

Second Series *December, 1927* *Vol. 30, No. 6*

THE

PHYSICAL REVIEW

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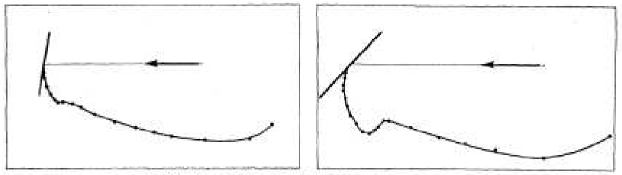
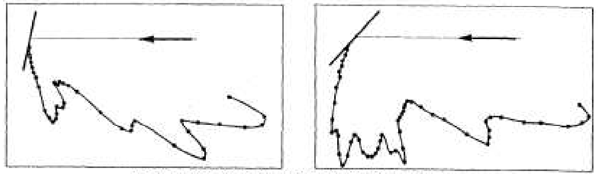
By C. Davisson and L. H. Germer

Abstract

The intensity of scattering of a homogeneous beam of electrons of adjustable speed incident upon a single crystal of nickel has been measured as a function of direction. The crystal is cut parallel to a set of its {111}-planes and bombardment is at normal incidence. The distribution in latitude and azimuth has been determined for such scattered electrons as have lost little or none of their incident energy.



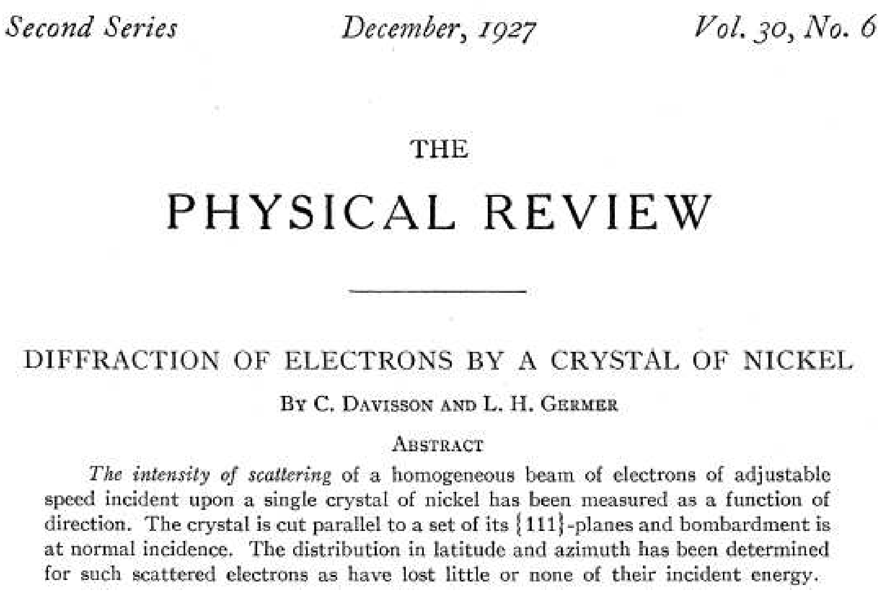
SCATTERING OF 75 VOLT ELECTRONS FROM A BLOCK OF NICKEL (MANY SMALL CRYSTALS)



SCATTERING OF 75 VOLT ELECTRONS FROM SEVERAL LARGE NICKEL CRYSTALS

THE investigation reported in this paper was begun as the result of an accident which occurred in this laboratory in April 1925. At that time we were continuing an investigation, first reported in 1921,[1] of the distribution-in-angle of electrons scattered by a target of ordinary (polycrystalline) nickel. During the course of this work a liquid-air bottle exploded at a time when the target was at a high temperature; the experimental tube was broken, and the target heavily oxidized by the inrushing air. The oxide was eventually reduced and a layer of the target removed by vaporization, but only after prolonged heating at various high temperatures in hydrogen and in vacuum.

When the experiments were continued it was found that the distribution-in-angle of the scattered electrons had been completely changed. Specimen



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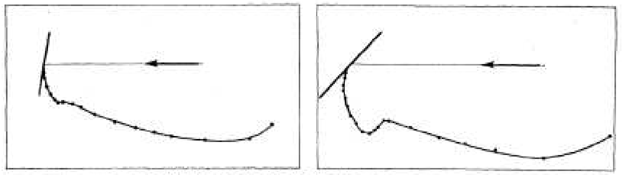

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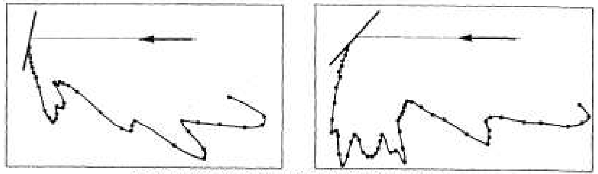

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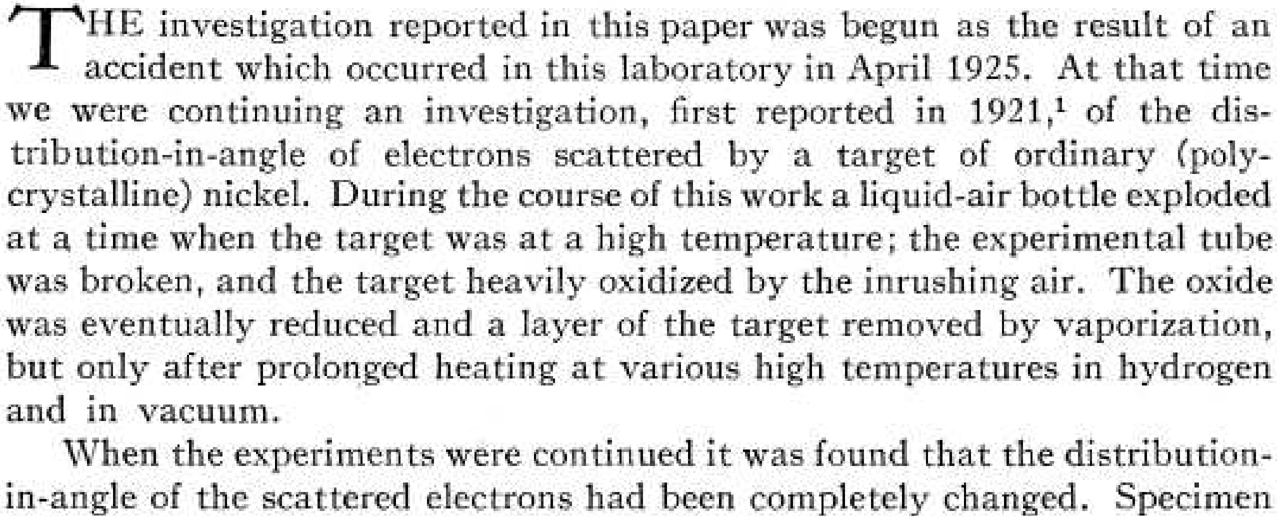

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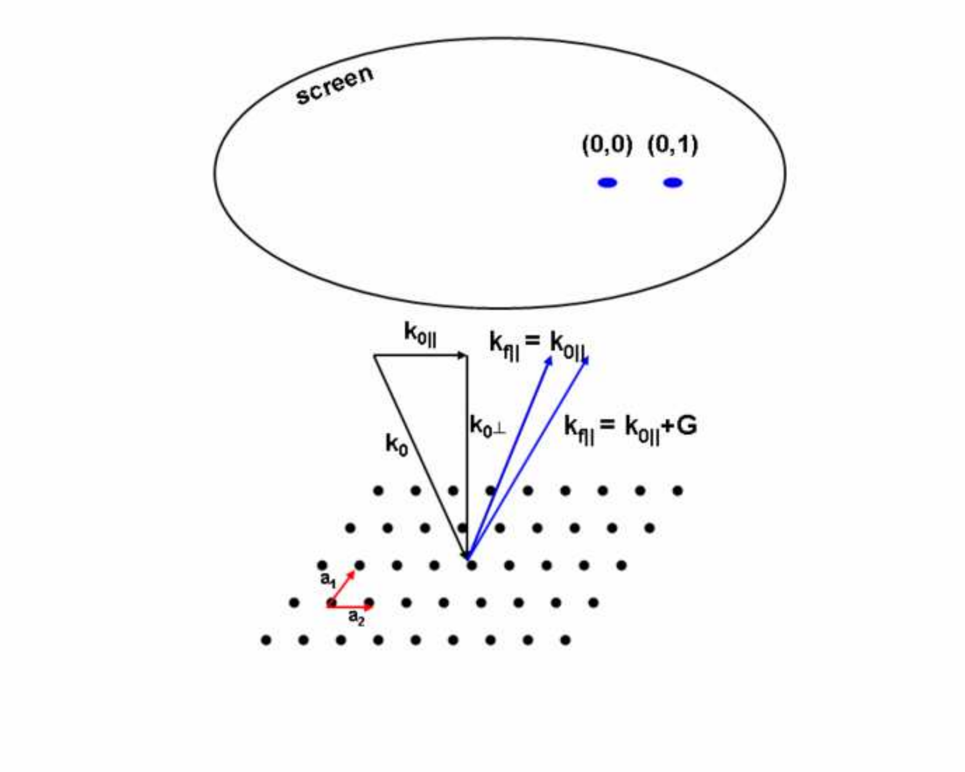
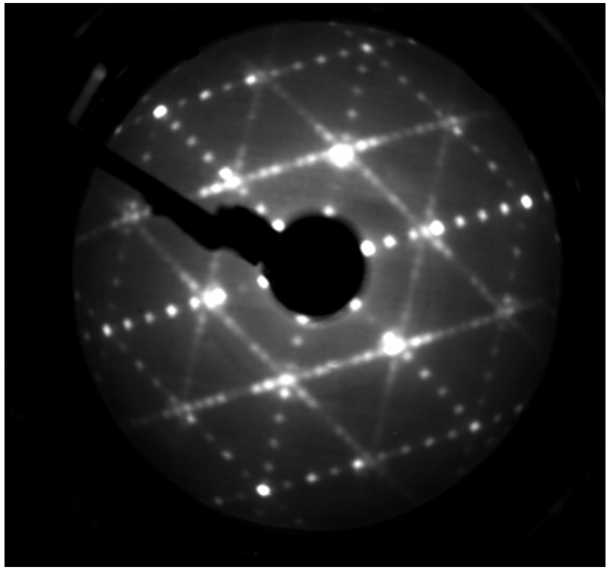
serendipity!

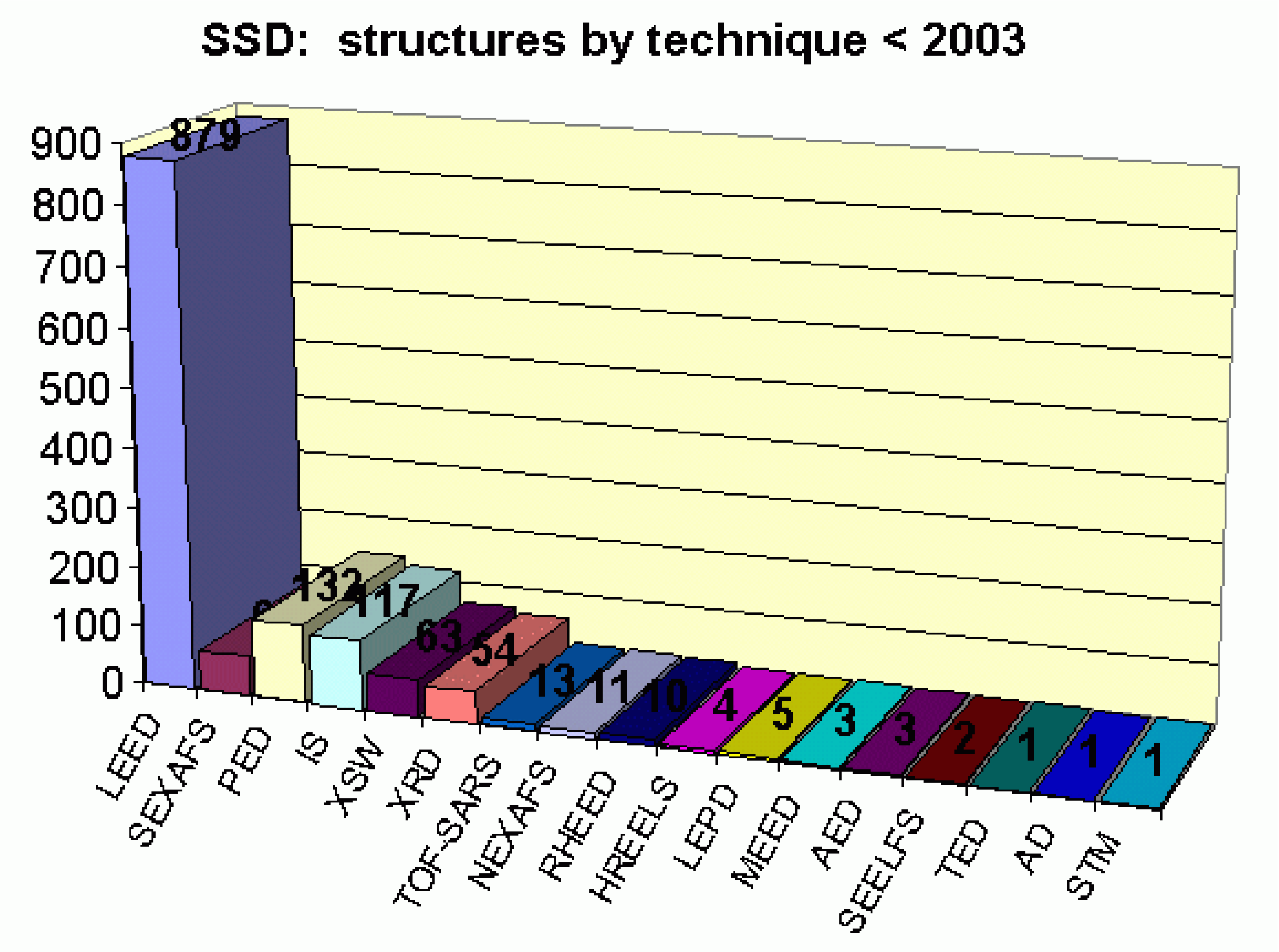
Low energy electron diffraction (LEED)





It took almost 40 years for LEED to become a tool for structure determination

LEED has been the dominant tool to determine surface structures



M. A. Van Hove, www.sitp.lbl.gov

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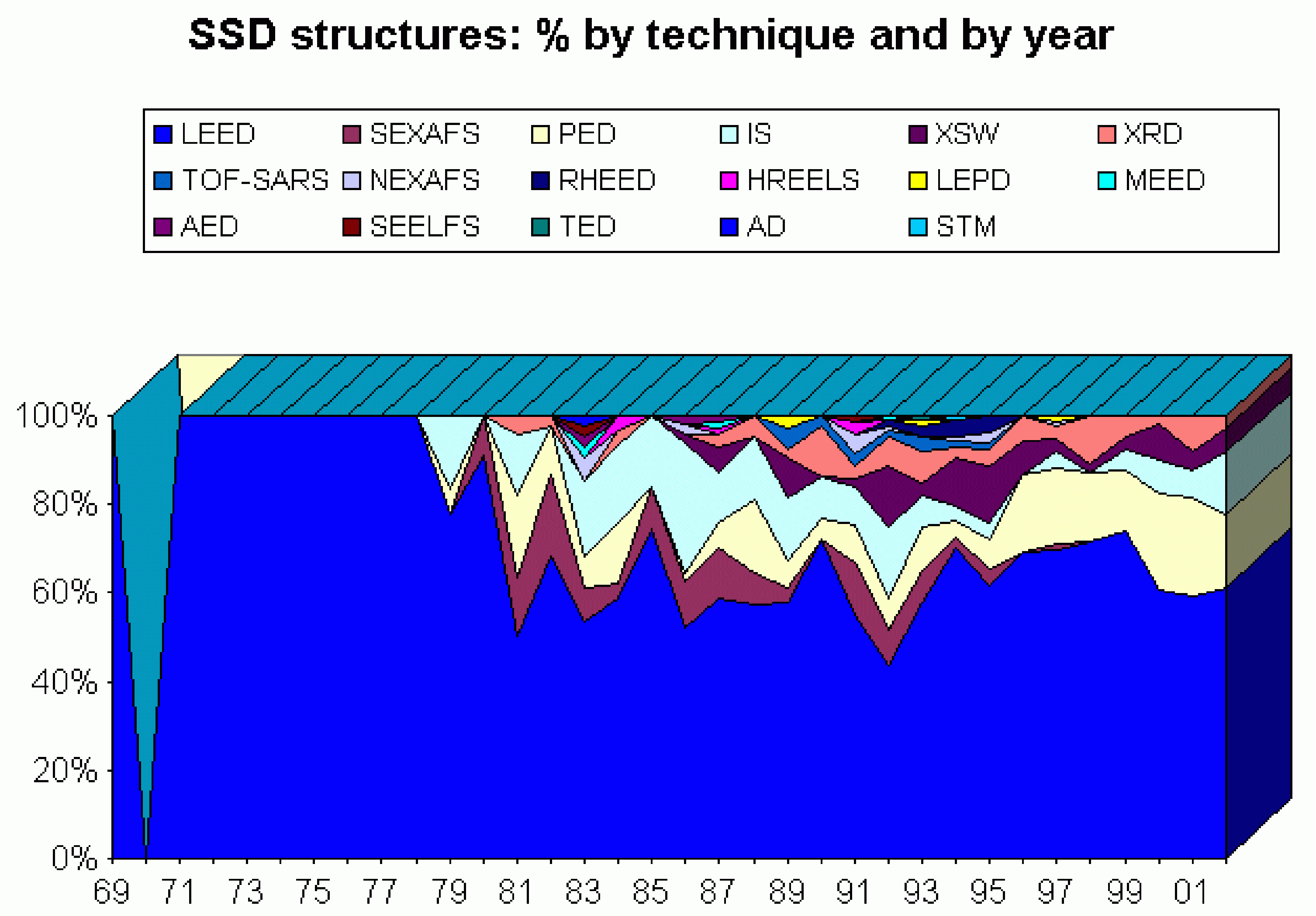
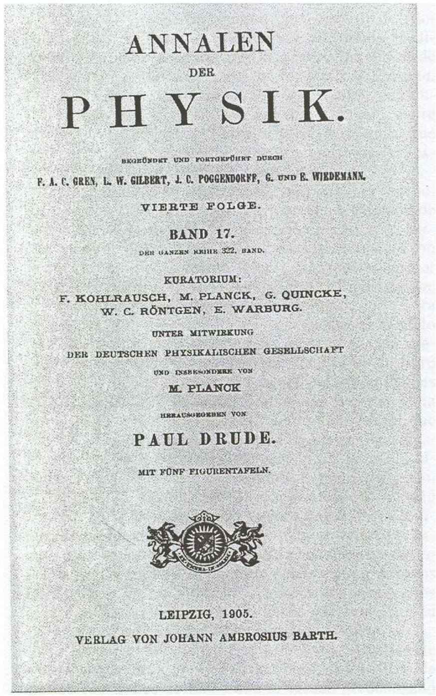


M. A. Van Hove, www.sitp.lbl.gov

photoelectric effect and photoemission

In 1905, Einstein described the photoelectic effect as the emission of electrons caused by the absorption of light quanta


ANNALEN
DER
PHYSIK.
BEGRÜNDET UND FORTGEFÜHRT DURCH
F. A. C. GREN, L. W. GILBERT, J. C. POGGENDORFF, G. UND E. WIEDEMANN.
VIERTE FOLGE.
BAND 17.
DER GANZEN REIHE 322. BAND.
KURATORIUM:
F. KOHLRAUSCH, M. PLANCK, G. QUINCKE,
W. C. RÖNTGEN, E. WARBURG.
UNTER MITWIRKUNG
DER DEUTSCHEN PHYSIKALISCHEN GESELLSCHAFT
UND INSBESONDERE VON
M. PLANCK
HERAUSGEGEBEN VON
PAUL DRUDE.
MIT FÜNF FIGURENTAFELN.

LEIPZIG, 1905.
VERLAG VON JOHANN AMBROSIUS BARTH.

On a heuristic viewpoint concerning the generation and conversion of light, Ann. Phys. **17**, 132 (1905).

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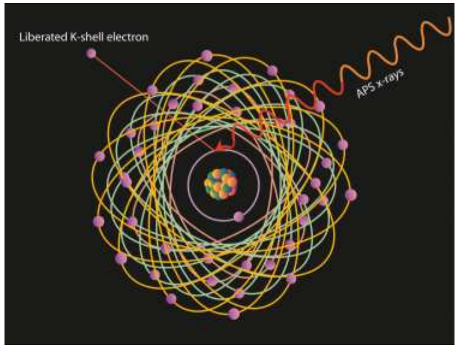

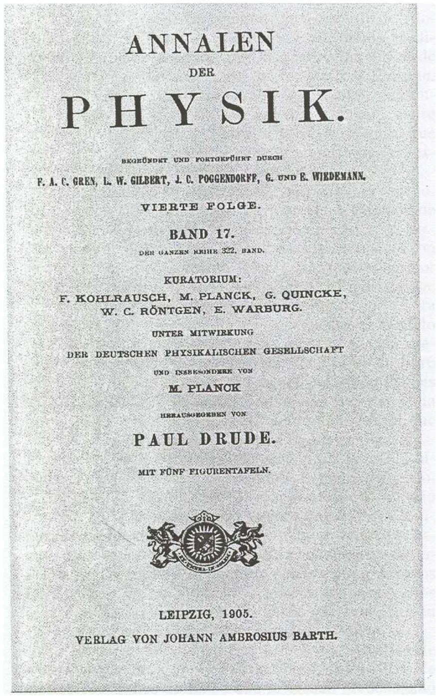

ANNALEN
DER
PHYSIK.
BEGRÜNDET UND FORTGEFÜHRT DURCH
F. A. C. GREN, L. W. GILBERT, J. C. POGGENDORFF, G. UND E. WIEDEMANN.
VIERTE FOLGE.
BAND 17.
DER GANZEN REIHE 322. BAND.
KURATORIUM:
F. KOHLRAUSCH, M. PLANCK, G. QUINCKE,
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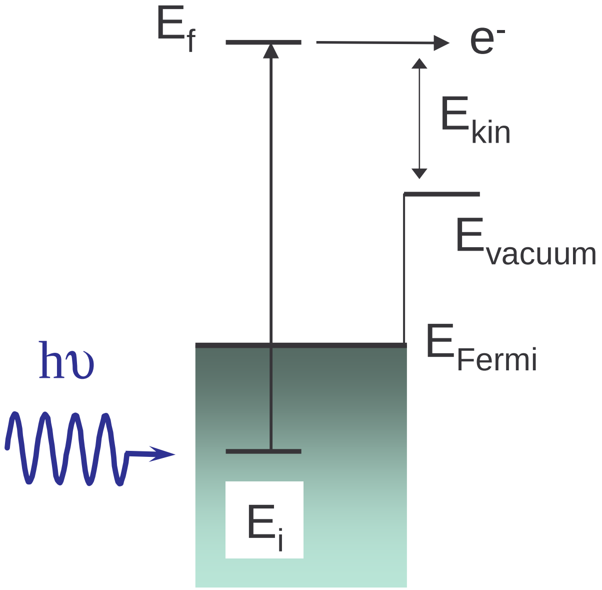
UNTER MITWIRKUNG
DER DEUTSCHEN PHYSIKALISCHEN GESELLSCHAFT
UND INSBESONDERE VON
M. PLANCK
HERAUSGEGEBEN VON
PAUL DRUDE.
MIT FÜNF FIGURENTAFELN.

LEIPZIG, 1905.
VERLAG VON JOHANN AMBROSIUS BARTH.

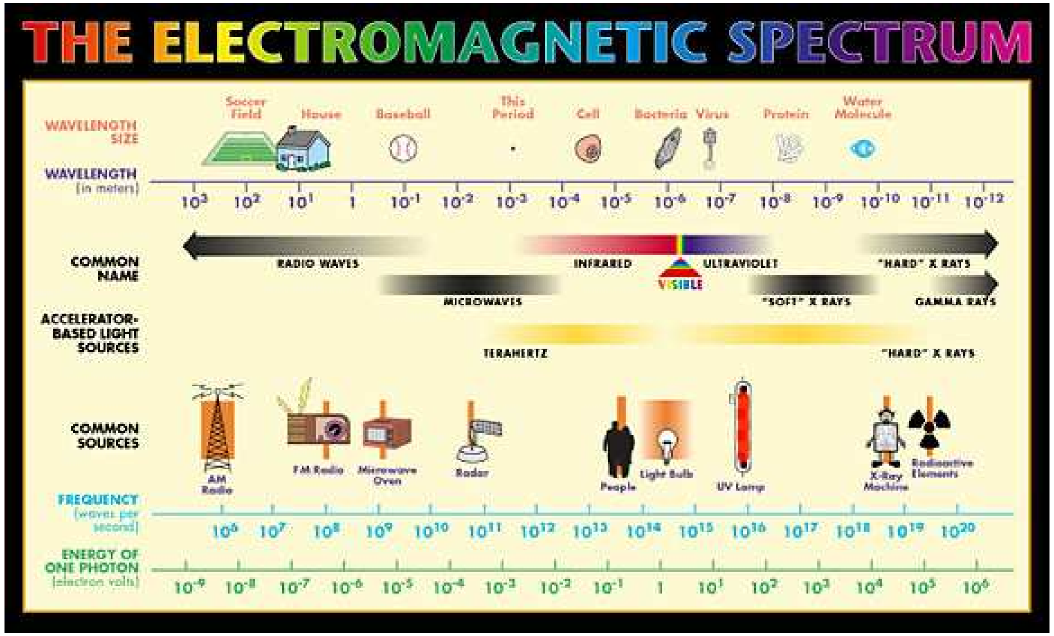
On a heuristic viewpoint concerning the generation and conversion of light, Ann. Phys. **17**, 132 (1905).

photons in à electrons out

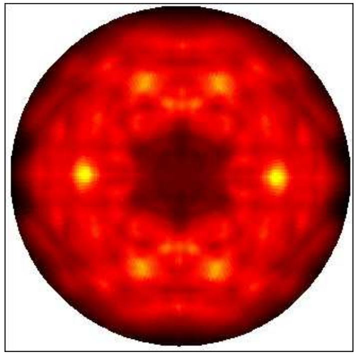
$$h\upsilon = E_{initial} - E_{final} = E_{binding} + E_{kinetic}$$



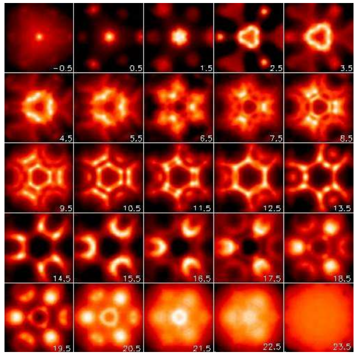
photoelectric effect and photoemission



synchrotron sources



X-rays:
structural properties

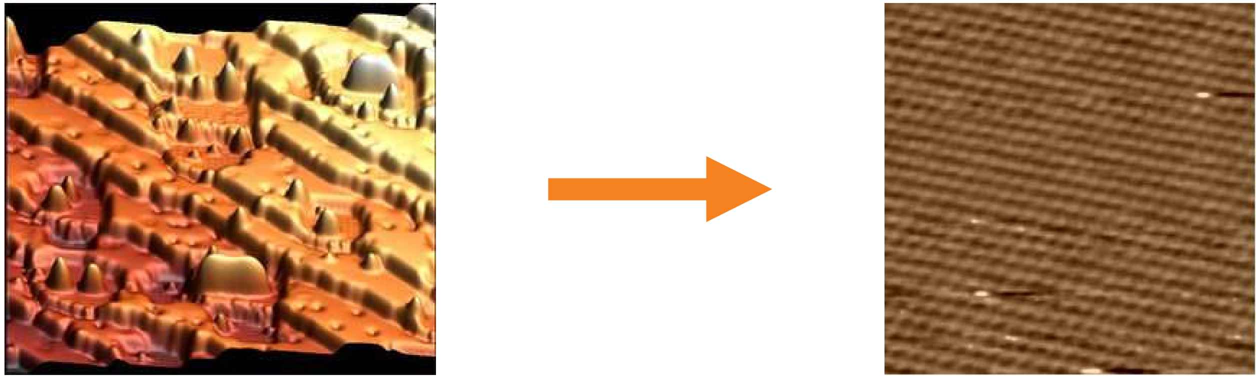


UV light:
electronic properties

the birth of surface science (as we understand it today)

Surface science, as it is understood today, started in the late 1960’s, mostly because of the confluence of three factors:

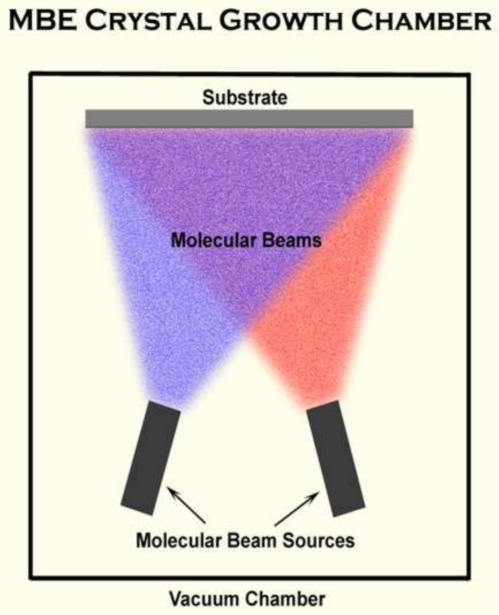
- Arrival of ultra high vacuum (UHV, i.e., $P < 10^{-7}$ Pascal) technology.
- Availability of single crystal samples.
- Improvements on the theory of electron-solid interactions.



from rough uncontrolled surfaces to crystalline clean surfaces

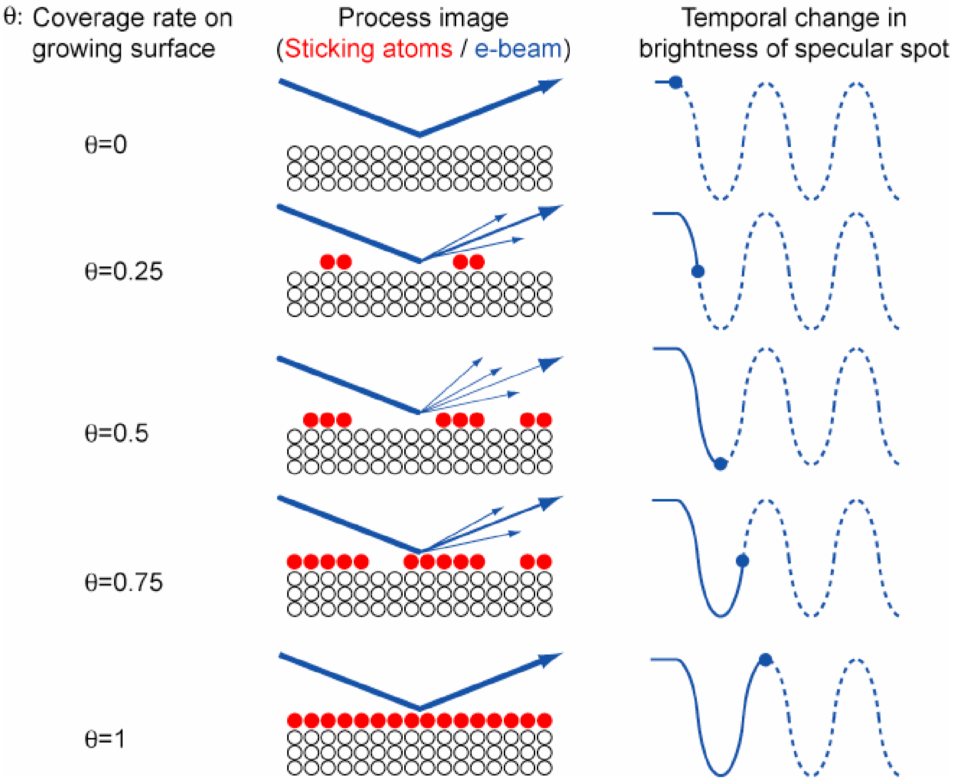
molecular beam epitaxy (MBE) and semiconductor electronics

Molecular beam epitaxy (MBE) started in the early 1970s as a mean of growing high-purity epitaxial layers of compound semiconductors. It was mostly developed at Bell Labs by J. R. Arthur and A. Y. Cho. Because of the high degree of control possible with MBE, it is a valuable tool in the development of sophisticated electronic and optoelectronic devices.



- •evaporation at very low deposition rates
- •typically in ultra-high vacuum
- •very well controlled
- •grow films with good crystal structure
- •expensive
- •often use multiple sources to grow alloy films
- •deposition rate is so low that substrate temperature does not need to be as high

molecular beam epitaxy (MBE) and semiconductor electronics

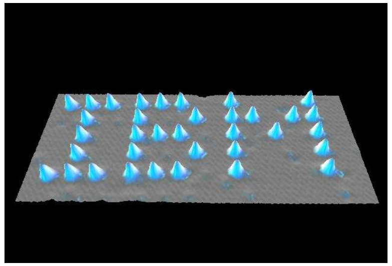


RHEED intensity oscillations can be used as an accurate, quick, direct measure of the growth rates in MBE. When growth is initiated on a smooth GaAs surface, the intensity of the RHEED pattern, especially the specular reflection, starts to oscillate. The oscillation frequency corresponds to the monolayer growth rate

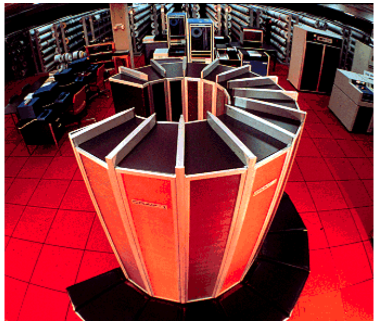
Surface Science: The First Thirty Years, written in 1992-1993, describes a field in which the basic techniques for the determination of **surface structure and composition** have been validated on **simple systems** such as clean low-index single crystal surfaces and monolayers of adsorbates thereon. Surface-phase diagrams of adsorbate systems were being mapped and the dynamics of surface diffusion were followed by field ion microscopy. Initial results on more complex systems such as steps on surfaces, buried interfaces, and the dynamics of simple surface chemical reactions were beginning to be reported. Although the scanning tunneling microscope (STM) had been invented, its application for spectroscopy was in its infancy. The extension of scanning probe notions to atomic force microscopy (AFM) was in a highly exploratory state.

C. B. Duke, PNAS 100, 3858 (2003)

... and then the STM
grew up



and computing
power too



"The importance of surfaces and interfaces cannot be overstated, with their reach extending from the hardware of the digital age to the processes of life. The past half-century has seen the development of a full and varied toolkit for characterizing them. This toolkit is now serving a growing interdisciplinary community and is providing a powerful platform for scientific research and manufacturing technology."

Dave Allara, Penn State University (Nature, 2005) http://dipc.ehu.es/ricardo/master/nanohistory.htm