

NBT 620 Arayüzler ve Kolloidler

- M. Serdar Önses (onses@erciyes.edu.tr)
- Textbook:
 - Physics and Chemistry of Interfaces (H.J. Butt, K. Graf and M. Kappl.) Wiley, 2006.
- Topics (Surface and Interface science)
 - Introduction to surface and interface science
 - Surface tension, Surface energy and Capillarity
 - Thermodynamics of interfaces
 - Electrical aspects of surfaces
 - Surface forces
 - Surface of solids
 - Solid-liquid interface – Contact angle
 - Solid-liquid interface – adsorption from solution
 - Surface modification,

NBT 620 Arayüzler ve Kolloidler

Ders notu = Vize %40 + Final %60

- Vize = Yazılı sınav
- Final = Makale sunumları

Makale sunumları

- Arayüzlerin önemli olduğu yayınlar
- Her öğrenci iki hafta birer makale sunumu yapacak

Interfaces

- An interface is the area which separates two phases from each other.
- If we consider the solid, liquid, and gas phase we immediately get three combinations of interfaces:
 - Solid–liquid,
 - Solid–gas
 - Liquid–gas
- These interfaces are also called surfaces (surface generally refers to the boundary between a condensed phase and a gas)
- **Interface is, however, a more general term than surface.**
- Interfaces can also separate two immiscible liquids such as water and oil.
 - These are called liquid–liquid interfaces.
- Solid–solid interfaces separate two solid phases. They are important for the mechanical behavior of solid materials.
- Gas–gas interfaces do not exist because gases mix.

Interfaces

- “Interfaces” (or “surfaces”) are the thin boundary regions separating macroscopic chunks of matter from their surroundings or from one another.
- While interfaces appear abrupt to the naked eye, they all have in fact a finite thickness, typically ranging from a few Ångströms to a few nanometers,

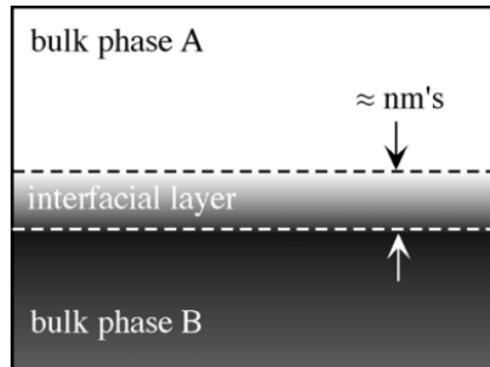


Fig. 1-1: Schematic of material interface, showing zone of inhomogeneity and adjacent bulk phases.

- These thin regions are first of all inhomogeneous, and its properties differ profoundly from those of material in a bulk phase state.
- No system is free of the influence of its interface(s), and in many applications or situations, it is essential that one know not just the bulk properties, but the *interfacial properties* as well

Interfaces

- The chemical composition of the interfacial stratum is also different from that of the bulk phases it separates.
- The apparent interface between a piece of metal, such as iron or aluminum, and air, as
 - Unless it is a noble metal, it will be covered with an oxide layer, which is at least partially hydroxylated from contact with water vapor in the air.
 - On top of this will probably be a layer of tightly bound water and possibly an additional layer of loosely bound water, depending on the relative humidity.
 - The very top layer is likely to be an adsorbed scum of grease or other organic contaminant.
- The ability of interfaces of all kinds to contain components that may or may not be present in the bulk phases at the instant of interest makes their composition more complex

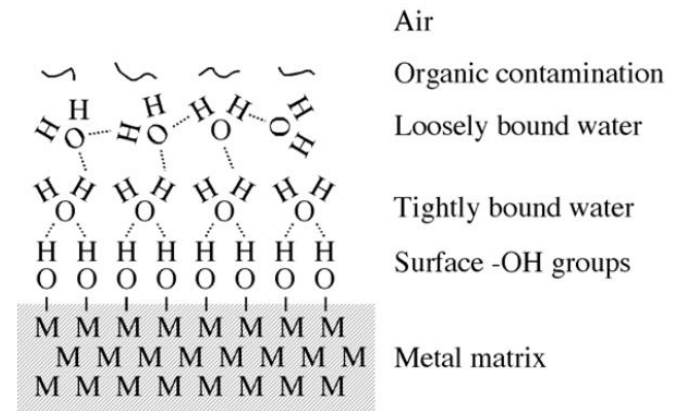
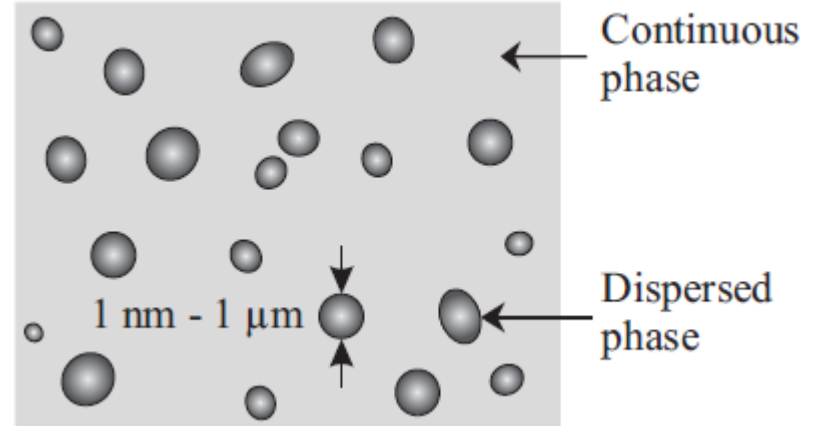


Fig. 1-2: Schematic representation of the typical chemistry at a nominal metal-air interface.

Colloids - dispersions

- Often interfaces and colloids are discussed together.
- Colloids are disperse systems, in which one phase has dimensions in the order of 1 nm to 1 μm



- Colloid science concerns systems in which one or more of the components has at least one dimension within the nanometer to micrometer range
 - It concerns systems containing large molecules and/or small particles
- The word “colloid” comes from the Greek word for glue and has been used the first time in 1861 by Graham
- A dispersion is a two-phase system which is uniform on the macroscopic but not on the microscopic scale. It consists of grains or droplets of one phase in a matrix of the other phase.

Colloids - dispersions

Historical data:

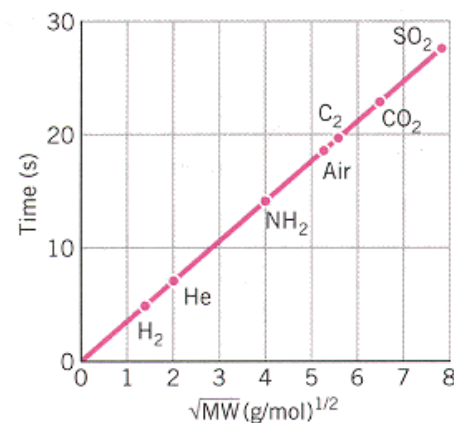
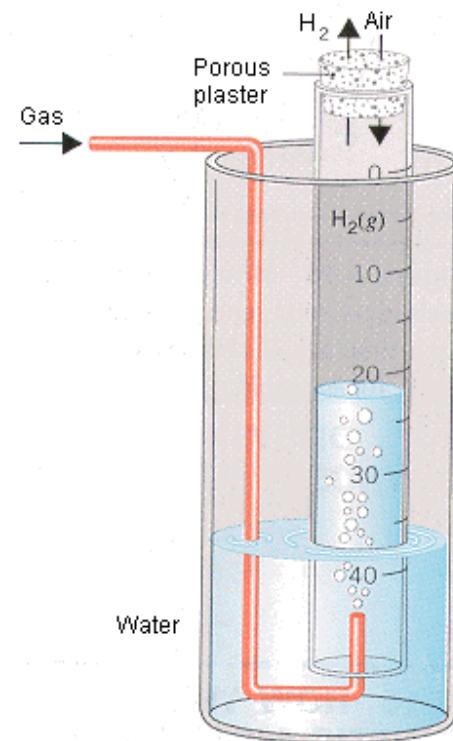
- Selmi (1845)
- described pseudosolution i.e particles that are larger than the usual molecules.
 - first to investigate colloidal system systematically e.g. preparation of colloidal sulphur, silver chloride and prussian blue, albumin and starch solutions.
- Michael Faraday (1857) - investigation of optical properties of gold sol (*Faraday sol/s* ~ 3 nm radius). Prepared by reduction of a gold chloride solution with phosphorus.
- Thomas Graham (1861) - classical experiment e.g. rate of diffusion from different substances.
- Coined the term “Colloid” (glue like) to describe Selmi’s pseudosolution. Displayed a low rate of diffusion and lack of crystallinity therefore the particles must be very large at least 1 nm. On the other hand, failure of the particle to sediment under the influence of gravity explained that the particles have an upper limit of about 1 micron.
- Tyndal (1869)
- light scattered by colloidal particles is polarised.

Thomas Graham: Founder of colloidal chemistry

Graham's Laws of Diffusion and Effusion (Thomas Graham)

- In 1829 Thomas Graham used an apparatus similar to the one shown at the right to study the diffusion of gases -- the rate at which two gases mix.
- This apparatus consists of a glass tube sealed at one end with plaster that has holes large enough to allow a gas to enter or leave the tube.
- When the tube is filled with H_2 gas, the level of water in the tube slowly rises because the H_2 molecules inside the tube escape through the holes in the plaster more rapidly than the molecules in air can enter the tube.
- By studying the rate at which the water level in this apparatus changed, Graham was able to obtain data on the rate at which different gases mixed with air.

Graham found that the rates at which gases diffuse is inversely proportional to the square root of their densities



Thomas Graham: Founder of colloidal chemistry

- Graham extended his diffusion studies to liquids.
- He was particularly interested in the way in which dissolved substances passed through tiny holes in a membrane (the skin from a pig's bladder was a favorite kind of membrane used).
- When they were dissolved in water, most crystalline substances (which Graham called "crystalloids") passed fairly easily through membranes and diffused relatively quickly from one part of the liquid to another.
- But non-crystalline substances (e.g. glue, or gelatine) diffused very slowly when they were dissolved.
- Graham called this second class of substances "colloids", and it became clear that the reason for the difference in their rates of diffusion was the difference in size of their particles.
- Colloid particles are far larger than the molecules and ions present in solutions crystalloids.

Colloids - dispersions

- Simple colloidal dispersions are two phase systems
 - Dispersed phase: the phase forming the particles
 - Continuous phase (dispersion medium): the medium in which the particles are distributed

Continuous phase	Dispersed phase	Term	Example
Gas	liquid	Liquid aerosol	clouds, fog, smog, hairspray
	solid	Solid aerosol	smoke, dust, pollen
Liquid	gas	Foam	lather, whipped cream, foam on beer
	liquid	Emulsion	milk
	solid	Sol, colloidal suspension	ink, muddy water, dispersion paint
Solid	gas	porous solids*	
		foam	styrofoam, soufflés
	liquid	solid emulsion	butter
	solid	solid suspension	concrete

Colloids - dispersions

Foams and liquid foams

liquid foam: dispersion of a gas in a liquid

solid foams: dispersion of a gas in a solid

liquid foams



soaps and detergents

aerogel (solid foam)



99 % air

Colloids - dispersions

Aerosol

liquid particles dispersed in gas

mist
(visibility higher)



fog
(visibility < 1 km)



clouds
(liquid or frozen droplets)

Colloids - dispersions

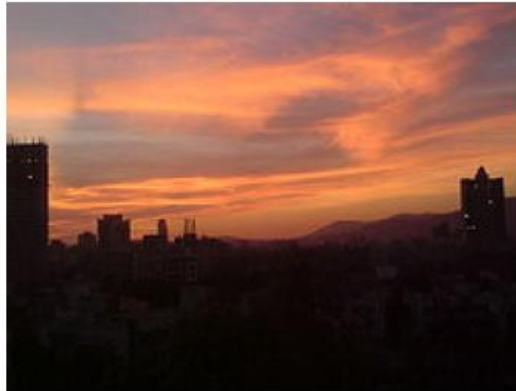
Solid aerosol

solid particles dispersed in gas



fire extinguisher:
tiny solid particles
(40% alkaline metal oxide)
suspended in gas
(60% CO₂, water vapor, N₂)

particulates in air



Colloids - dispersions

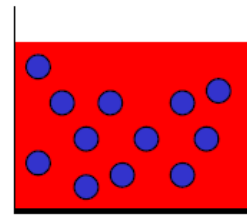
Emulsion

mixture of 2 immiscible liquids:
liquid dispersed in another continuous liquid



oil in water

emulsifier
→



emulsion

dispersed oil droplets in water

Milk is an emulsion of fat in water.
Butter is an emulsion of water in fat



Oil in water (o/w)--
->mayonnaise,
milk



water in oil (w/o)---butter

Colloids - dispersions

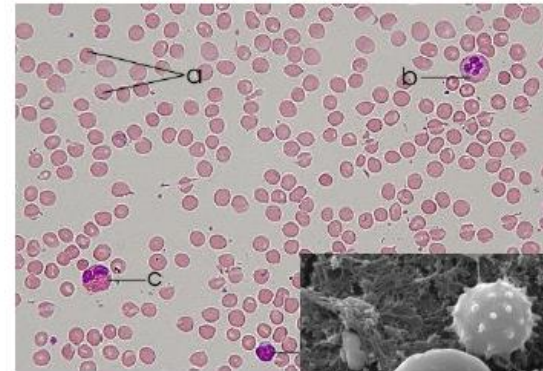
Sols

solid particles in a liquid

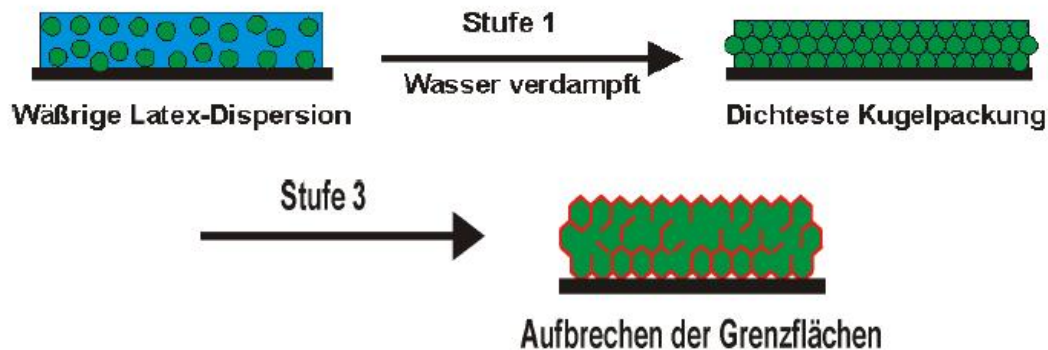
paints



blood



red and white
blood cells

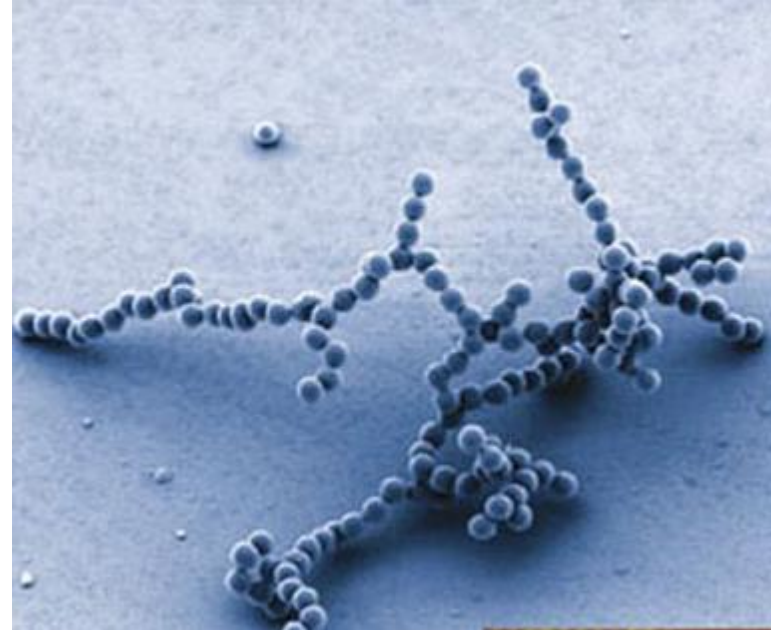


Colloids and interfaces

- Colloids and interfaces are intimately related.
- This is a direct consequence of their enormous specific surface area.
- Their interface-to-volume relation is so large, that their behavior is completely determined by surface properties.
- Gravity is negligible in the majority of cases.
- For this reason we could define colloidal systems as systems which are dominated by interfacial effects rather than bulk properties.
- This is also the reason why interfacial science is the basis for nanoscience and technology and many inventions in this new field originate from surface science.

An example

- A system dominated by surface effects
- SEM image shows aggregates of quartz (SiO_2) particles (diameter $0.9\ \mu\text{m}$).
- *These particles were blown as dust into a chamber filled with gas.*
- While sedimenting they formed fractal aggregates due to attractive van der Waals forces.
- On the bottom they were collected.
- These aggregates are stable for weeks and months and even shaking does not change their structure.
- Gravity and inertia, which rule the macroscopic world, are not able to bend down the particle chains.
- Surface forces are much stronger...

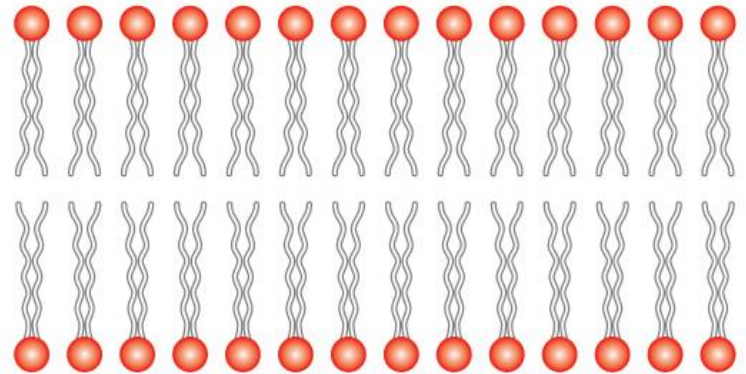


Interest in interfaces

There are two good reasons to study and understand this intrinsic difference between surface and bulk properties:

1. *scientific curiosity*
2. *the desire to gain control over the so important interface processes such as corrosion, passivation, materials processing such as film growth and etching, and heterogeneous catalysis, etc.*

- A better understanding of natural processes.
- In biology the surface tension of water allows to form lipid membranes.
 - This is a prerequisite for the formation of compartments and thus any form of life.
- In geology the swelling of clay or soil in the presence of water is an important process.



- The formation of clouds and rain due to nucleation of water around small dust particles is dominated by surface effects.
- Many foods, like butter, milk, or mayonnaise are emulsions.
- Their properties are determined by the liquid–liquid interface. Washing and detergency are examples which any person encounters every day.

Interest in interfaces

- Surfaces and interfaces are phase boundaries
- Phase boundaries are the locations of gradients, and gradients are a driving force for processes.
- If, for instance, we put a piece of rock candy into a glass of tea, the sugar crystal and the water occupy separate volumes, separated by a sharp phase boundary.
- With time, however, water molecules attack the crystal (at the surface) and sugar molecules are detached and diffuse into the liquid phase.
- We observe the process of dissolution, which continues until the distribution of water and sugar molecules is uniform throughout the glass, until there is no more phase boundary between sugar and water.



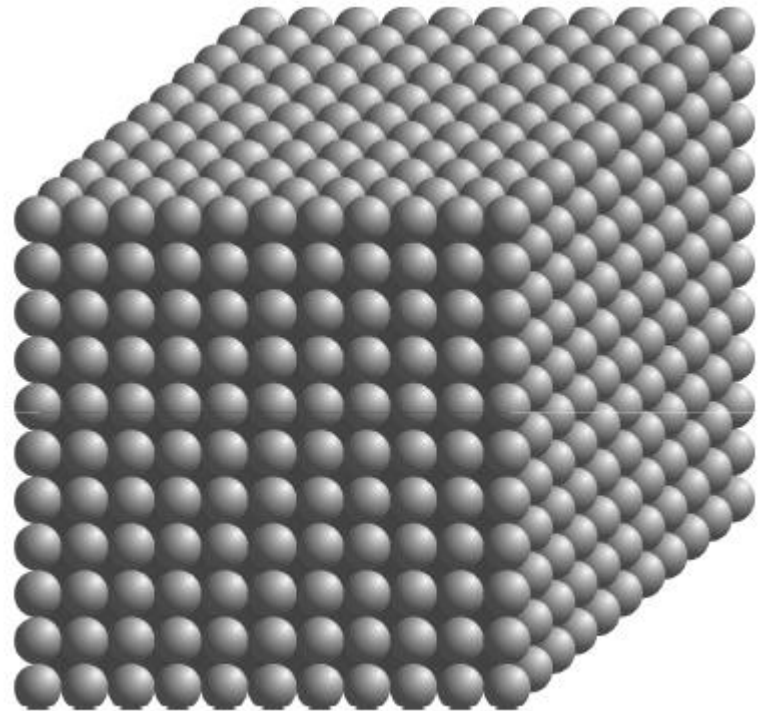
Interest in interfaces

- A similar “decay process” destroys our car despite all our care to maintain and protect its surface as mentioned above.
- Thus, the gradients at interfaces drive spontaneous processes, irrespective of whether we want them to occur or not.
- We want the sugar to sweeten our tea homogeneously, but we do not want the decomposition of our car.
- The respective process, of course, depends on the nature of the two phases on either side of the phase boundary (an acidic solution attacks the surface of our car much more effectively than pure water).
- More precisely, the respective process depends on the properties of both phases within their area of immediate contact.
- These interface properties ultimately determine the mechanism, the speed, and the final product of the process.



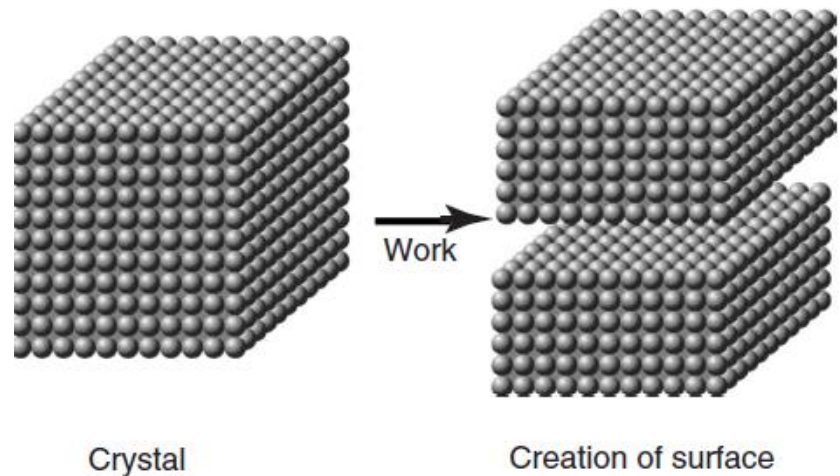
Bulk vs. Surface

- Why are surfaces so peculiar?
- Basic deviations between the surface and the bulk of a condensed phase.
- These obvious deviations will lead to the natural insight that surface and bulk properties must be different.
- Take a crystal in vacuum as our test sample.
- The facets of a crystal are planar surfaces
- These facets include characteristic angles.
- This simple geometric habitus of crystals suggests that the basic building blocks, atoms, ions, and molecules are also piled up in a regular way (as verified by diffraction techniques).



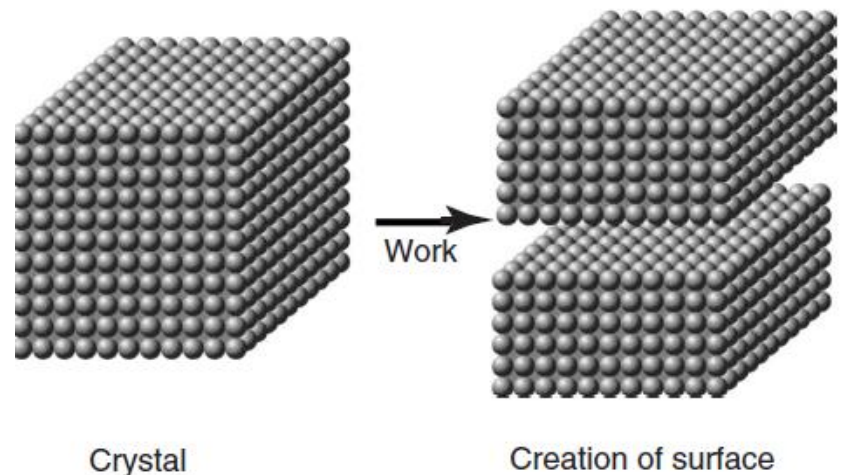
Bulk vs. Surface

- Attractive interactions between these building blocks, for example, electrostatic forces between the chloride anions and sodium cations in rock salt; metallic bonds in metals such as iron, copper, platinum, or tungsten; or “covalent bonds” in silicon or diamond, keep the building blocks together.
- These attractive forces can be very strong, which becomes obvious if we try to cut up a crystal; it costs a lot of work to cleave a piece of rock salt or to cut a piece of metal or even a diamond.
- This energy is needed to sever, to cut the “bonds” between all atoms on both sides of the section plane.
- As a result, two new surfaces have been created, and all atoms at these two new surfaces have been bereaved of their bonds to their former neighbors (which are now at the distant opposite surface).



Bulk vs. Surface

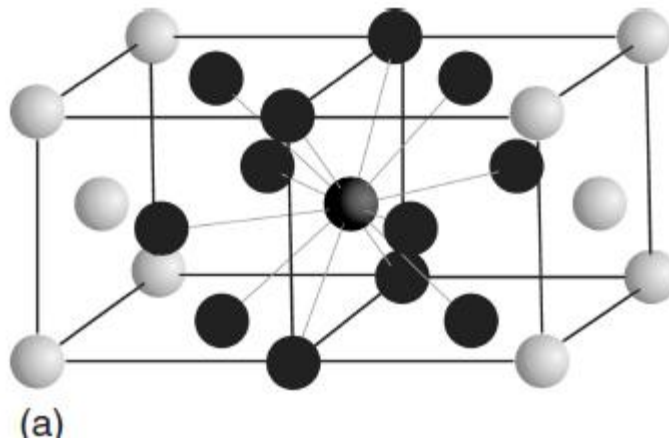
1. The first consequence of this rupture is that all surface atoms find themselves in an asymmetric environment.
 - While the bulk atoms are symmetrically surrounded by their nearest neighbors, the surface atoms have no neighbors on one side, but only vacuum.
2. Surface atoms are freely accessible from the vacuum side.
 - On the one hand, they are freely accessible by experimental probes, and, on the other hand, they would be the first to be exposed to atoms or molecules of an adjacent (gaseous, liquid, or solid) phase.
3. The applied energy needed to rupture the bonds must now (to a large extent) be stored in the “unsaturated bonds” of all surface atoms at the newly created surfaces (energy conservation).



Bulk vs. Surface

Effects that can be anticipated on the basis of these three consequences.

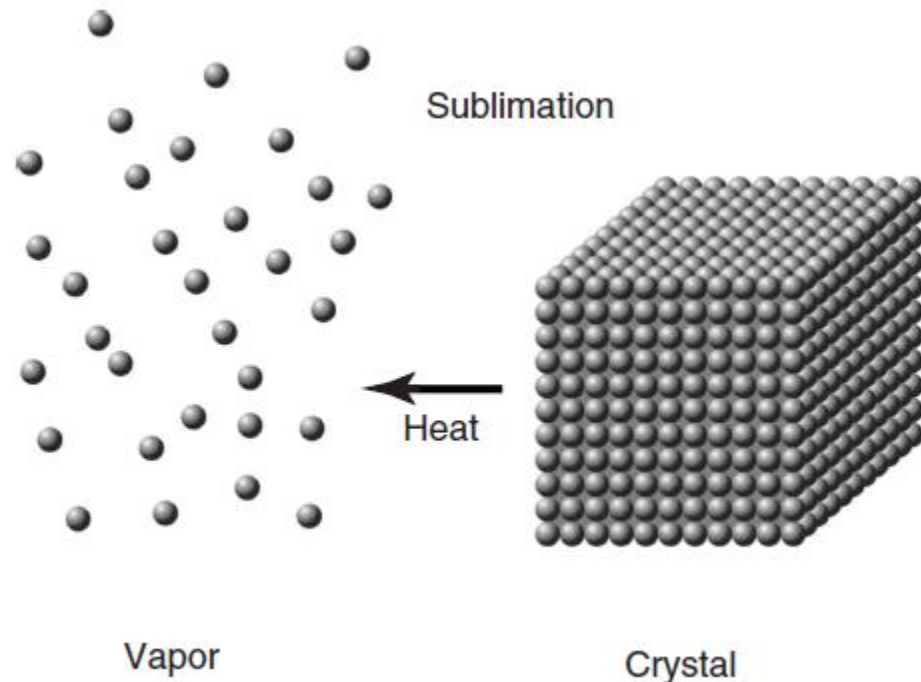
- It is easily seen that surface atoms must have a higher energy than bulk atoms, and it is even straightforward to estimate their excess energy.
- In the interior of the crystal, every atom has, depending on the specific crystal structure of the material, for example, in copper (Cu), 12 nearest neighbors



Bulk vs. Surface

Effects that can be anticipated on the basis of these three consequences.

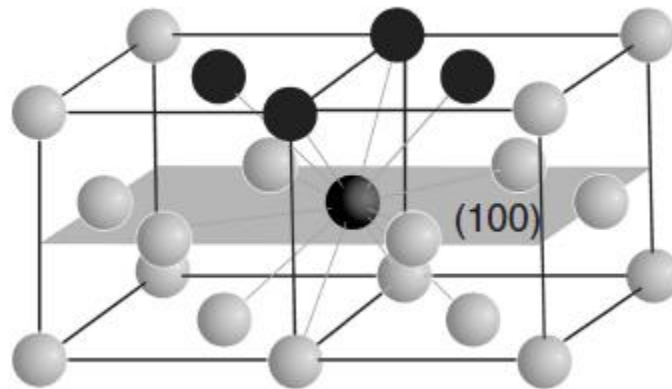
- If we heat the copper crystal to such a high temperature that it completely evaporates, we break all bonds between all copper atoms in the crystal (Figure 1.3).
- The minimum energy to achieve this is the sublimation energy E_{sub} , a well-known and tabulated thermodynamic quantity for 1 mol of most elements and compounds.
- Thus, the sublimation energy is required to break $12 N_A$ bonds,
- N_A being the number of atoms per mole copper (Avogadro's number).
- Thus, dividing the sublimation energy by $12 N_A$ yields the energy $E_{\text{Cu-Cu}}$ to break one Cu–Cu bond.
- Since every broken Cu–Cu bond creates two separated Cu atoms per broken bond, the energy per Cu atom increases by $\frac{1}{2} E_{\text{Cu-Cu}}$



Bulk vs. Surface

Effects that can be anticipated on the basis of these three consequences.

- *All that remains to be done is to count, on the basis of the crystal structure, the number of interrupted bonds per surface atom, which is equal to*
 - $(12 - \text{the number of remaining neighbor atoms per surface atom}) \times \frac{1}{2} E_{\text{Cu-Cu}}$
- *So, if we cut a copper crystal along the plane denoted (100), every surface atom is left with eight neighbors, four bonds are unsaturated (between the central atom and the four black atoms).*

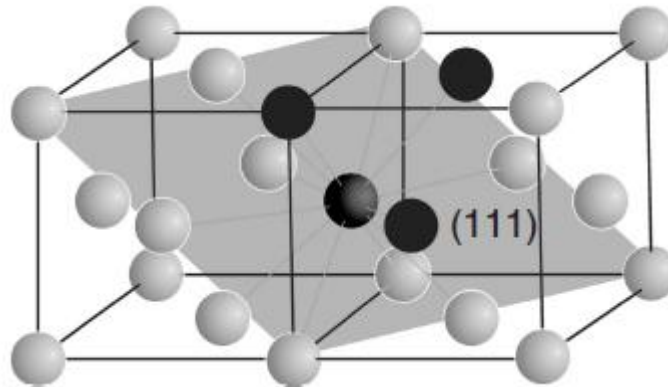


- These unsaturated bonds are called “dangling bonds.”
- Thus, the excess energy per surface Cu atom in the (100) plane is $2 E_{\text{Cu-Cu}}$.
- Surface atoms of high coordination number are more stable

Bulk vs. Surface

Effects that can be anticipated on the basis of these three consequences.

- If instead we cut the crystal along the plane denoted (111), every surface atom retains nine neighbors, that is, only three bonds become dangling bonds, and the excess energy per Cu atom in the (111) plane is $3/2 E_{Cu-Cu}$.



Bulk vs. Surface

Effects that can be anticipated on the basis of these three consequences.

- As a general rule, every physical system prefers to assume a state of minimum total energy.
- If the temperature is high, say 5000 K, the copper atoms will form a vapor of individual atoms: Their high thermal energy (motion) overcompensates the attractive forces between them and prevents them from bonding to each other.
- If the temperature is low, for example, room temperature, the copper atoms form a solid piece of metal (attractive forces between the copper atoms).
- Energy increase dissociates the bonds, whereas bond formation leads to a lower state of energy.
- The lowest state of energy is reached once every copper atom binds to the maximum possible number of neighbors, that is, 12 other copper atoms
- Only the very surface atoms suffer an unavoidable lack of neighboring atoms and are thus *not in the lowest* possible energy state of an atom within the crystal lattice.
- Existence of under-coordinated surface atoms increases the total energy of the crystal.
- The total surface-induced excess energy is given by the total number of “dangling bonds” of all surface atoms times $1/2 E_{Cu-Cu}$.

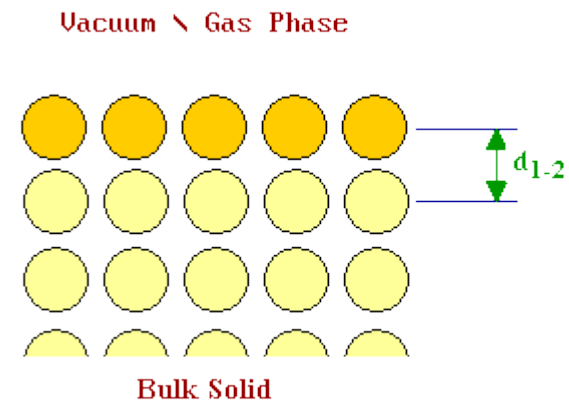
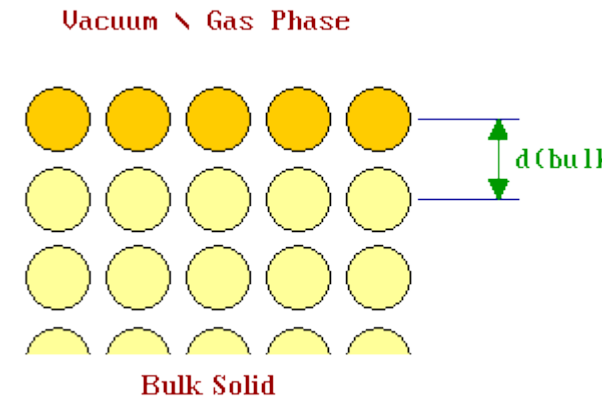
Bulk vs. Surface

- *All surfaces are energetically unfavourable in that they have a positive free energy of formation.*
- *A simple rationalisation for why this must be the case comes from considering the formation of new surfaces by cleavage of a solid and recognizing that 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, so the surface free energy contribution to the total free energy of a system must therefore be positive.*
- *The unfavourable contribution to the total free energy may, however, be minimised in several ways :*
 - *By reducing the amount of surface area exposed*
 - *By predominantly exposing surface planes which have a low surface free energy*
 - *By altering the local surface atomic geometry in a way which reduces the surface free energy*

Bulk vs. Surface

How to reduce excess surface energy? - Surface relaxation

- Surface atoms have neighbors only in and below the surface, but not on the outside.
- This asymmetry causes an obvious imbalance of bonding forces acting on the surface atoms perpendicular to the surface.
 - We expect the surface atoms to be pulled downward,
- This reduction of distance between the first and second atomic layer, and, thus, reduction of Cu–Cu bond lengths is called “**surface relaxation**.”
- *In this case, the change in bond length between atoms of the first and second layer leads*
 - to a decrease of the total surface excess energy, and,
 - to a decrease of the energy per surface atom (the atomic arrangement *parallel to the surface* remains unchanged).



Bulk vs. Surface

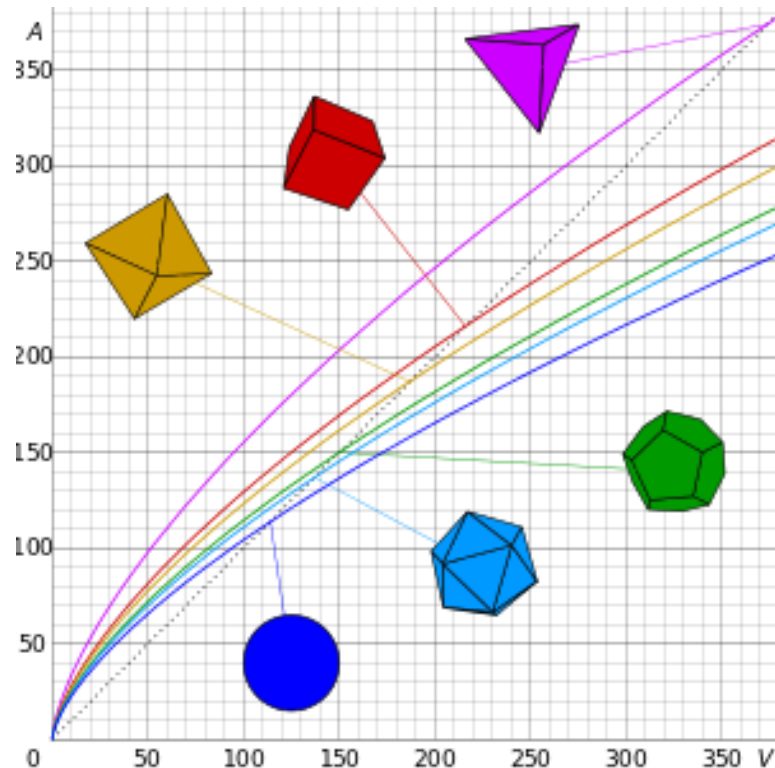
How to reduce excess surface energy? – Surface segregation

- Suppose we do not have a pure copper crystal but a copper–nickel alloy (of the same crystal structure).
- The sublimation energy of copper is lower than that of nickel.
- Consequently, the energy per dangling Cu bond is lower than that of nickel.
- Given again the chance, a Cu–Ni crystal would thus prefer to be totally surrounded by a layer of Cu atoms rather than Ni atoms.
- Since this requires the diffusion of Cu atoms out of the bulk to the surface in order to replace surface Ni atoms, this “chance is given” when the crystal is heated and the diffusion of atoms is activated.
- This phenomenon of “**surface segregation**,” that is, the enrichment of the alloy component with the lower heat of sublimation at the surface, has again been verified experimentally for many systems.
- **Important conclusion:** in equilibrium, the surface composition of multicomponent systems, for example, alloys, must be different from the bulk composition, as long as the sublimation energies of the components are different.

Bulk vs. Surface

How to reduce excess surface energy? – Reduce the total # of dangling bonds

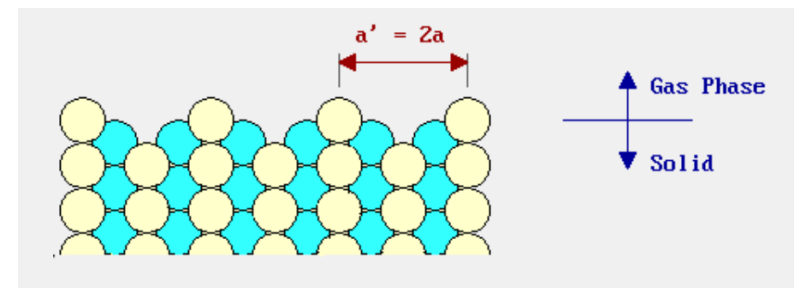
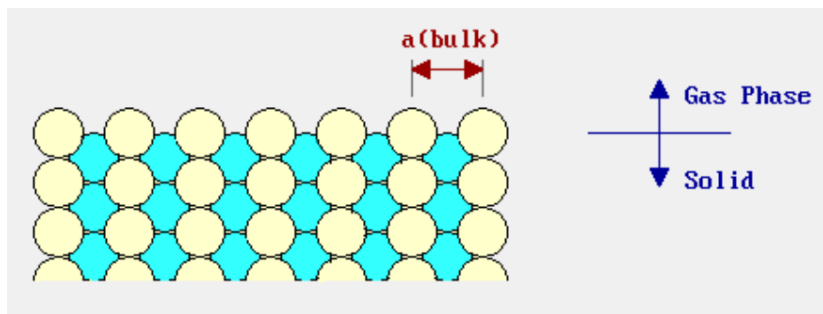
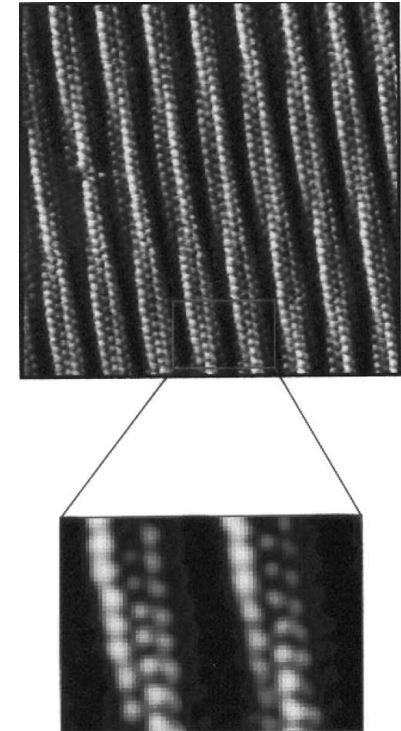
- Reduction of the number ratio of surface-to-bulk atoms at constant total number of atoms
- For instance, if we melt the copper crystal and let the drop solidify, the number ratio of surface-to-bulk atoms of the resulting *sphere*, to a first approximation, and, as a consequence, the surface excess energy is lowest.



Bulk vs. Surface

How to reduce excess surface energy? – Surface reconstruction

- Reduction of the number of dangling bonds per surface atom
- We could restructure a crystal such that it is terminated only by (111)-facets
 - With only three dangling bonds per surface atom rather than by (100) facets, etc, with higher numbers of dangling bonds per surface atom,
- The surface excess to the total energy of the crystal would also decrease.
- This restructuring, of course, would also require mass transport because the atomic density of a hexagonal (111) plane is $\sim 20\%$ higher than that of a (100) plane, and, hence, thermal activation.
- This phenomenon of “**surface reconstruction**,” can indeed be observed experimentally if certain clean surfaces are heated in vacuum (STM).



Bulk vs. Surface

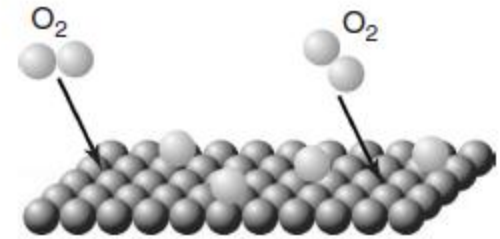
How to reduce excess surface energy? Summary

- **Surface relaxation** - reduction of distance between the first and second atomic layer
- **Surface segregation** - the enrichment of the alloy component with the lower heat of sublimation at the surface
- **Minimization of the total surface area** –
- **Surface reconstruction** - Reduction of the number of dangling bonds per surface atom
- ❖ While “surface relaxation” leaves the structure (periodicity) within the first atomic layer unchanged from that of the second (and any parallel deeper) layer, “surface reconstruction” leads to a dramatic change of the structure of (at least) the first atomic layer.
- ❖ **As a consequence of all this, *all typical solid state properties of a given piece of solid matter* are different at its surface compared to its bulk.**

Importance of Surfaces and Interfaces

Adsorption

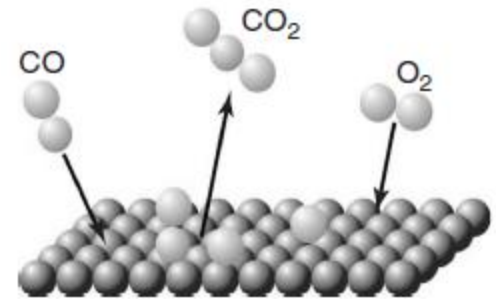
- The most obvious way to reduce the excess surface energy is to expose the surface atoms to new bonding partners that saturate the dangling bonds.
- Atomically clean surfaces, freshly prepared in vacuum, once exposed to gases, are indeed prone to the attachment, that is, “adsorption,” of gas molecules or atoms – if the formation of the new bonds leads to a lowering of the total energy, notably the surface excess energy.
- Clean metal surfaces immediately adsorb oxygen from the atmosphere
- If this oxygen uptake process proceeds into the interior of the metal, we are faced with **oxidation and corrosion**.
- Any chemical reaction of a solid A with an adjacent phase B, that is, a gas or a liquid (or another solid), necessarily starts at and proceeds through the interface between A and B.
- Likewise, the mere physical deposition of atoms or molecules from a gaseous or liquid phase B on a solid surface A leads to the formation of thin films of material B on the substrate A.
- In all cases, the primary step is the attachment of particles B (the adsorbate) on the bare surface A (the substrate)



Importance of Surfaces and Interfaces

Adsorption is a fundamental surface process of enormous economic relevance.

- It is easy to conceive that on adsorption, molecules change their properties.
- Owing to the extra bond to the surface, the electronic and vibrational properties of the adsorbed molecules most likely differ from those of the same molecules in the gas (or liquid) phase.
- This difference is the basis of *heterogeneous catalysis*.
- Two *adsorbed, and thereby modified, molecules may react easier with each other* and, due to quite different sterical constraints, to different products than the same two molecules in the gas phase
- Both the adsorption-induced enhancement as well as the altered selectivity of this reaction toward specific reaction products may be tuned by the choice of the adsorbing surface, that is, the “catalyst.”
 - In cars, convert poisonous into (more or less) harmless exhaust gases.
 - Fuel cells, promising alternative energy sources for the future, are based on similar catalytic process



Importance of Surfaces and Interfaces

Nanoscience and technology

- The surface acts as a mere support for these tiny objects.
- This role of surfaces becomes particularly important in nanoscience and nanotechnology.
- Nanosized entities of solid matter are not easy to handle, let it be ultrathin films of nanometer thickness (nanosized in one dimension), nanowires (nanosized in two dimensions), or nanodots (clusters, bigger molecules) being nanosized in all three dimensions.
- A convenient way to study their properties is to attach them to the surface of a solid, which of course is possible due to interactions between them and the supporting surface.

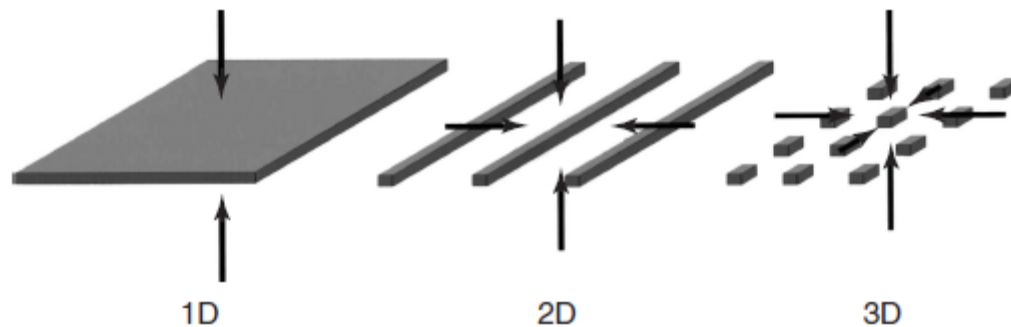
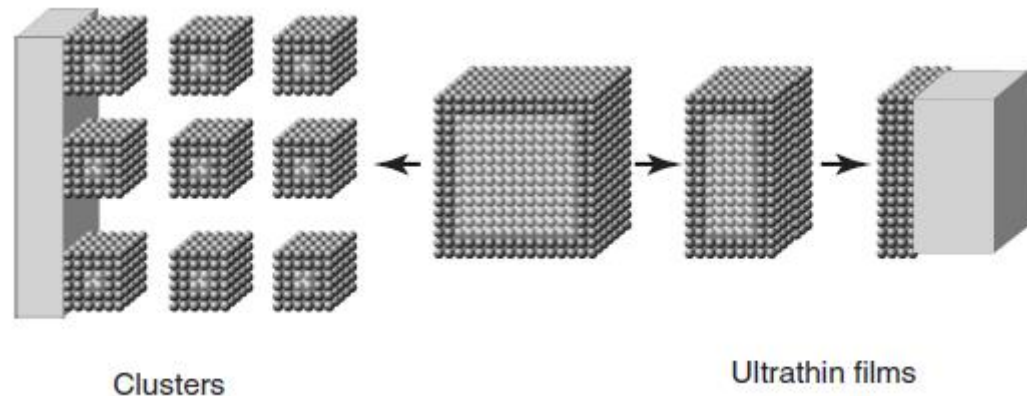


Figure 1.7 Nanosized materials: ultrathin films (nanosized in one dimension), nanowires (nanosized in two dimensions), and nanodots (clusters) nanosized in all three dimensions.

Importance of Surfaces and Interfaces

Nanoscience and technology

- These interactions may alter the properties of these nanosized entities to some extent, the properties of matter must change once its dimensions shrink to nanosize.
- One reason for this expectation is that surfaces must have different properties than the bulk of the respective material.
- Ultrathin, only a few-atomic-layers-thick films, nanowires, and small clusters are dominated by surfaces; there is hardly any bulk (Figure 1.8).
- The properties of these clusters must be dominated by those of their surface atoms.
- Moreover, to a first approximation, the average properties of a cluster as a whole should vary with its size due to the variation of the number ratio of surface-to-“bulk” atoms.
- By selecting the cluster size, it is, thus, possible to “tune” the properties of one and the same material



Importance of Surfaces and Interfaces

Summary

- Surfaces/interfaces cause “confinement” of assemblies of atoms as well as their itinerant valence electrons and that the atoms at the surface/interface find themselves in an asymmetric environment
- Differences between the surface and bulk properties of one and the same piece of matter.
- Often cited statement by Wolfgang Pauli (Nobel Prize in Physics 1945)

“God made the bulk; the surface was invented by the devil”