

Surface phenomena at the micro- and nano- scale

Master's Degree in Materials Science



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A.A. 2024-2025

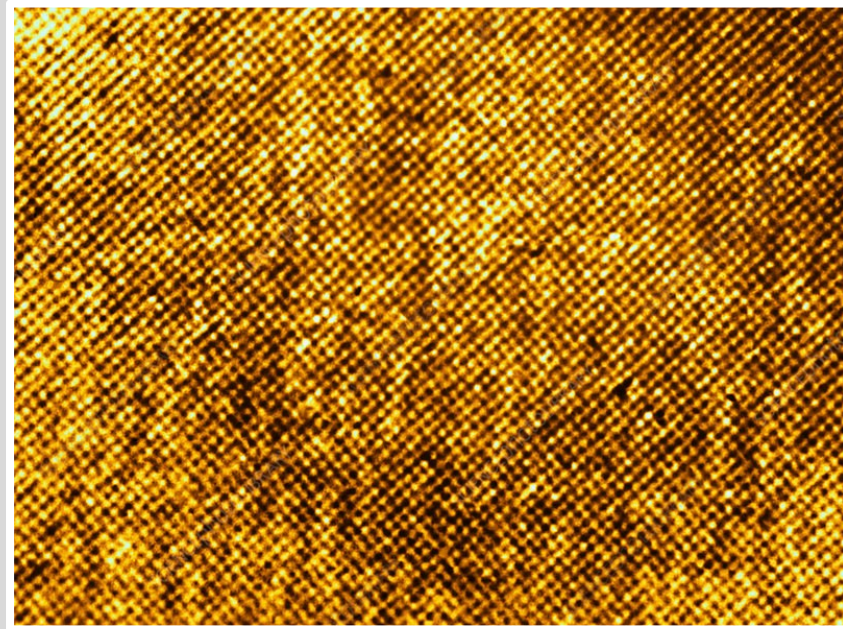
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1. Introduction to surfaces & surface science



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TABLE OF CONTENTS

1. Definition of interface and surface
2. Surface science
3. Thermodynamic at surfaces
 - 3a. Surface tension for liquids
 - 3b. Minimization of the surface tension for solids
 - Adsorption from the gas phase
 - Relaxation and reconstruction
 - Assuming a spherical shape
4. Nano-scale effects on the materials properties

DEFINITION OF SURFACE

What is an interface? And a surface?

An **interface** is the boundary between two phases.

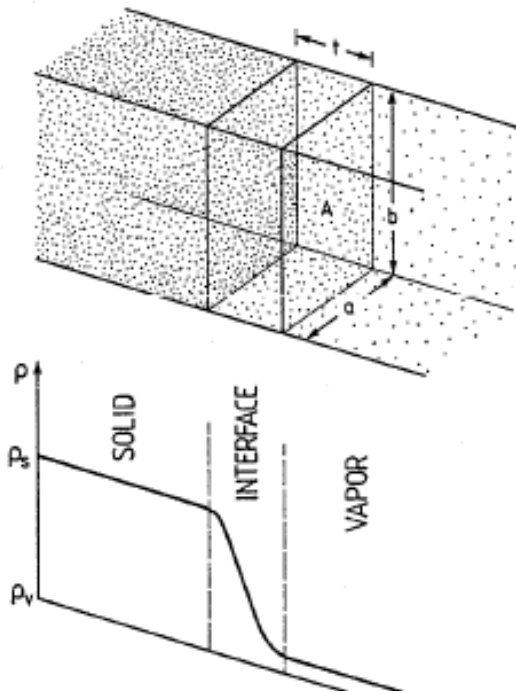


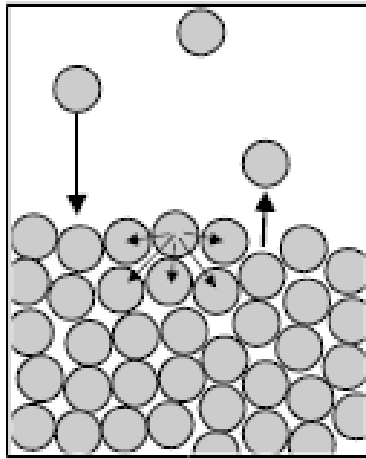
Fig.3.1. Schematic description of a solid/vapor interface (area A , thickness t). The solid is in thermodynamic equilibrium with its vapor. In the interface region the density ρ of the material changes gradually from its solid value ρ_s to its vapor value ρ_v .

At the border of a solid or liquid in contact with vapour there is usually no abrupt change in density, but more or less continuous transition from high density to low density. The interface consists either of evaporating bulk material or condensing material from the gas phase.

The words **interface** and **surface** are often used synonymously, although *interface* is preferred for the boundary between two condensed phases and in cases where the two phases are named explicitly, e.g. the solid/gas interface, but the surface of a solid.

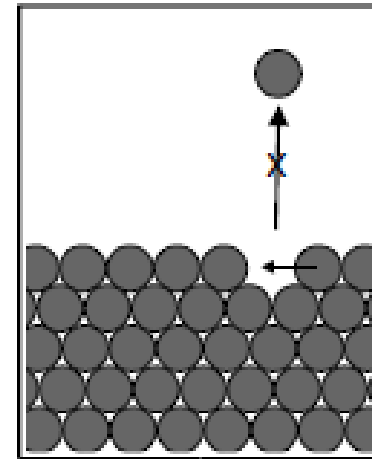
Different interface/surface scenarios

liquid / vapor



- liquid highly mobile & disordered
- constant evaporation and recondensation at surface

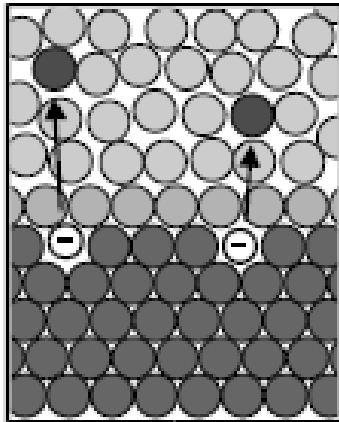
solid / vapor (vacuum)



- solid highly immobile
- crystalline solids highly ordered / structured
- usually no evaporation of surface atoms & molecules, only lateral diffusion (depends on T)

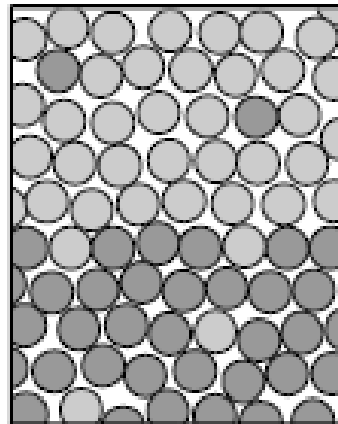
Different interface/surface scenarios (cont.)

solid / liquid



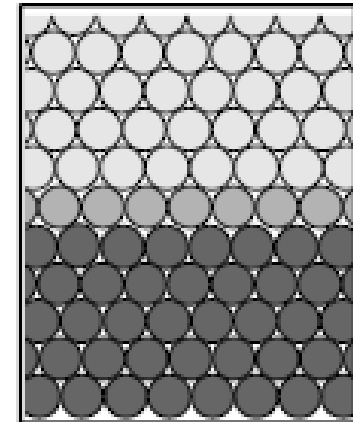
- liquid can dissolve surface atoms \rightarrow may lead to surface charges
- liquid molecules at the interface can be much higher ordered than in the bulk

liquid₁ / liquid₂



- both phases highly mobile \rightarrow shape of interface is controlled by surface tension
- depending on solubility molecules will migrate from one phase to the other \rightarrow controlled by chemical potential (partition coeff.)

solid₁ / solid₂



- if two crystalline solids are in atomic contact the different lattice constants will generate strain @ interface
- if both materials react together new compound will be formed in contact region \rightarrow **interphase**
- at high T interdiffusion possible (e.g. Cr & Au)

When does the surface matter?

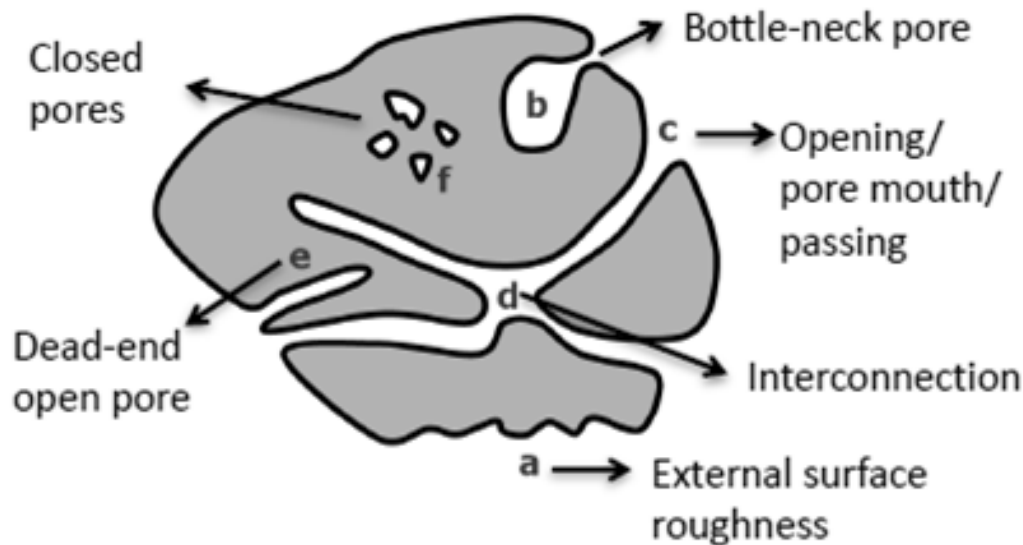
The surface of an object determines its optical appearance, stickiness, wetting behaviour, frictional behaviour, and chemical reactivity.

- In *large* objects with small surface area (A) to volume (V) ratio (A/V) the physical and chemical properties are primarily defined by the bulk (inside).
- In *small* objects with a large A/V ratio the properties are strongly influenced by the surface.

Surface differs substantially from the interior of the solid both in chemical composition and physical properties.

Internal surface and porosity

Finely divided solids possess not only a geometrical surface, as defined by the different planes exposed by the solid, but also **an internal surface** due to the primary particles aggregation, which generates pores of different size according to both the nature of the solid and origin of the surface.



Porosity (%)	$\frac{\text{Volume of pores}}{\text{Total volume of solid}} \times 100$
Specific Surface Area (m ² /g)	$\frac{\text{Total surface area}}{\text{mass of solid}}$
Specific Pore Volume (cm ³ /g)	$\frac{\text{Total volume of pores}}{\text{mass of solid}}$

It is important to discriminate between external and internal surface area. The pores must be characterized in terms of pore volume, pore size and pore size distribution

Classification of pores

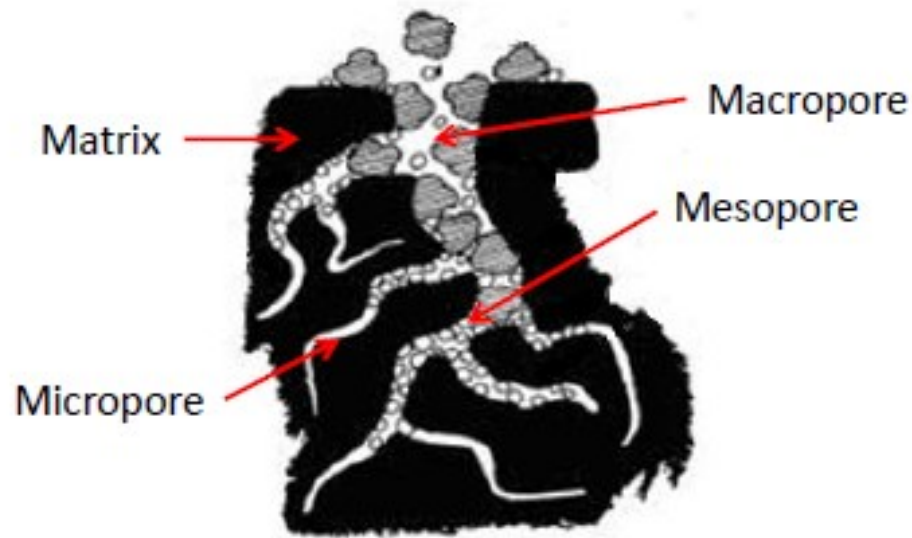
Pores are classified on the basis of their width w , which represents either the diameter of a cylindrical pore, or the distance between the sides of a slit-shaped pore:

- **Micropores:** $w < 20 \text{ \AA}$ (2 nm)
- **Mesopores:** $20 \text{ \AA} \leq w \leq 500 \text{ \AA}$ (2 and 50 nm)
- **Macropores:** $w > 500 \text{ \AA}$ (50 nm)



Classification of pores (cont.)

Some materials, like charcoal and silico-alumina, have irregular pores with widely variable diameters in a normal shape. Conversely, other materials such as zeolites and clay minerals are entirely micro- or meso-porous, respectively. In these cases, the porosity does not arise from the primary particles aggregation, but is an intrinsic structural feature of the solid material.



External, internal, and nano-surface

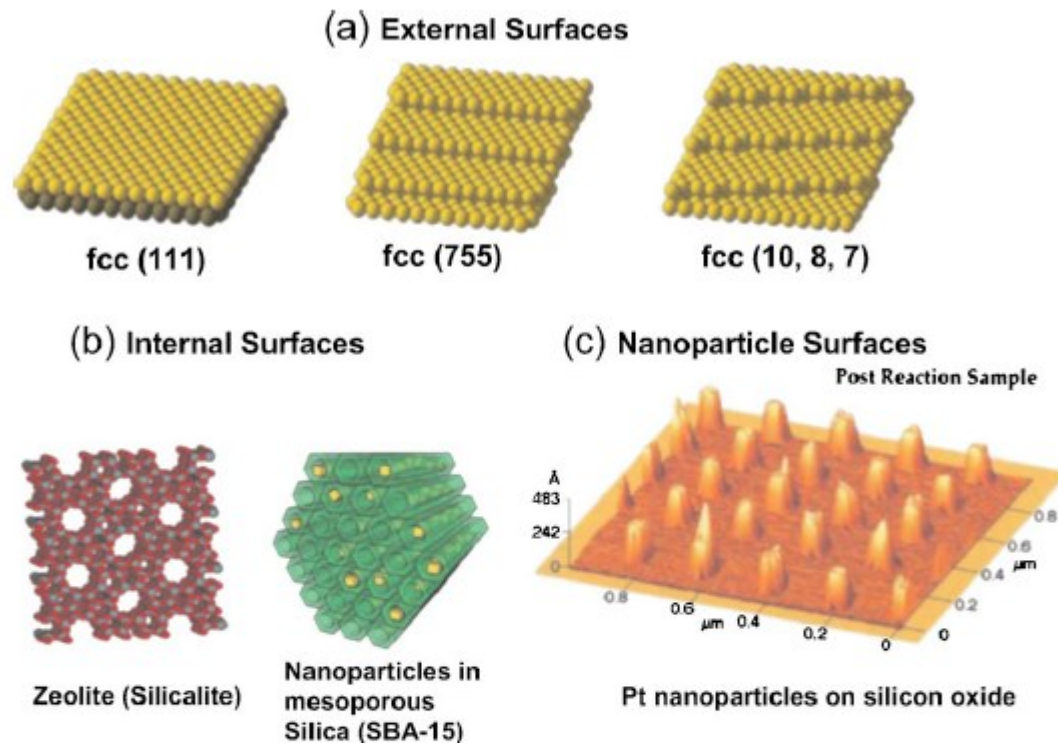


FIG. 3. (Color online) Three types of surfaces, (a) external surfaces such as single crystals with different surface phases, (b) internal surfaces such as Zeolite or SBA-15, where most of the surface area is located inside the micropores or mesopores. Zeolite has ordered pores (size less than 2 nm) with interconnections. SBA-15 has ordered pores with 2–50 nm distribution, and (c) nanoparticles of platinum. The atomic force microscopy (AFM) image of Pt nanoparticles on SiO_2 fabricated with electron beam lithography is shown.

TABLE OF CONTENTS

1. Definition of interface and surface
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Why surface science?

Surface science in everyday's life

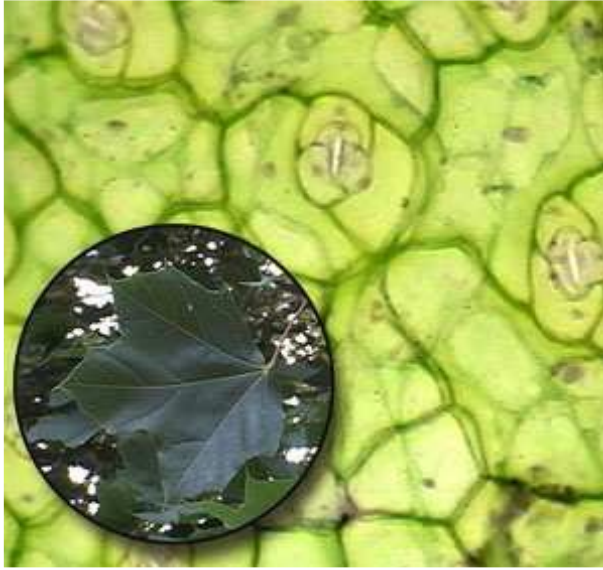
Why surface science?

The main drivers of surface science

- Catalysis
- Micro/nanoelectronics
- Energy (photovoltaics, fuel cells...)

- Biological issues (tissue/prosthetic compatibility, membrane chemistries...)
- Neuronetworks, biological and not

Surface, complexity, functionality

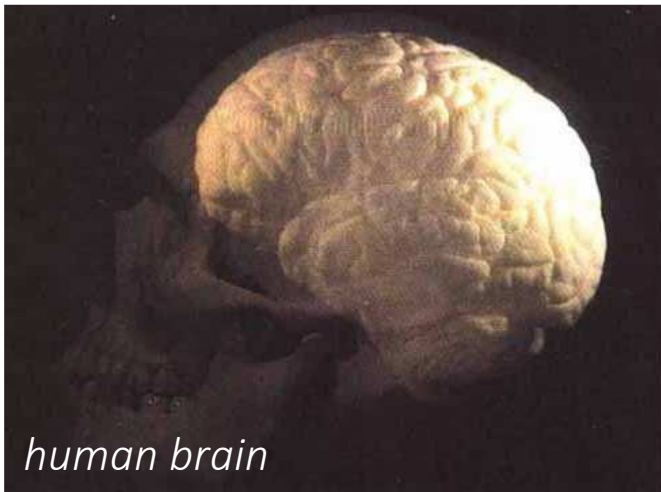


green leaf (primary site of photosynthesis in plants)

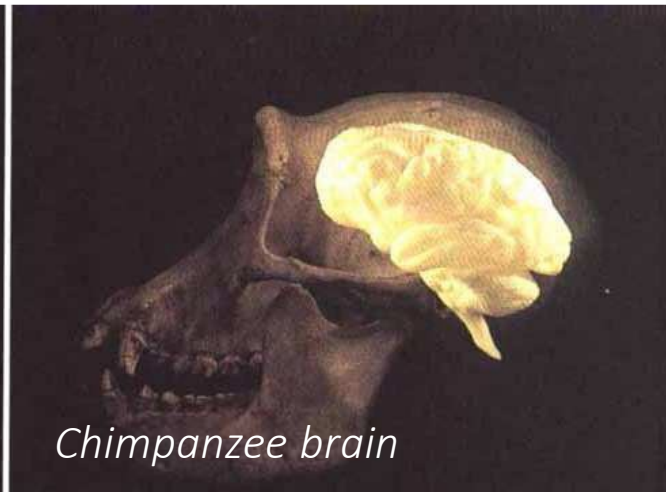
Surfaces and interfaces are the favorite media of **evolution**. Both photosynthetic and biological systems evolve and improve by ever increasing their interface area or their interface/volume ratio.

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



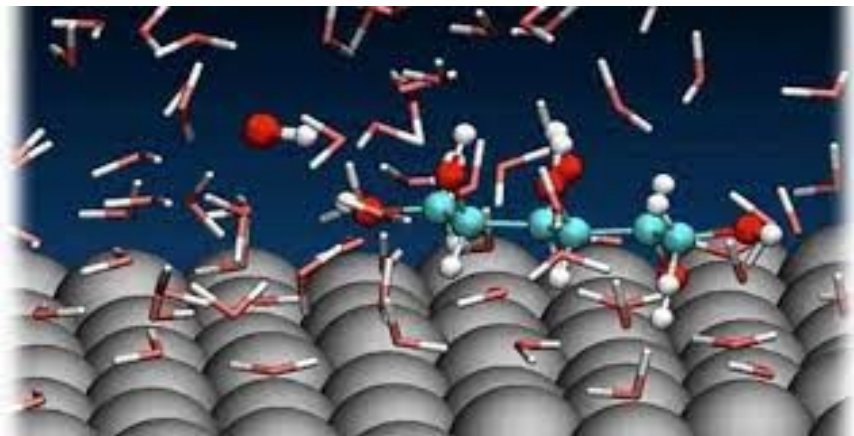
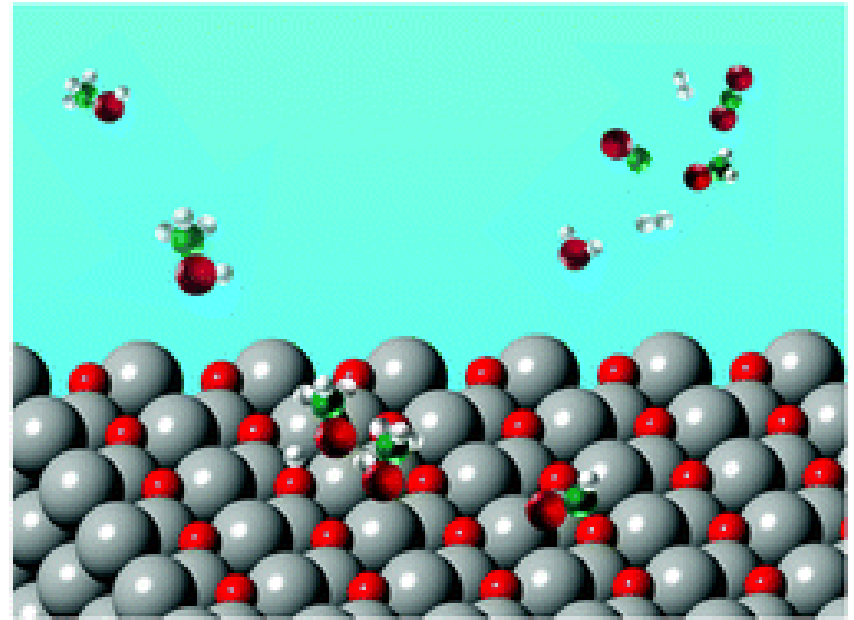
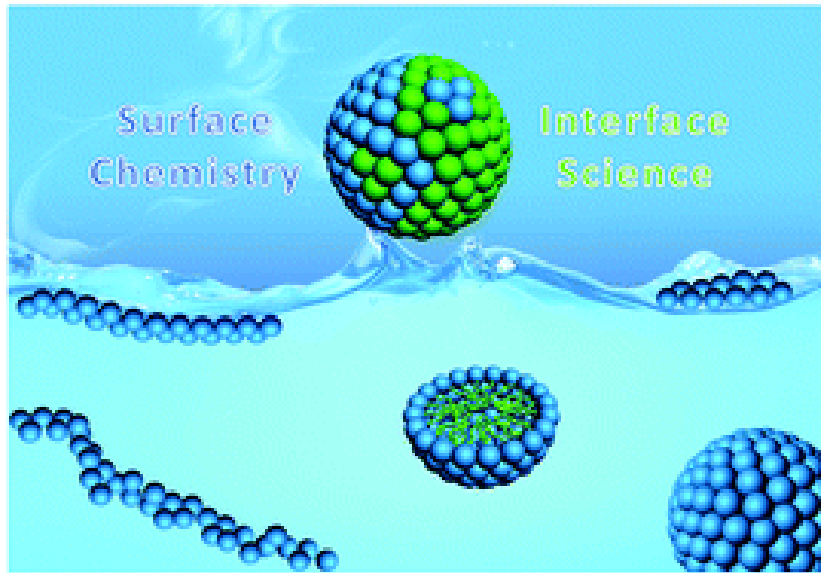
Chimpanzee brain

Surface science

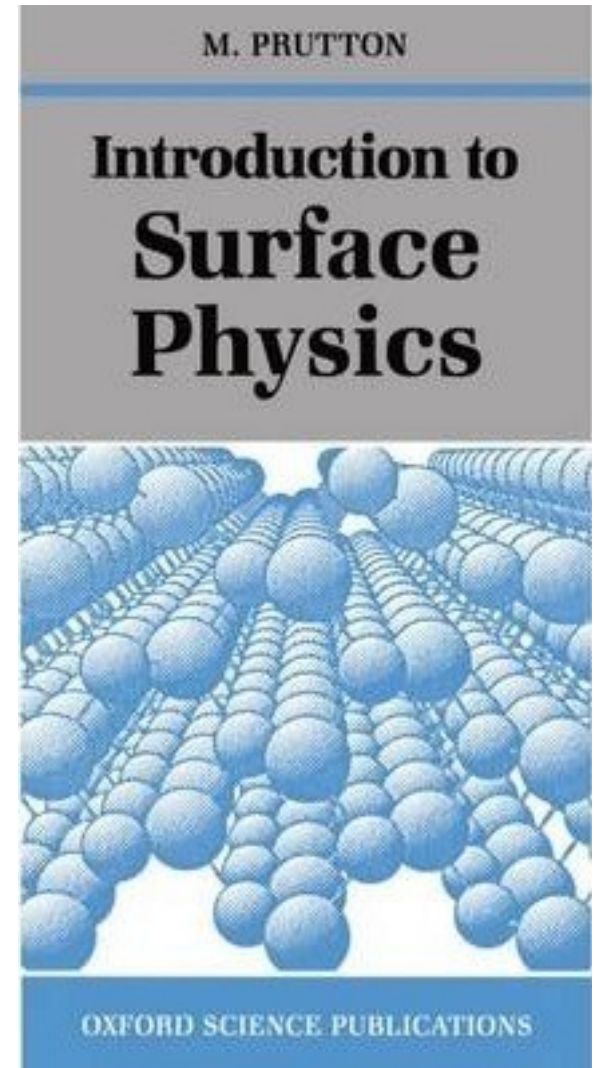
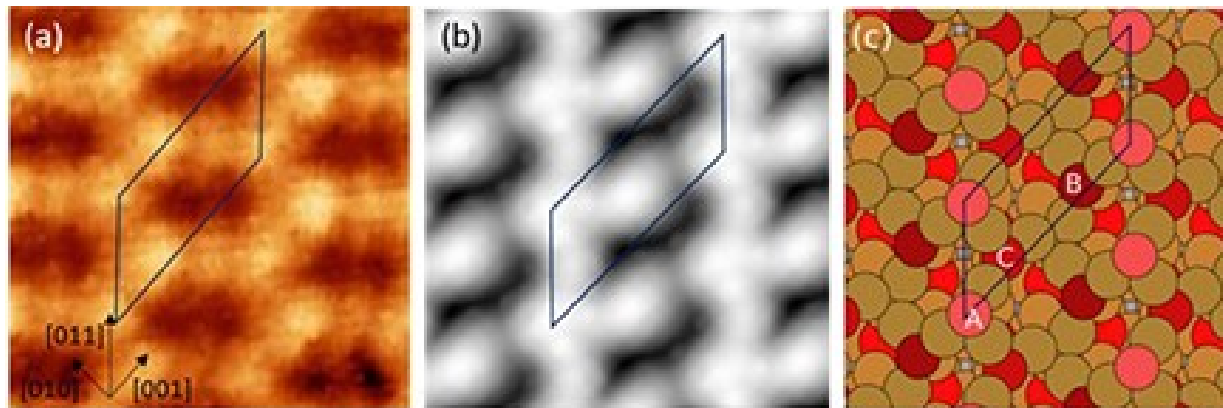
Surface science is the study of physical and chemical phenomena that occur at the surfaces. It includes the fields of surface chemistry and surface physics.

Very often, surface physics overlaps with surface chemistry, particularly at the very ultimate atomic or molecular scale, where physics and chemistry are no longer distinct by the traditional definition.

Surface chemistry in the web



Surface physics on the web



Surface physics

Surface physics can be roughly defined as the **study of physical changes that occur at interfaces.**

Some of the things investigated by surface physics include surface states, surface diffusion, surface reconstruction, surface phonons and plasmons, epitaxy and surface enhanced Raman scattering, the emission and tunneling of electrons, spintronics, and the self-assembly of nanostructures on surface.

- What does the new surface look like?
- What is the energy required to create the two new surfaces?
- Is the surface identical to an internal crystal plane of the un-cleaved solid? Or do atoms move to new positions forming a structure not found in the bulk of a single crystal?
- What kind of defects exist – steps, kinks, vacancies?
- What are their concentrations and how can they be minimized?

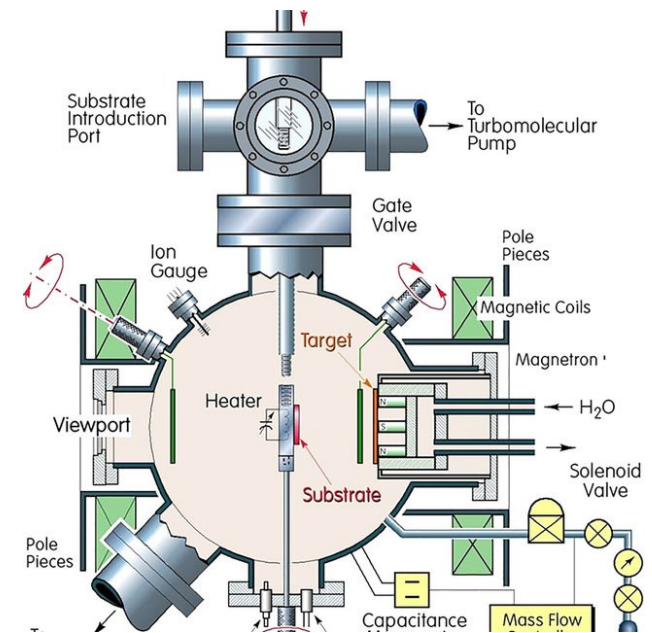
What is this?



Early surface physics and the need for UHV

The ideal situation in early surface physics was a solid surface created by cleaving a solid body into two halves, thereby exposing two surfaces, without any interference from surrounding gas or liquid. In other words, the cleavage had to occur in a **perfect, ultra-high vacuum**.

A more common way, in practice, to create the clean surface was to mount a single crystal, cut and polished to expose a low index crystal plane, in a vacuum chamber, pumping down to an ultra-high vacuum, and then removing any surface dirt, like oxides or contamination, by a combination of **repeated ion sputtering and annealing** until a well-ordered single crystal surface was exposed.



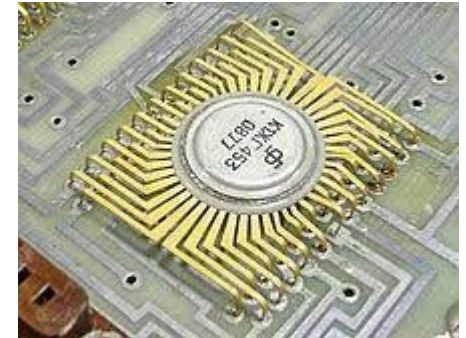
Why do we need a vacuum?

- Atoms at the surface directly interact with gases in the environment
- Reactions occur at the surface that don't occur in the bulk

A boost from advances in microelectronics

At the dawn of this era, simple metals and semiconductors were the main objects of investigation. Successively, over several decades, more complex surfaces were addressed such as alloys, oxides, carbides and polymers. Also, interactions with gases and liquids were approached, and similar questions were asked for these ad-atoms and ad-molecules as for the clean surface.

Pure surface physics got a boost in the late 1950s and through the 60s from **developments in semiconductor technology and microelectronics**.



Nobel Prize in Physics

1956: Bardeen, Brattain and Shockley for the *transistor*.

2000: Kilby, for the *integrated circuit* (IC).

Development of UHV technology

Integrated circuits and their active elements, including transistors and diodes, were strongly dependent on the understanding and processing of clean surfaces, particularly silicon and silicon oxides.

These needs resulted in the **rapid development of ultra-high vacuum (UHV) technology**, to be able to prepare and study clean surfaces, and of many new analytical methods to study surfaces.



Nobel Prize in Physics

1937: for *electron diffraction*.

1981: Siegbahn, for *XPS*.

1986: Binnig and Rohrer for *STM and AFM*

2 parallel tracks: surface physics & chemistry

The early situation in pure surface physics contrasted with that in early surface chemistry, the other branch of surface science. In surface chemistry, **the presence of molecules, in either the gas or liquid phase, which could interact with the surface** was a central and inherent ingredient from the beginning.

A famous and early example is heterogeneous catalysis, an active field already at the beginning of the 20th century, both practically and scientifically.

While the classical surface chemistry path and the surface physics path of surface science were quite separate early on, with some but weak interactions, the situation changed gradually from the 1970s onward.

Surface chemistry

Surface chemistry can be roughly defined as the **study of chemical reactions at interfaces**, aiming at modifying the chemical composition of a surface by incorporation of selected elements or functional groups that produce various desired effects or improvements in the properties of the surface or interface. Particularly, the adhesion of gas or liquid molecules to the surface is known as adsorption.

Converging surface physics & surface chemistry

As surface science matured and the knowledge of pure surfaces grew and new methods developed, surface physics began to address a larger diversity of surfaces and more complex surface systems, and included gas-surface and liquid-surface systems, like those of classical surface chemistry.

At the same time, surface chemistry started to employ the theories, methods and concepts of surface physics and the boundaries between surface physics and surface chemistry diminished.

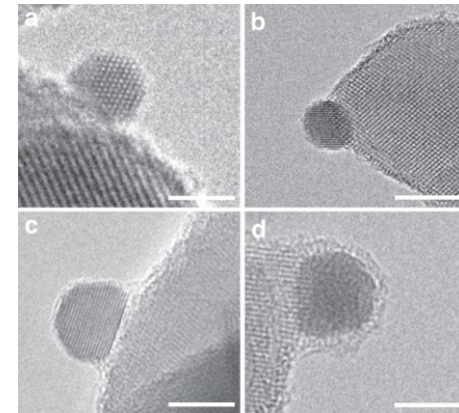
Bridging gaps

Contrast between:

UHV pressure studies in surface physics (at $10^{-6} - 10^{-9}$ torr) and the practical, industrial systems at 1-100 atmospheres

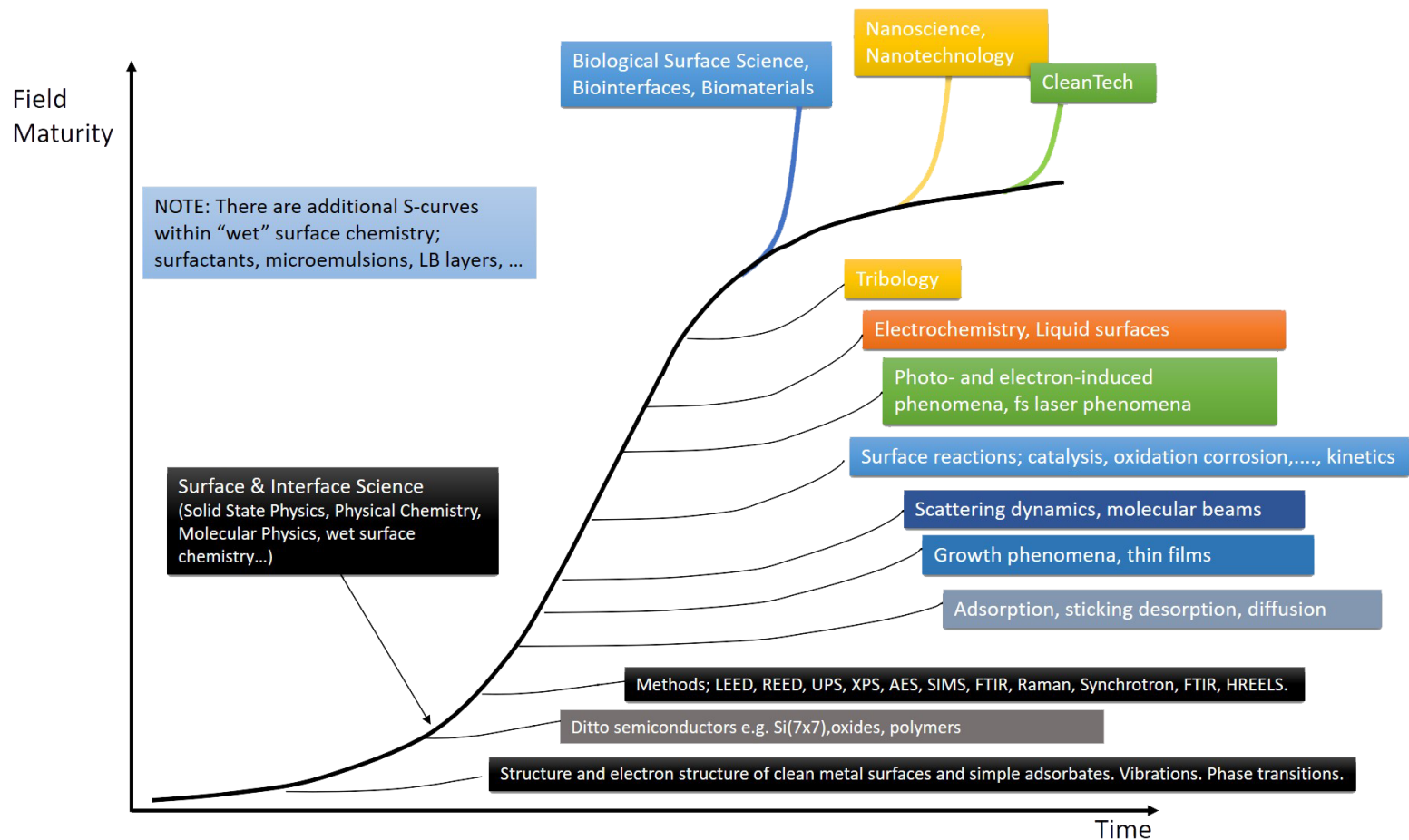


ideal single crystal surfaces as model systems and the practical systems consisting of nm sized particles exposing different facets or being non-crystalline.



Could UHV studies at 10^{-6} torr on single crystals really tell us anything about the situation on nanoparticles on oxide supports at six to nine orders of magnitude higher pressures?

The S-curve evolution of surface science



The S-curve evolution of surface science, from early days to a mature area, and scientific fields that have emerged along the way

The early days of surface science: static properties

In the early development of surface science and particularly in surface physics, the focus was on the “static properties” of simple surfaces. It was challenging enough to describe the surface, with or without adsorbates, in a “frozen” situation, without involving temporal changes and dynamics.

For many years, the determination of structural aspects of adsorbed atoms and molecules, both as single adsorbates and as dense monolayers, and the associated electron structure, was a primary field. Bond positions of atoms, bond lengths, and vibrational properties were in focus together with the associated electron structure aspects, such as bond orbitals, surface band structure and charge distributions.

More complex static systems

Today the position(s), orientation(s) and electron **structure of simple adsorbates**, like, e.g., CO molecules, on single crystal metal surface like Ni, Cu, Pt can be described in atomistic detail and with chemical accuracy in the energies.

Also **“simple” compound surfaces**, like metal oxides, are fairly well described.

Challenges of static systems still remain as the systems addressed become more complex, like molecules with many atoms or more complex compound surfaces. Oxides, carbides, polymers and “soft” surfaces, and biological surfaces like lipid bilayers are now in focus, as are larger, e.g., organic or even biological molecules.

Dynamics: studies of temporal changes

While the static approach addresses the frozen state, the dynamics concern the **time evolution of reversible or irreversible changes of the surface system.**

Examples are adsorption processes and diffusion, reaction, and desorption of adsorbates.

Theoretically, static systems can be described by solving the time-independent Schrödinger equation, while dynamic systems require the even more challenging task to solve the time-dependent equation.

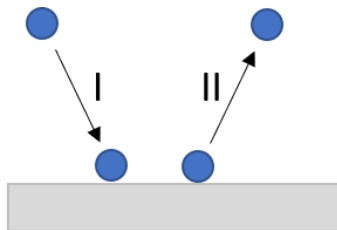
Moving on to dynamic interactions

The overall ambition in dynamics studies is thus to understand, at an atomic level, **how things happen and evolve at the surface**.

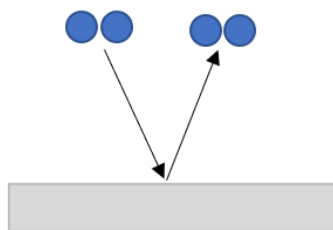
Typical questions asked are:

- How can a molecule that bounces towards a surface lose enough energy to stick to it?
- Which are the detailed steps involved in desorption of atoms and molecules from surfaces?
- What causes or prevents dissociation of simple molecules like H_2 , CO , O_2 on different surfaces?
- How do two different atoms/molecules react on a surface to create a new molecule, as in a catalytic reaction?

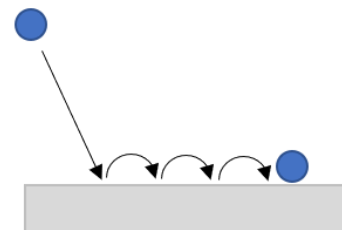
Examples of gas-surface interaction events



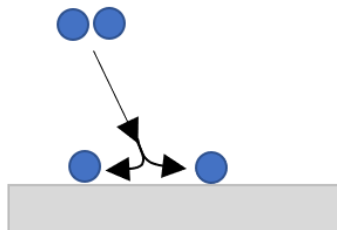
a. I. Direct adsorption (sticking)
II. Direct desorption



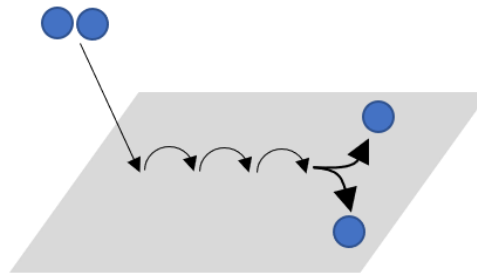
b. Direct elastic or inelastic scattering



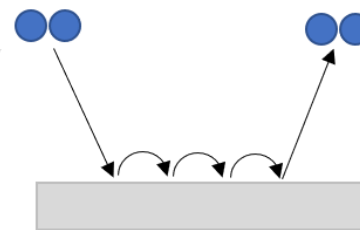
c. Adsorption (sticking) via diffusion or precursor motion



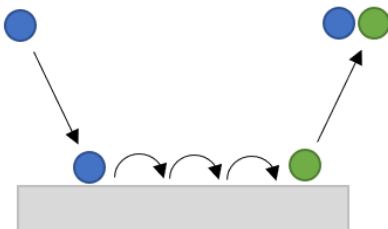
d. Direct, dissociative adsorption



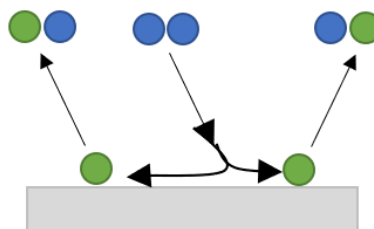
e. Dissociative adsorption via precursor motion



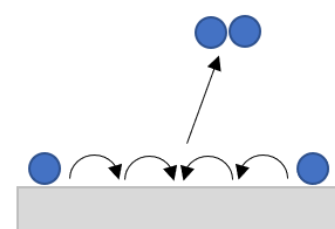
f. Trapping-desorption



g. Reactive scattering via precursor motion



h. Reactive scattering via diffusion



i. Associative desorption

Training yourself

TABLE OF CONTENTS

1. Definition of interface and surface
2. Surface science
- 3. Thermodynamic at surfaces**
 - 3a. Surface tension for liquids**
 - 3b. Minimization of the surface tension for solids
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Thermodynamic at surfaces

All surfaces are energetically unfavourable in that they have a positive free energy of formation.

Let's consider the formation of a new surface of area σ by cleavage of a solid: chemical bonds have to be broken between atoms on either side of the cleavage plane in order to split the solid and create the surfaces. **Breaking bonds requires work to be done on the system.**

The total internal energy of the system must increase by an amount proportional to σ , since otherwise this process would occur spontaneously.

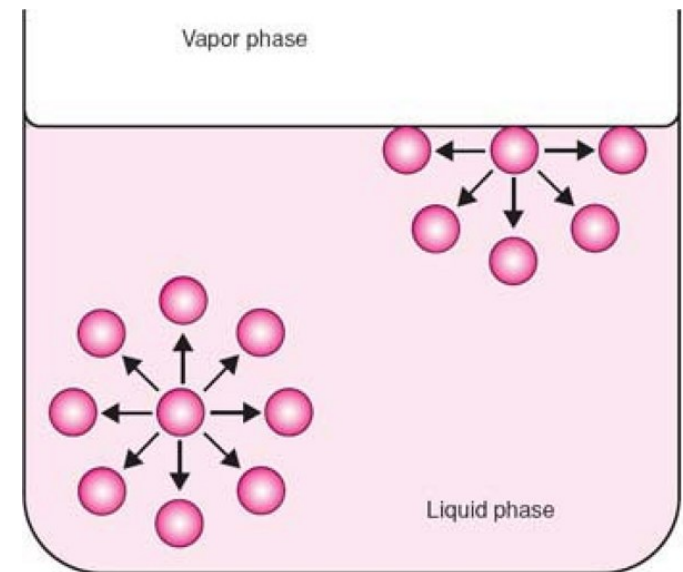
Liquid interfaces

Molecules in the bulk liquid are surrounded in all directions by other molecules for which they have an equal attraction.

Molecules at the surface (i.e., at the liquid–air interface) can only develop attractive cohesive forces with other liquid molecules that are situated below and adjacent to them.

The net effect is that the molecules at the surface of the liquid experience an inward force toward the bulk.

Such a force pulls the molecules of the interface together and, as a result, contracts the surface, resulting in a *surface tension*.



Surface tension and surface energy

The work made to increase the surface σ of a small amount $d\sigma$ can be described as $dw_s = -\gamma d\sigma$, where γ is the surface tension, measured as energy/area (Jm^{-2} or Nm^{-1})

The work used to make the surface (keeping constant the temperature and the pressure) is the Gibbs free energy:

$$-dw_s = dG_s = \gamma d\sigma \qquad \gamma = \left(\frac{\partial G_s}{\partial \sigma} \right)_{P,T}$$

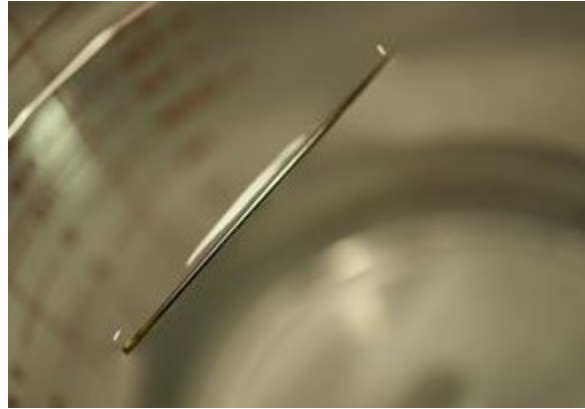
At the simplest level, we can ascribe the existence of surface tension to the reduction in bonds for molecules at the liquid surface. Formally it is the **additional free energy per unit area required to remove molecules from the bulk liquid to create the surface.**

Examples of surface tension



Walking on water.

Small insects such as the water strider can walk on water because their weight is not enough to penetrate the surface.



Floating a needle.

A carefully placed small needle can be made to float on the surface of water even though it is several times as dense as water. If the surface is agitated to break up the surface tension, then the needle will quickly sink.



Droplets.

Surface tension is responsible for the shape of liquid droplets. Although easily deformed, droplets of water tend to be pulled into a spherical shape by the cohesive forces of the surface layer.

Surface tension of water

Surface tension of different liquids

The table shows the surface tensions of several liquids at room temperature.

Note especially that:

- hydrocarbons and non-polar liquids such as ether have rather low values;
- one of the main functions of soaps and other surfactants is to reduce the surface tension of water;
- mercury has the highest surface tension of any liquid at room temperature. It is so high that mercury does not flow in the ordinary way, but breaks into small droplets that roll independently.

substance	surface tension (dyne/cm)
diethyl ether $(\text{CH}_3\text{-CH}_2)_2\text{O}$	17.0
n-octane	21.8
Benzene C_6H_6	40.0
glycerin $\text{C}_3\text{H}_2(\text{OH})_3$	63
water H_2O	72.7
sodium oleate (soap) solution in water	25
sodium chloride solution (6M in water)	82.5
mercury (15°C)	487

The stronger the intermolecular forces acting between the particles in a liquid, the stronger the cohesive forces, the greater the surface tension of the liquid.

Factors influencing surface tension

Surface tension always decreases with temperature as thermal motions reduce the effect of intermolecular attractions.

This is one reason why washing with warm water is more effective; the lower surface tension allows water to more readily penetrate a fabric.

Minimization of surface tension for liquids

The smaller the surface area, the lower the potential energy. Thus intermolecular attractive forces act to minimize the surface area of a liquid.

In a liquid the surface tension γ is **isotropic**: a liquid tends to form **spherical particles** to minimize the surface area.

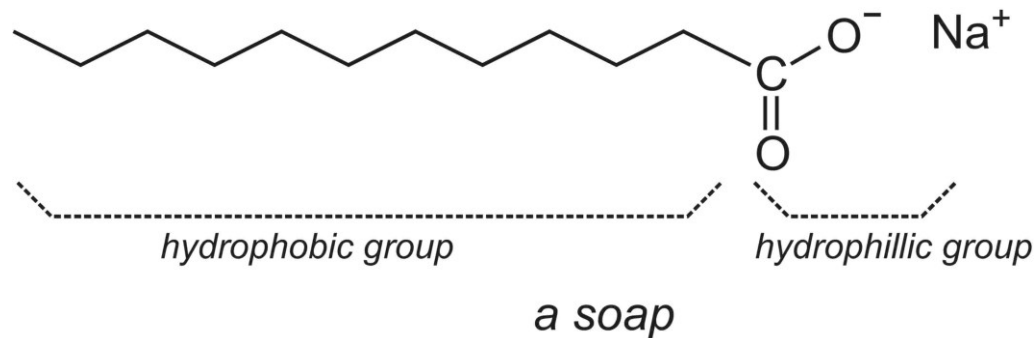
The geometric shape that has the smallest ratio of surface area to volume is the *sphere*, so very small quantities of liquids tend to form spherical drops.



Adsorption at liquid interfaces & surfactants

Certain molecules and ions, when dispersed in the liquid, move of their own accord to the interface. The surface free energy and the surface tension of the system are automatically reduced.

Molecules and ions that are adsorbed at interfaces are termed *surface-active agents* or *surfactants* or *amphiphile*.

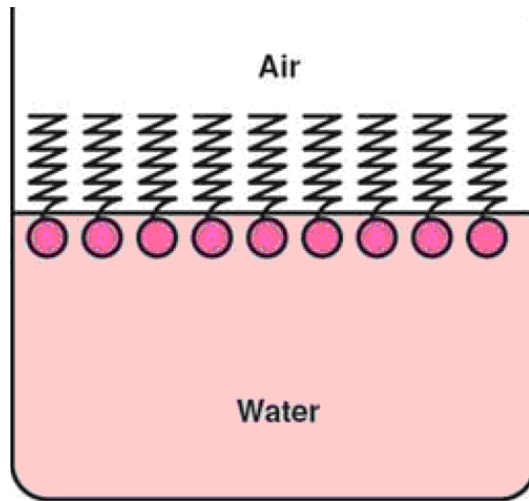


A surfactant molecule can be depicted schematically as a cylinder representing the hydrocarbon (hydrophobic) portion with a sphere representing the polar (hydrophilic) group attached at one end.

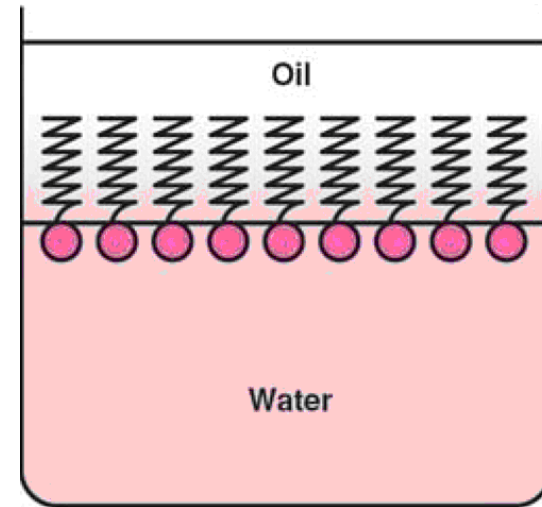
Surface-active agents

It is the amphiphilic nature of surface-active agents that causes them to be absorbed at interfaces. Thus, in an aqueous dispersion of amphiphile, the polar group is able to associate with the water molecules. The nonpolar portion is rejected.

As a result, **the amphiphile is adsorbed at the interface.**



At the air–water interface, the lipophilic chains are directed upward into the air



at the air–oil interface, they are associated with the oil phase

TABLE OF CONTENTS

1. Definition of interface and surface

2. Surface science

3. Thermodynamic at surfaces

3a. Surface tension for liquids

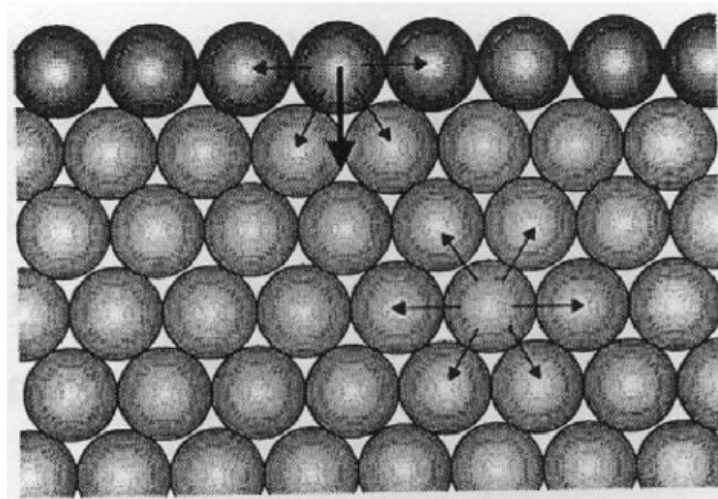
3b. Minimization of the surface tension for solids

- **Adsorption from the gas phase**
- **Relaxation and reconstruction**
- **Assuming a spherical shape**

4. Nano-scale effects on the materials properties

Thermodynamic at solid surfaces

Surfaces, as places that divide two different phases or places where crystalline periodicity is interrupted, are characterized by a higher free energy. An atom inside a piece of matter is surrounded by atoms, while an atom on a surface is only partially surrounded by atoms: **there are asymmetric forces that act on an atom located on the surface**. The atom try to move inside the bulk and it has an higher potential energy.



Moving an atom from the bulk to the surface requires energy.



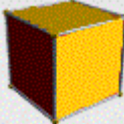

Minimization of the surface free energy

Surface phenomena are driven by the minimization of the surface free energy achieved either:

- 1) by reducing the area of the surface by assuming a spherical shape
- 2) by adsorption from the gas phase;
- 3) by altering the local surface atomic geometry reconstructing in a way which reduces the surface free energy;

Anisotropic surface tension γ

The table compares the surface areas of different three-dimensional shapes that have a volume of 1 cm³. Increasing the number of sides enclosing a given volume, decreases the surface area.

3D shape		volume = 1 cm ³	surface area	surface area to volume ratio
sphere		volume = $V = 1 \text{ cm}^3$ $V = \frac{4}{3} \pi r^3$ $r = (\frac{3V}{4\pi})^{1/3}$ radius = $r = 0.62 \text{ cm}$	surface area = $4\pi r^2$ $= 4\pi(0.62)^2$ $= 4.83 \text{ cm}^2$	4.83 : 1
octahedron		volume = $V = 1 \text{ cm}^3$ $V = \frac{1}{3} \sqrt{2} l^3$ $l = [(3V)^2/2]^{1/3}$ length = $l = 1.65 \text{ cm}$	surface area = $2\sqrt{3} l^2$ $= 2\sqrt{3} (1.65)^2$ $= 5.72 \text{ cm}^2$	5.72 : 1
cube		volume = $V = 1 \text{ cm}^3$ $V = l^3$ $l = V^{1/3}$ length = $l = 1 \text{ cm}$	surface area = $6l^2$ $= 6 \times 1^2$ $= 6 \text{ cm}^2$	6 : 1
tetrahedron		volume = $V = 1 \text{ cm}^3$ $V = (\sqrt{2} l^3)/12$ $l = [(12V)^2/2]^{1/3}$ length = $l = 4.16 \text{ cm}$	surface area = $\sqrt{3} l^2$ $= \sqrt{3} (4.16)^2$ $= 7.21 \text{ cm}^2$	7.21 : 1

Anisotropic surface tension γ (cont.)

In a solid the surface tension γ is anisotropic, and the surface energy depends on the exposed surface: crystalline solids are not with spherical morphologies.

The more modern methods for predicting the morphologies of crystals are based on the calculation of the energies of the various faces. The methods are based on the intuitive consideration that **the closed polyhedron describing the shape of the crystal is determined by the faces with the lowest surface free energy** and that the extension of these faces is inversely proportional to the respective surface free energy.

Anisotropic surface tension γ (cont.)

The surface tension of a planar solid depends on the crystallographic orientation of the sample.

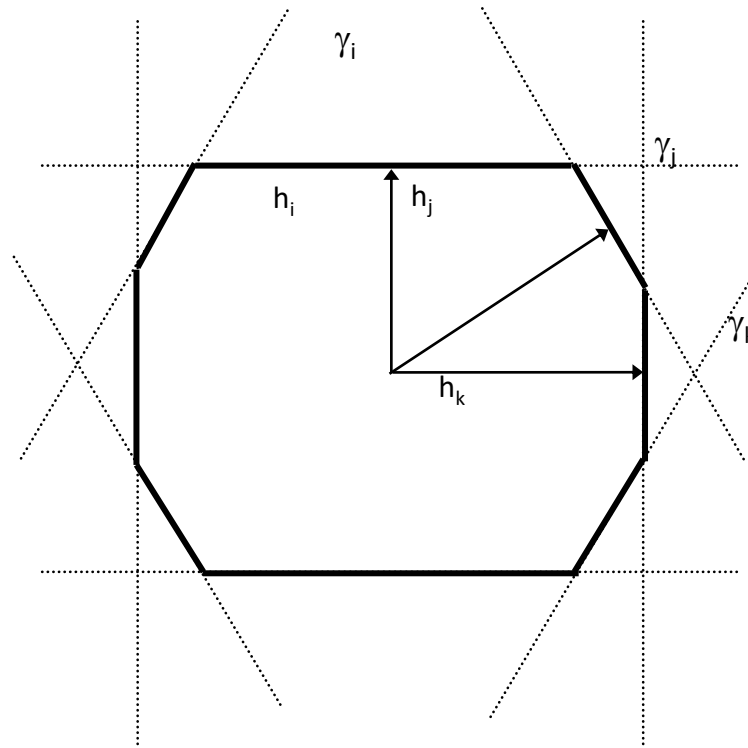
The anisotropy of the surface tension is represented via the γ -plot constructed by drawing a vector from the origin in the direction n (defined by its polar and azimuthal angles θ and ϕ) with a length equal to the surface tension, $\gamma(n)$, of the surface plane perpendicular to n .

γ has minima in the directions corresponding to close-packed surfaces.

The equilibrium shape must minimize the excess surface free energy while preserving the volume.

Wulff construction

- 1) The surface energy for each surface (h,k,l) is plotted in a polar plot so that the length of the vector is proportional to the surface energy;
- 2) At the end of the vector a surface plane is defined orthogonal to the vector;
- 3) The inner envelope of these surfaces defines the equilibrium shape.

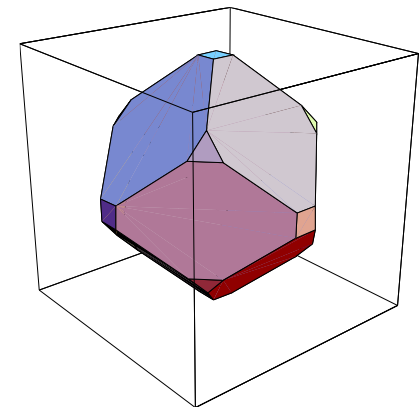
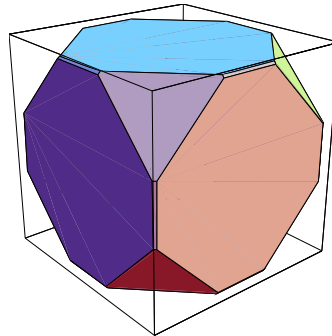
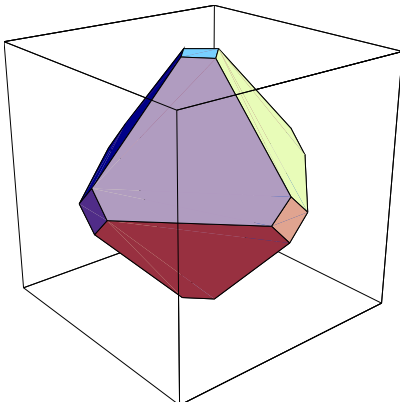
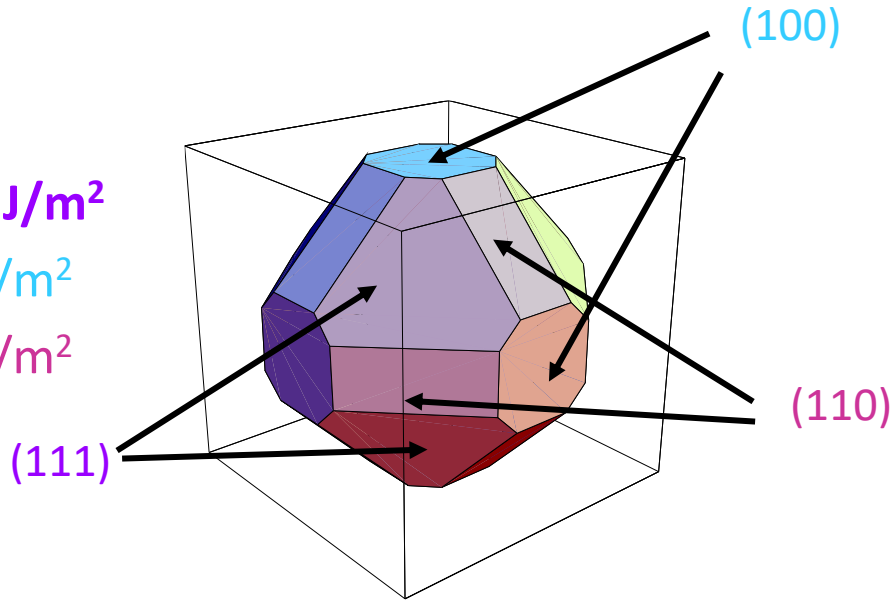


Wulff construction (cont.)

$$g_{111} = 1.97 \text{ J/m}^2$$

$$g_{100} = 2.2 \text{ J/m}^2$$

$$g_{110} = 2.1 \text{ J/m}^2$$



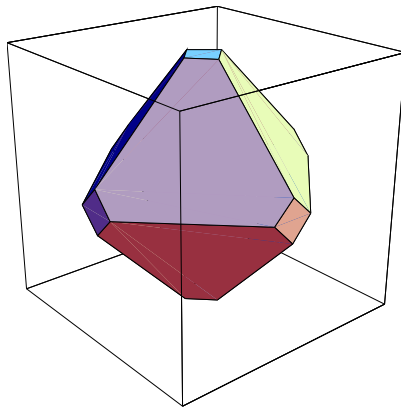
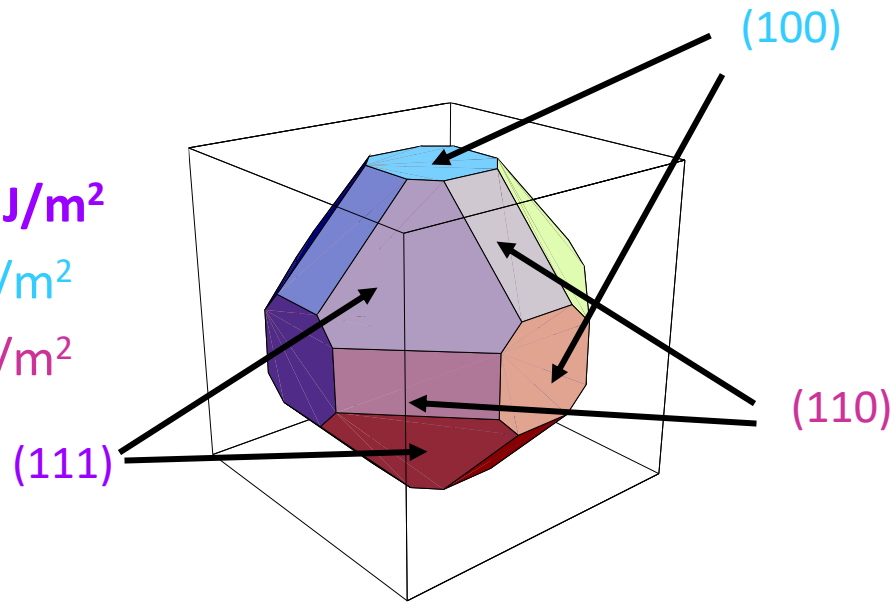
The polyhedra are terminated by the same (hkl) surfaces, but with a different extension. Assign each of them to the correct set of surface tension values $g(\text{hkl})$ in J/m^2 .

Wulff construction (cont.)

$$g_{111} = 1.97 \text{ J/m}^2$$

$$g_{100} = 2.2 \text{ J/m}^2$$

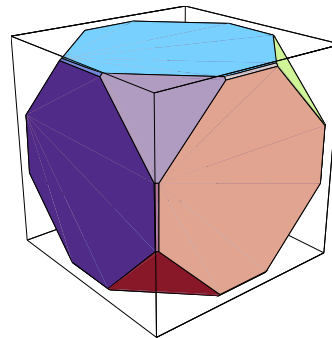
$$g_{110} = 2.1 \text{ J/m}^2$$



$$g_{111} = 1.5 \text{ J/m}^2$$

$$g_{100} = 2.2 \text{ J/m}^2$$

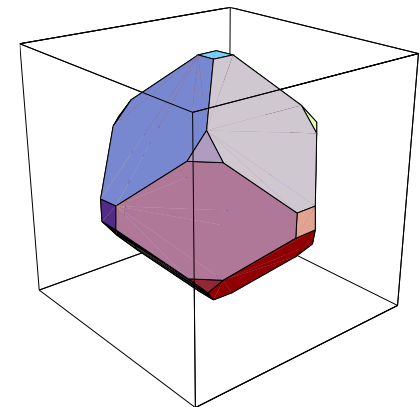
$$g_{110} = 2.1 \text{ J/m}^2$$



$$g_{111} = 1.97 \text{ J/m}^2$$

$$g_{100} = 1.5 \text{ J/m}^2$$

$$g_{110} = 2.1 \text{ J/m}^2$$



$$g_{111} = 1.97 \text{ J/m}^2$$

$$g_{100} = 2.2 \text{ J/m}^2$$

$$g_{110} = 1.7 \text{ J/m}^2$$

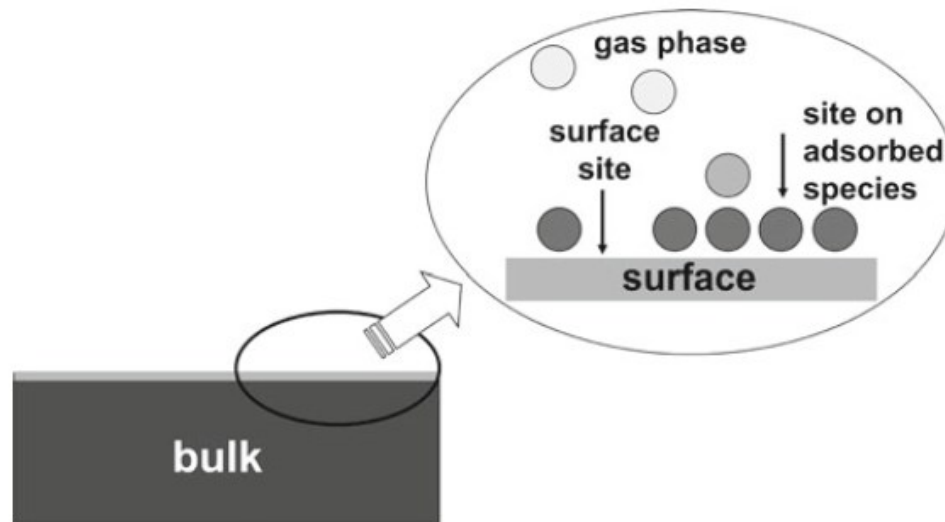
ABSORPTION & ADSORPTION

Let's have a look to the following video:

<https://youtu.be/djIzXvwIz5U>

Gas adsorption

The surface atoms of a solid, which are coordinatively unsaturated with respect to the bulk atoms, become saturated thanks to the interaction with molecules of the environment. **Adsorption is the process whereby molecules from the gas (or liquid) phase are taken up by a solid surface;** it is distinguished from absorption which refers to molecules entering into the lattice (bulk) of the solid material.



Adsorption is governed by either physical or chemical forces. In the former case the adsorption is named physical adsorption (*physisorption*) whereas in the latter case chemical adsorption (*chemisorption*).

Relaxation and reconstruction

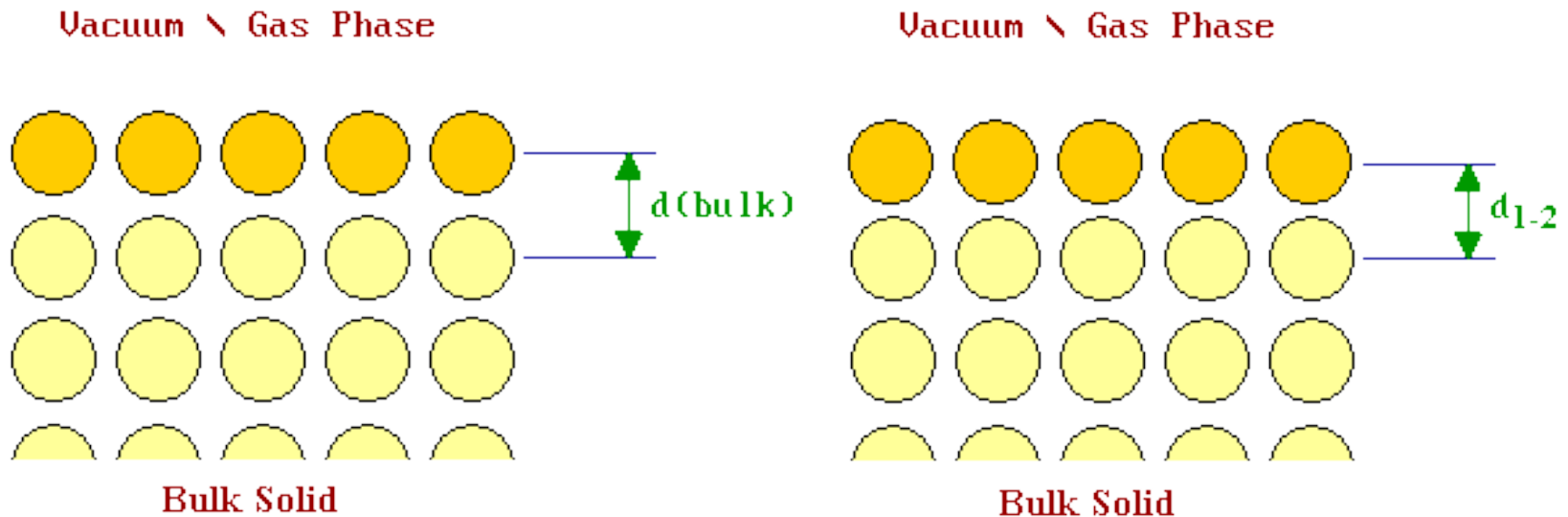
The phenomena of relaxation and reconstruction involve **rearrangements of surface (and near surface) atoms**. This process is driven by the energetics of the system i.e. the desire to reduce the surface free energy. There may be kinetic limitations which prevent or hinder these rearrangements at low temperatures.

The minimisation of surface energy means that even single crystal surfaces will not exhibit the ideal geometry of atoms to be expected by truncating the bulk structure of the solid parallel to a particular plane. The differences between the real structure of the clean surface and the ideal structure may be imperceptibly small (e.g. a very slight *surface relaxation*) or much more marked and involving a change in the surface periodicity in one or more of the main symmetry directions (*surface reconstruction*).

Relaxation

Relaxation is a small and subtle rearrangement of the surface layers which may nevertheless be significant energetically, and seems to be commonplace for metal surfaces.

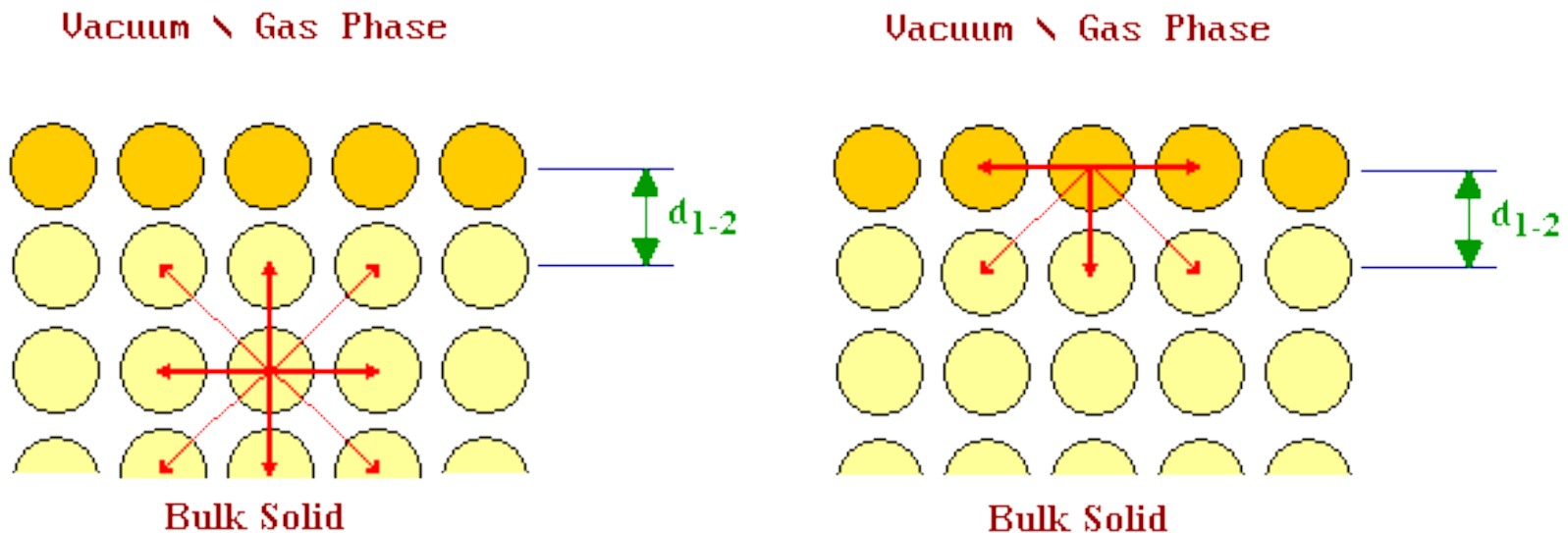
It involves adjustments in the layer spacing perpendicular to the surface. There is no change either in the periodicity parallel to the surface or to the symmetry of the surface.



Relaxation (cont.)

Which is the driving force for this process at the atomic level?

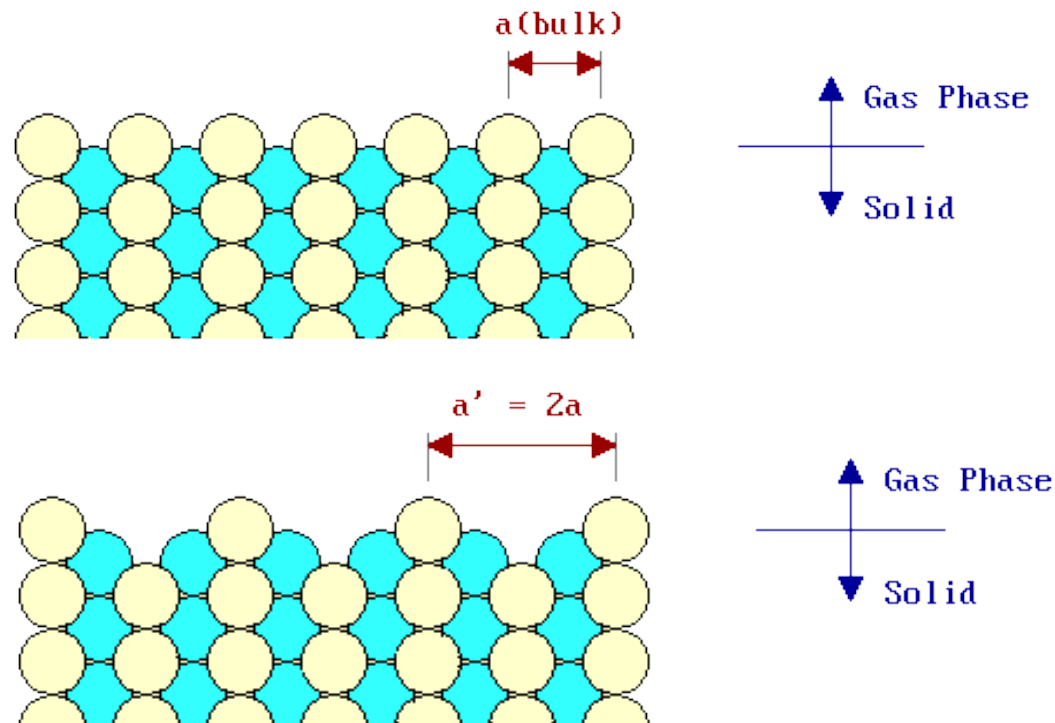
An atom in the bulk is acted upon by a balanced, symmetrical set of forces. On the other hand, an atom at the unrelaxed surface suffers from an imbalance of forces and the surface layer of atoms may therefore be pulled in towards the second layer.



The magnitude of the contraction in the first layer spacing is generally small ($< 10\%$). Compensating adjustments to other layer spacing may extend several layers into the solid.

Reconstruction

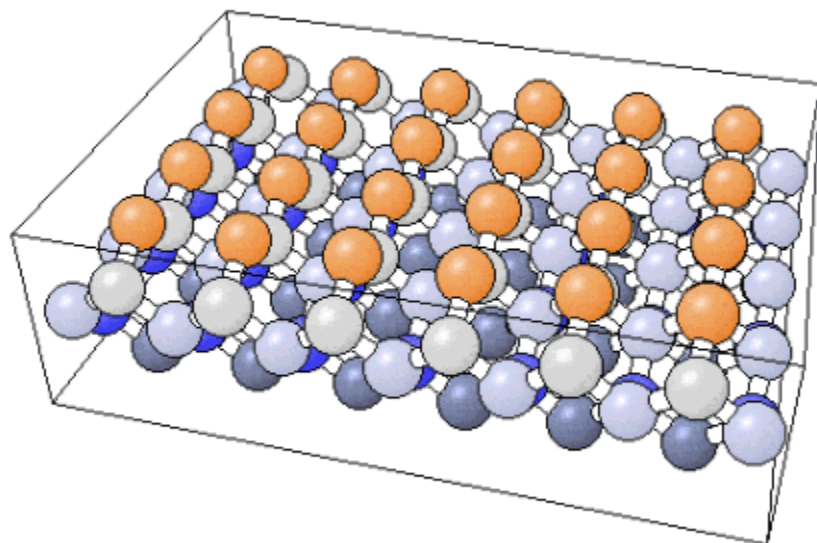
The reconstruction of surfaces is a much more readily observable effect, involving **larger displacements of the surface atoms**. It occurs with many of the less stable metal surfaces, but it is much more prevalent on semiconductor surfaces. Unlike relaxation, the phenomenon of reconstruction involves **a change in the periodicity of the surface structure**.



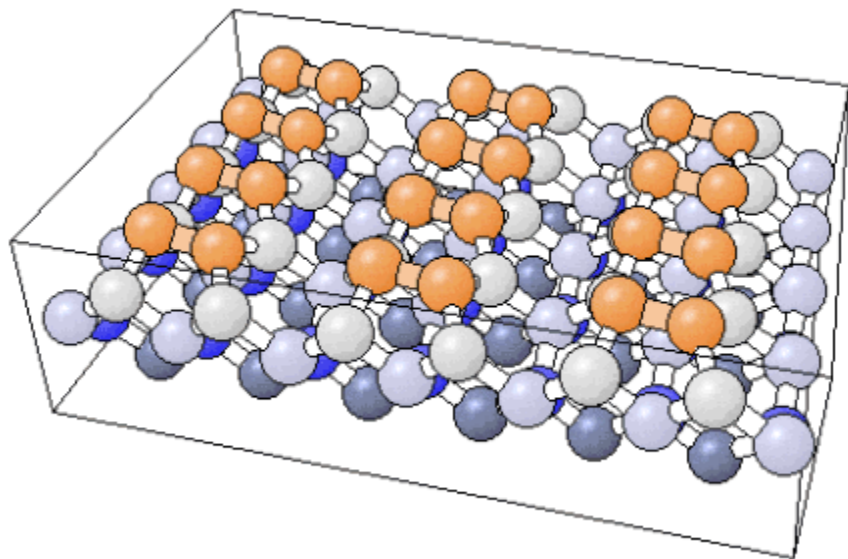
Since reconstruction involves a change in the periodicity of the surface and in some cases also a change in surface symmetry, it is readily detected using surface diffraction techniques (e.g. LEED and RHEED).

Reconstruction (cont.)

Reconstruction of Si(100)



Unreconstructed Si(100)-(1x1) surface. The Si atoms of the topmost layer are highlighted in orange; these atoms are bonded to only two other Si atoms, both of which are in the second layer (shaded grey).



Reconstructed Si(100)-(2x1) surface. The Si atoms of the topmost layer form a covalent bond with an adjacent surface atom are thus drawn together as pairs; they are said to form "*dimers*".

Surfaces and defects

If no major reconstruction processes are required in order to minimize the surface atoms energy, and if no structural/compositional defects are present, an ideal perfect homogeneous surface is obtained which can be properly represented by cutting a slab of the solid structure. Such an **ideal perfect homogeneous surface** is very rarely encountered, unless especially prepared for surface science studies.

Real solid surfaces (mostly in the case of finely divided, nanometric sized solids) are made up of a combination of flat regions (terraces), structural defects (steps, kinks, corners, edges), point defects (vacancies of ions/atoms in the solid).

Surfaces and defects (cont.)

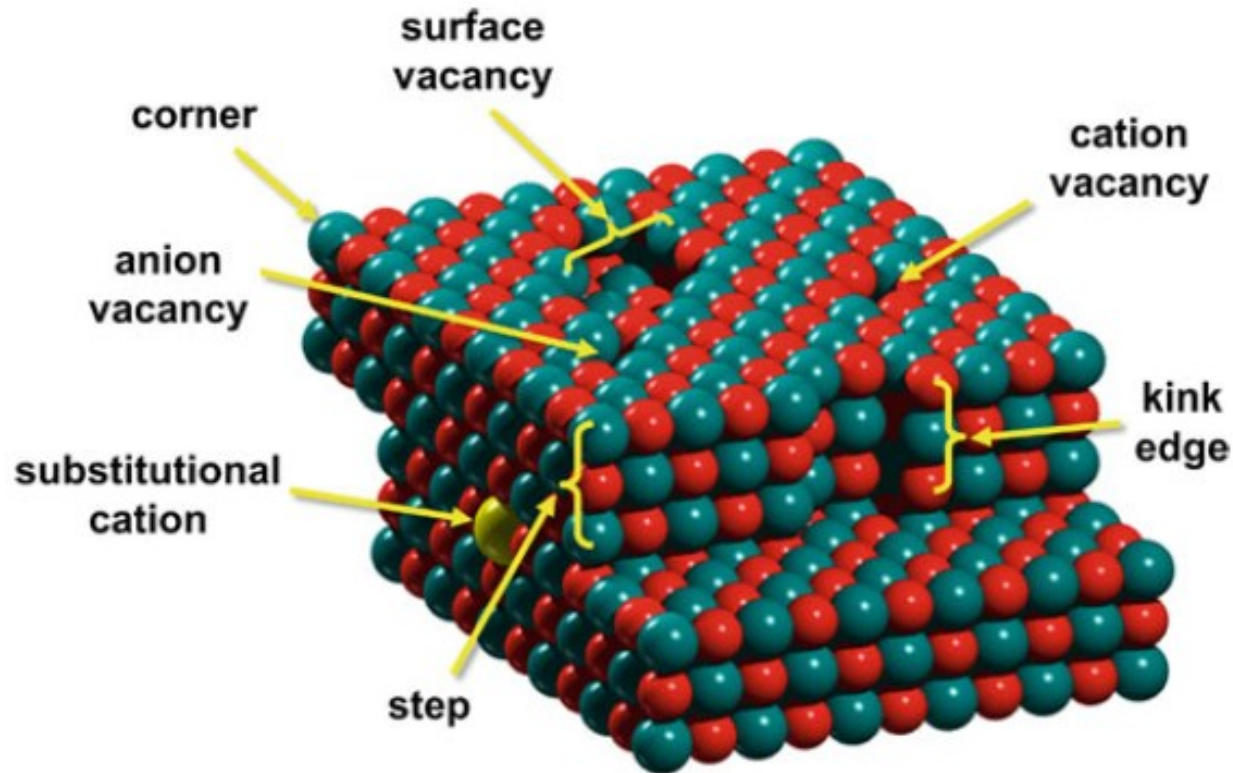


Fig. 1.1 Cartoon of a piece of realistic MgO nanocrystal, which exhibits both structural (steps, kinks edges and corners) and point (anionic and cationic vacancies) defects along the flat regions (terraces). The presence of a compositional defect (substitutional cation) is also outlined. By courtesy of Prof. Piero Ugliero, University of Torino

Surface is different electronically

Electron density trails off exponentially away from the surface into the vacuum. This partially depletes negative charge just below the surface. Redistribution of charge near surface sets up the surface dipole.

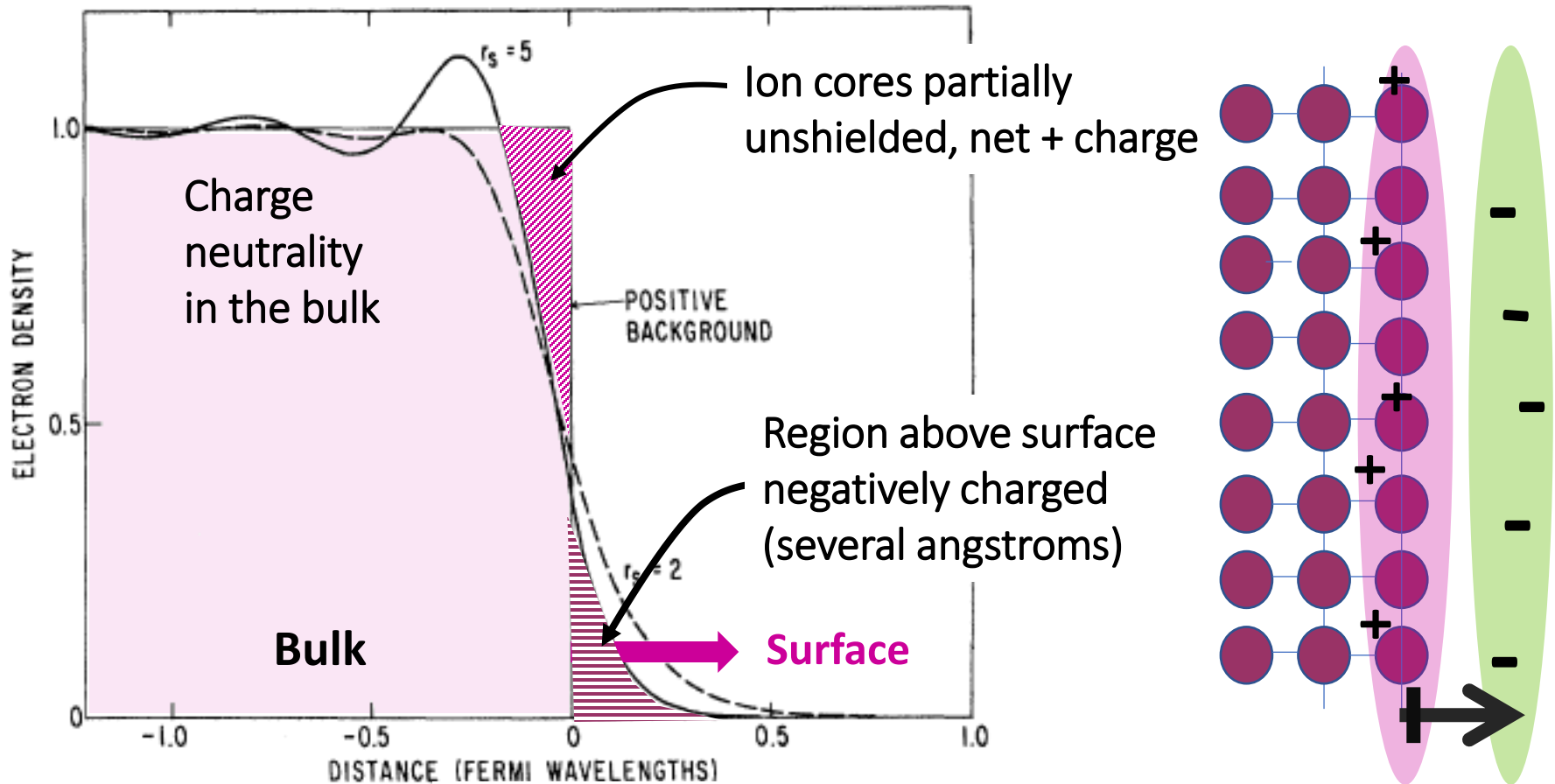
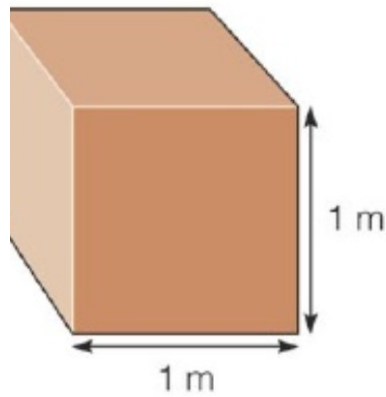


TABLE OF CONTENTS

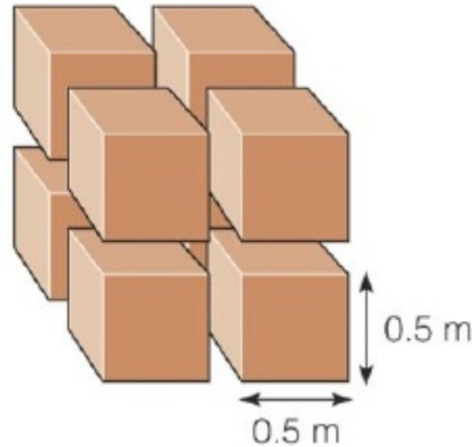
1. Definition of interface and surface
2. Surface science
3. Thermodynamic at surfaces
 - 3a. Surface tension for liquids
 - 3b. Minimization of the surface tension for solids
 - Adsorption from the gas phase
 - Relaxation and reconstruction
 - Assuming a spherical shape
- 4. Nano-scale effects on the materials properties**

Surfaces & nanoparticles

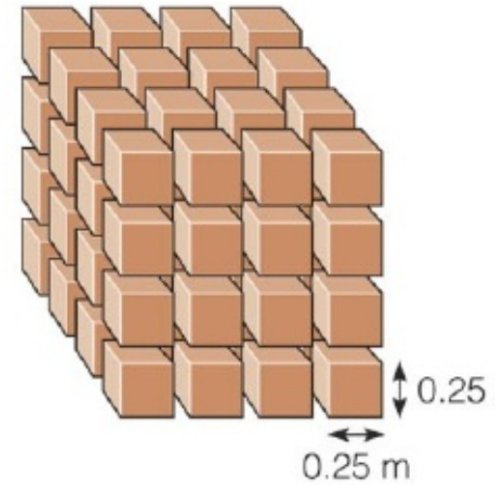
Which is the surface area of:



(a)



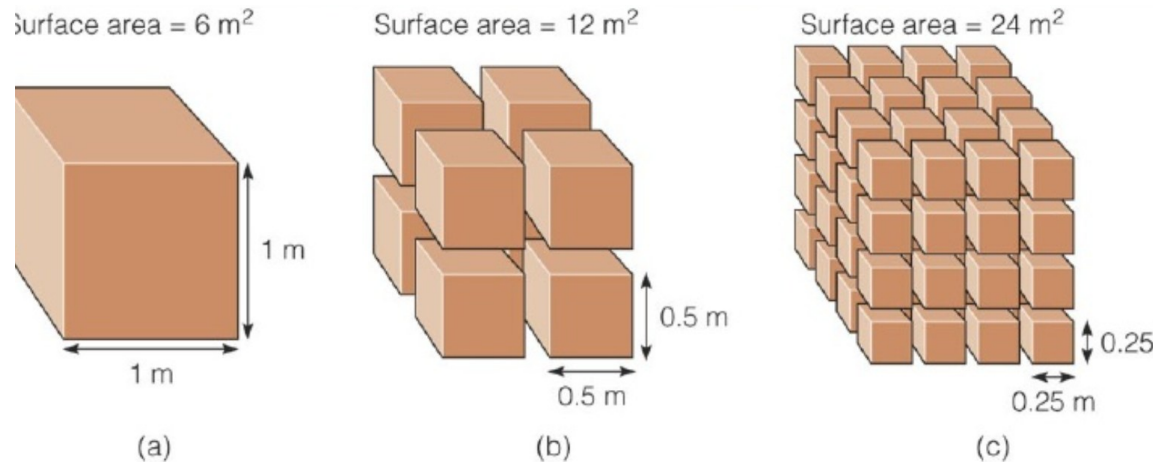
(b)



(c)

- 1) 1 cube, 1 meter per side
- 2) 8 cubes, 0.5 meter per side
- 3) 64 cubes, 0.25 meter per side

Surfaces & nanoparticles (cont.)



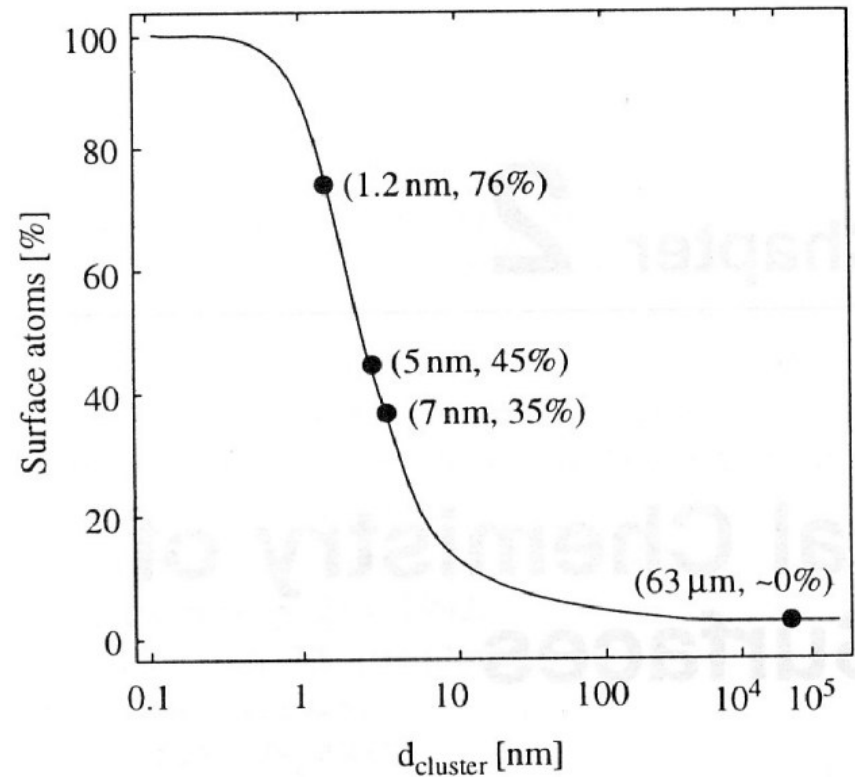
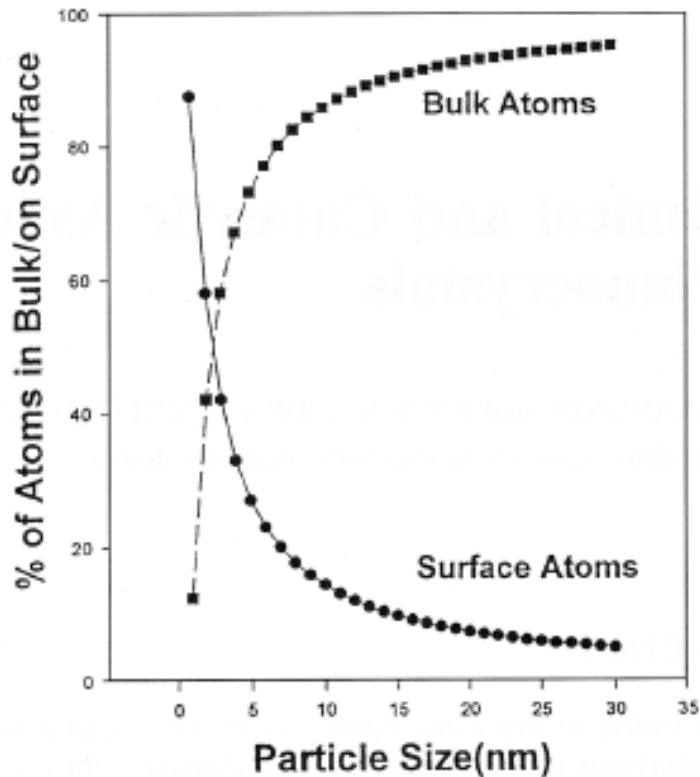
Let us consider one cubic volume shown in figure. Its surface area is 6 m². When it is divided into eight equal pieces its surface area becomes 12 m². When the same volume is divided into 64 pieces its surface area becomes 24 m².

Thus, when a given volume is divided into smaller pieces the surface area increases. Hence, **as particle size decreases a greater proportion of atoms are found at the surface compared to those inside.**

The same applies to a sphere. Let us consider a sphere of radius “r”. Its Surface Area = $4\pi r^2$, its volume = $\frac{4}{3}\pi r^3$. Surface Area to Volume Ratio = $\frac{3}{r}$. Thus **when the radius of the sphere decreases, its surface to volume ratio increases.**

Surface/bulk atom ratio

spherical iron nanocrystals



The fraction of atoms at the surface in a cube of Pd having 1 cm edge is almost zero, while it increases to 10% for a cube of 10 nm, and is close to 100% in the case of 1 nm cube.

Dispersion

“Dispersion” in a solid is defined as the ratio between the number of atoms at the surface in respect to the number of atoms in the bulk:

$$D = \left(\frac{N^{surf}}{N^{bulk}} \right)$$

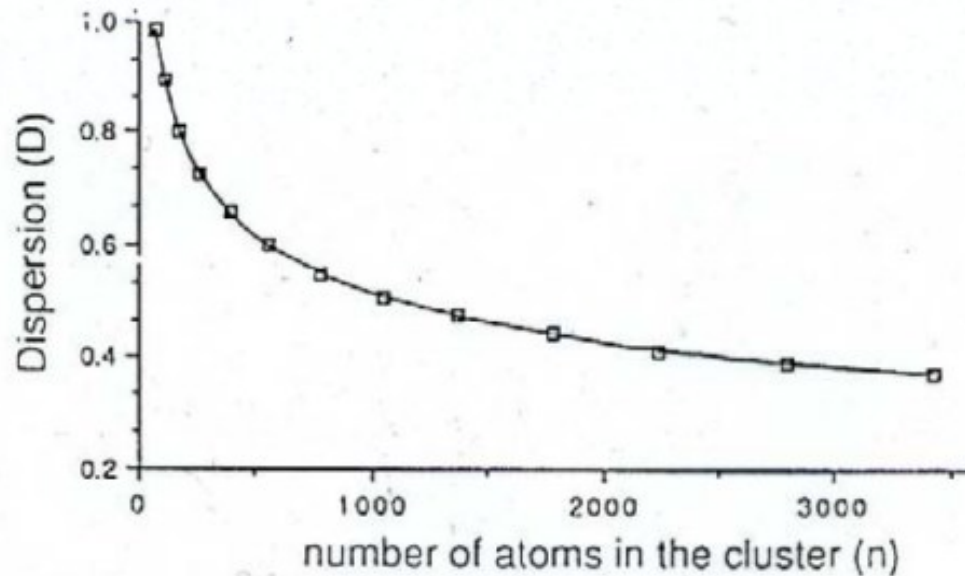


Figure 1.7. Clusters of atoms with single cubic packing having 8, 27, 64, 125, and 216 atoms. In an eight-atom cluster, all of the atoms are on the surface. However, the dispersion, \mathcal{D} , defined as the number of surface atoms divided by the total number of atoms in the cluster, declines rapidly with increasing cluster size. this is shown in the lower part of the figure.

Sintering as a way to minimize the surface energy

In a solid, in order to reduce surface energy, particles try to agglomerate and sintering.

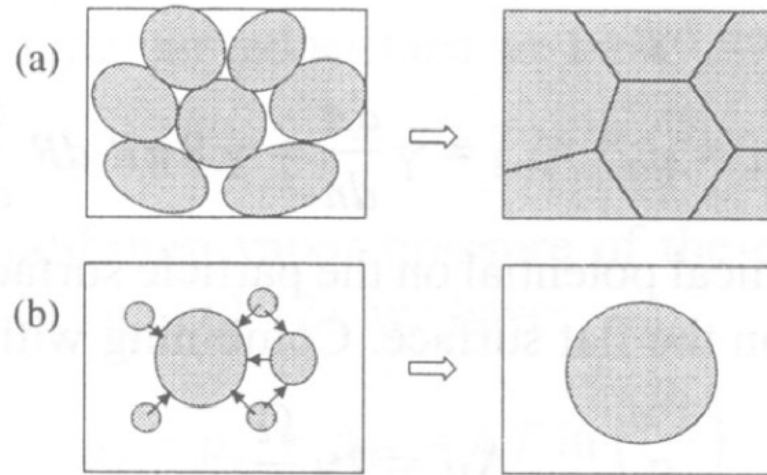


Fig. 2.9. Schematic showing sintering and Ostwald ripening processes. (a) Sintering is to combine individual particles to a bulk with solid interfaces to connect each other (b) Ostwald ripening is to merge smaller particles into a larger particle. Both processes reduce the solid–gas surface area.

Nano-scale effects

The nanometric dimension affects many properties of materials, such as:

- Structure
- Melting (and boiling) point
- Band gap
- Optical properties
- Electrical properties
- Magnetic properties
- ...others

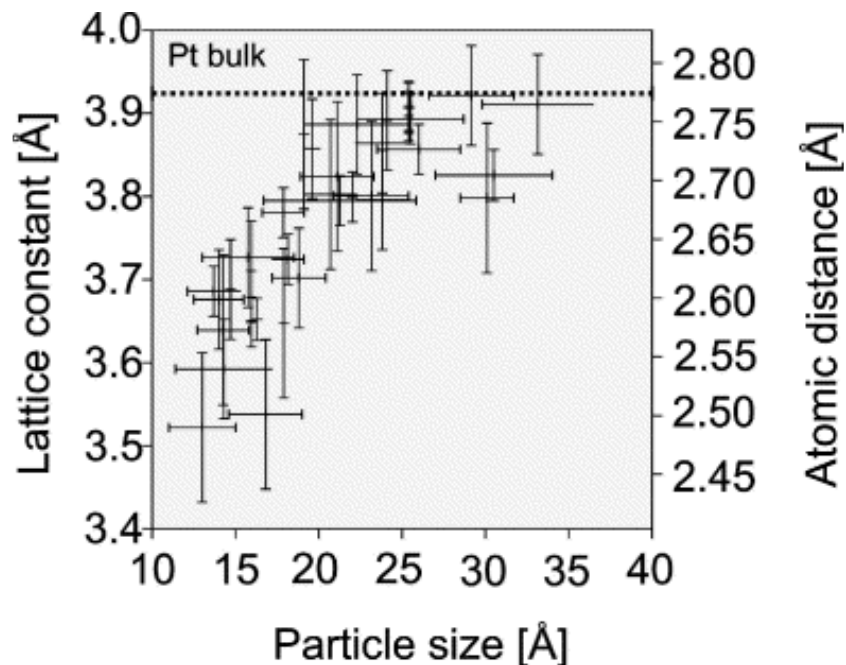
For example, composites made from particles of nano-size ceramics or metals smaller than 100 nanometers can suddenly become much stronger than predicted by existing materials-science models.

Metals with a so-called grain size of around 10 nanometers are much harder and tougher than their ordinary counterparts with grain sizes in the micro-meter range.

Nano-scale effects: structure

The crystal structure of nano particles is the same as bulk structure with different lattice parameters.

The inter atomic spacing decreases with size and this is due to long range electrostatic forces and the short range core-core repulsion.

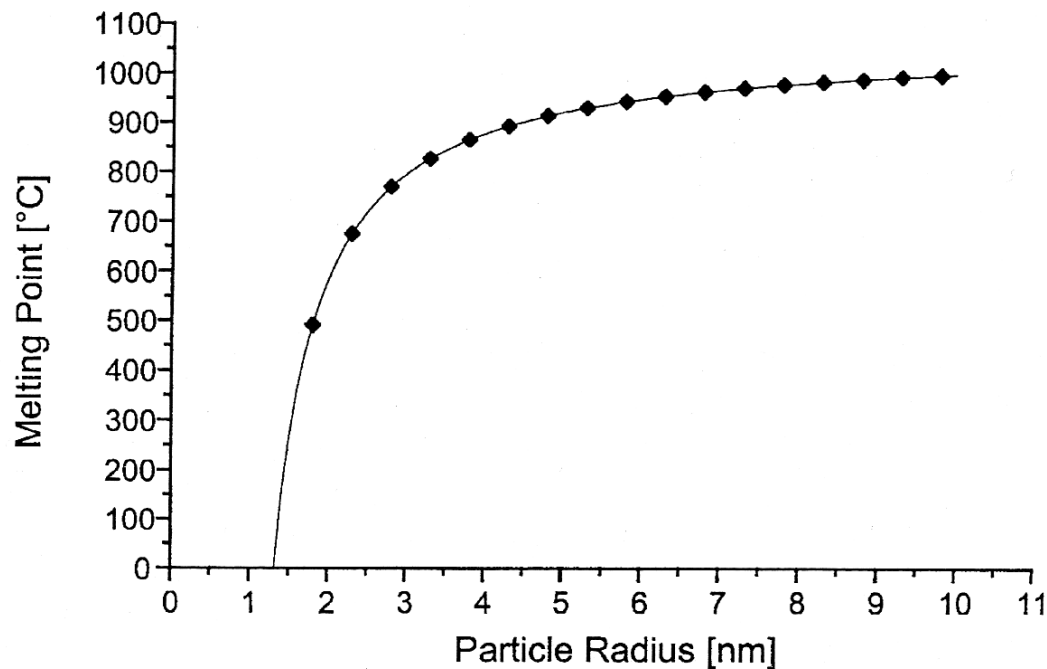


Interatomic distances in Pt-Pt decreases substantially for nano-particles. Reticular parameter tends to the massive Pt value for particles of 30 Å.

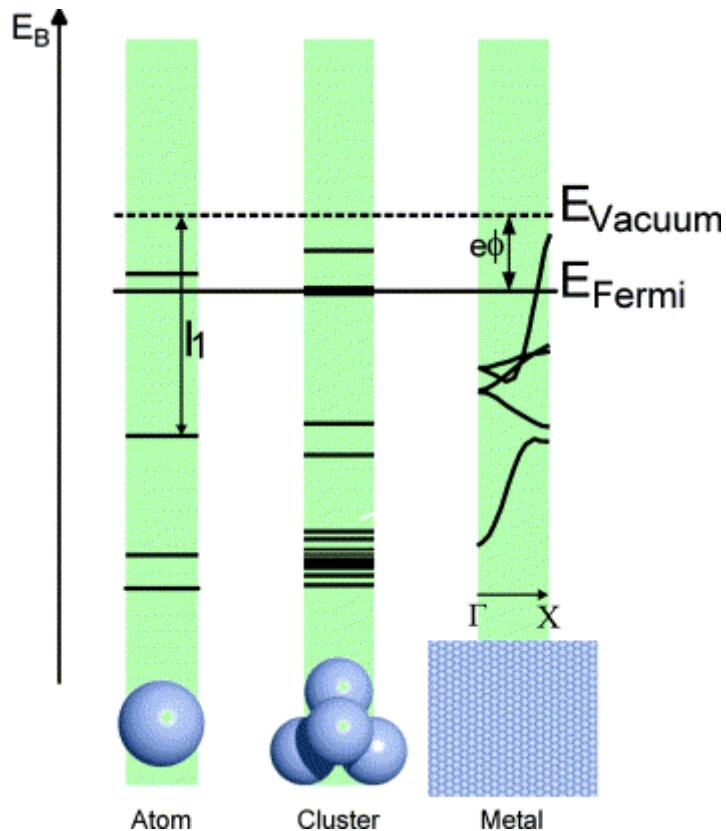
Lattice constants and interatomic distances of Pt particles grown on $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ as a function of their size (the horizontal bars represent the difference of the widths and the lengths of the clusters, while the vertical bars are error bars).

Nano-scale effects: melting point

The melting point decreases dramatically as the particle size gets below 5 nm

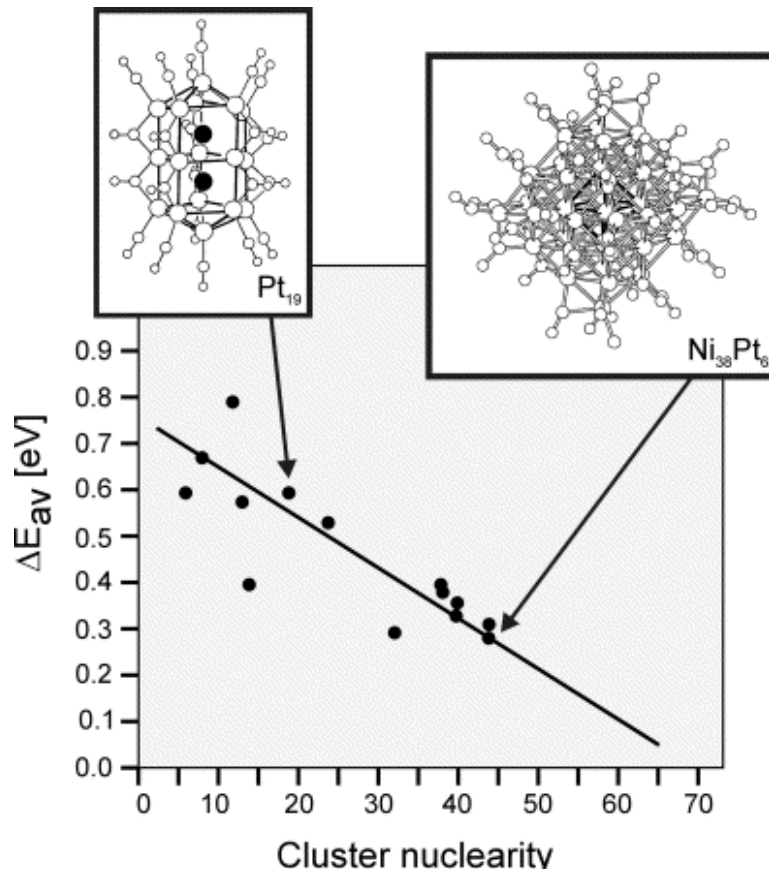


Nano-scale effects: electronic properties

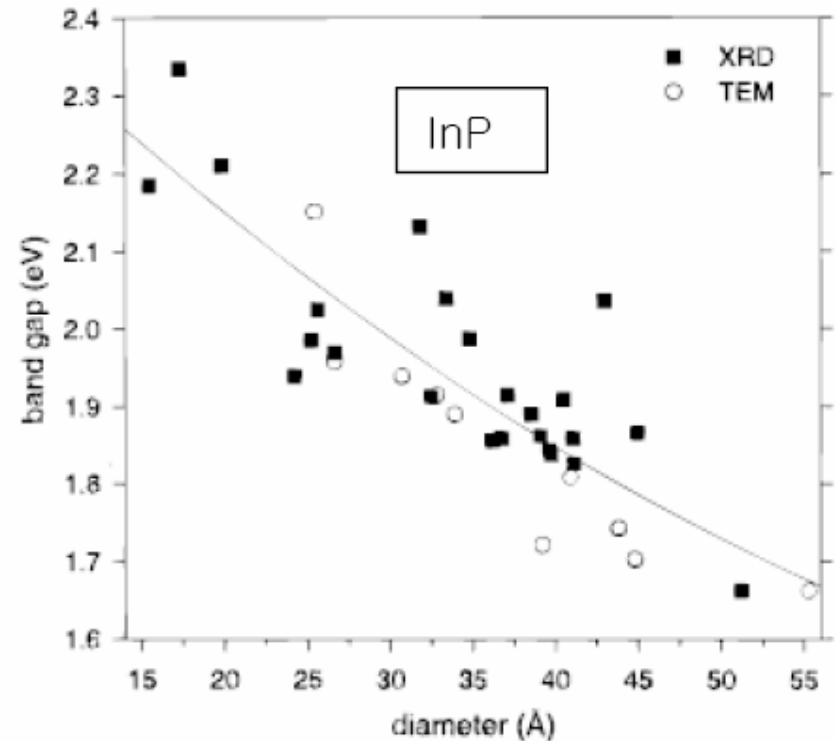


In nano-crystals the electronic energy levels are not continuous as in the bulk, but are discrete (finite density of states), because of the confinement of the electronic wave function to the physical dimensions of the particles. This phenomenon is called **quantum confinement**.

Nano-scale effects: electronic properties (cont.)



ΔE_{av} is the energy gap between occupied and unoccupied electronic states. 70 atoms seems the bounder between a “cluster” and a solid. Cu, Ag, Au, Al and alkaline metals show a higher limit.



The band gap increases with reducing the size of the particles

Training yourself 1

Training yourself 2

Training yourself 3