

# 1

## Introduction: An Intuitive Approach to Surface and Interface Science

*Klaus Wandelt*

Let us imagine – just for a moment – a world without surfaces and interfaces.

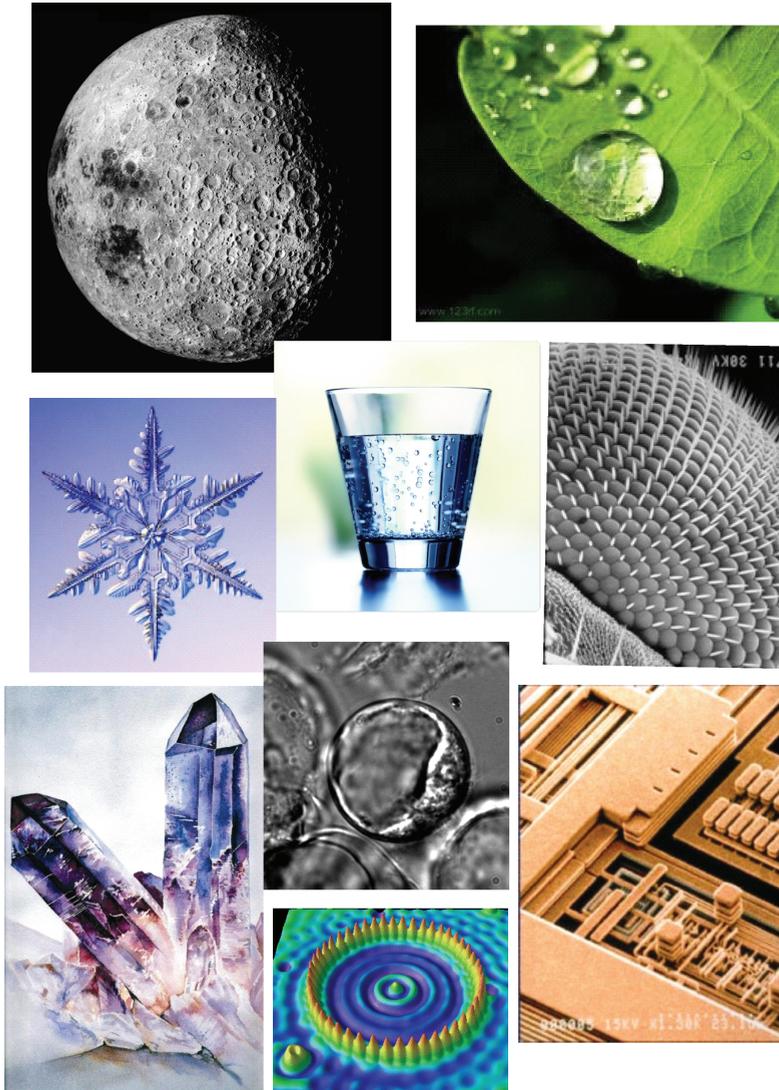
This world would be totally uniform, monotonous, and boring. There were not all these many distinct things that actually make our world so diverse and beautiful: celestial bodies, rocks, lakes, plants, animals, and all manmade structures such as buildings, cars, tools, computers, and so on. How do we marvel at the beauty of an ice crystal. How do we admire the diversity of green leaves. How do we dream by looking at a mountain lake and the waves and reflections at its surface. How much care do we give to clean and polish the surface of our cars. And how impressive are the delicate structures of a fly's eye and a modern computer chip (Figure 1.1).

### 1.1

#### Peculiarities of Surfaces

Surfaces and interfaces are “phase boundaries”, that is, they delimit distinguishable regions of matter (phases) and define the shape of these regions as long as they are solid.

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. 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



**Figure 1.1** Moon: NASA; Eye of a fly: “Münsters Universitätszeitung” of 2000, 15 Dec; Ice crystal: “Mandala”, online contribution by Hans Jürgen Wevers, 2006, 21 June; Computer chip: IBM Research News 4/97; Quantum Corral: IBM Corp. 1995.

phases within their *area of immediate contact*. These interface properties ultimately determine the mechanism, the speed, and the final product of the process.

It appears quite intuitive that the mere contact between two unlike phases leads to an alteration of their properties *at the interface* from their respective properties *in the bulk*. For instance, the interface between a piece of pure iron and air will be

enriched with oxygen compared to the bulk of either adjacent phase. It is, however, much less intuitive that the properties of the surface of a phase are different from the bulk properties if this phase is in contact with nothing, that is, vacuum.

It is part of the success story of surface science of the past 40 years that shows clearly that in equilibrium also the bare surfaces of solid materials in contact with ultrahigh vacuum (UHV) have, and indeed *must have*, properties that are different from those of the bulk. In essence, this means that even though we may know the bulk properties of iron, copper, silicon, or alloys *we do not know the properties of the atomically clean and well equilibrated surfaces* of iron, copper, silicon, or these alloys.

There are two good reasons to study and understand this intrinsic difference between surface and bulk properties: (i) *scientific curiosity* and (ii) *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.

Why are surfaces so peculiar? We start by drawing the attention to some 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. Following this insight, we also draw the attention to some fundamental as well as economic consequences of the peculiar physical and chemical properties of surfaces and interfaces.

Let us take a crystal in vacuum as our test sample. The facets of a crystal are planar surfaces as seen in Figure 1.1 and schematically depicted in Figure 1.2. 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). 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

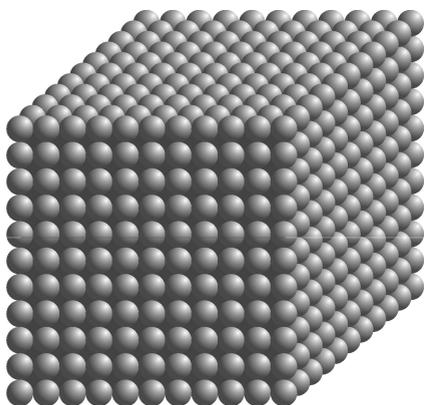
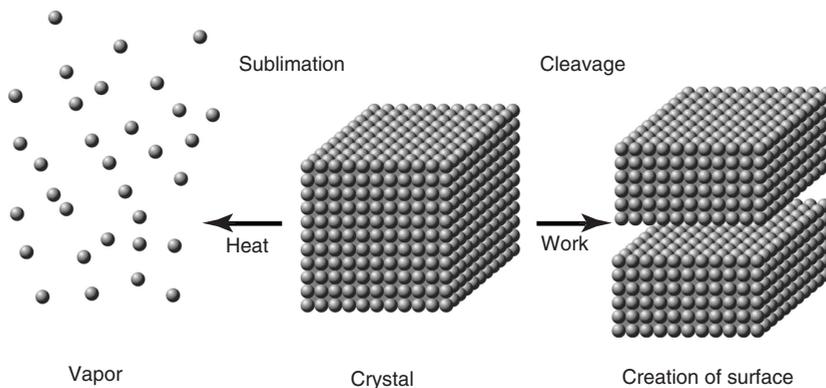


Figure 1.2 Schematic crystal.



**Figure 1.3** Cleavage breaks some bonds whereas sublimation breaks all bonds that previously held a crystal together.

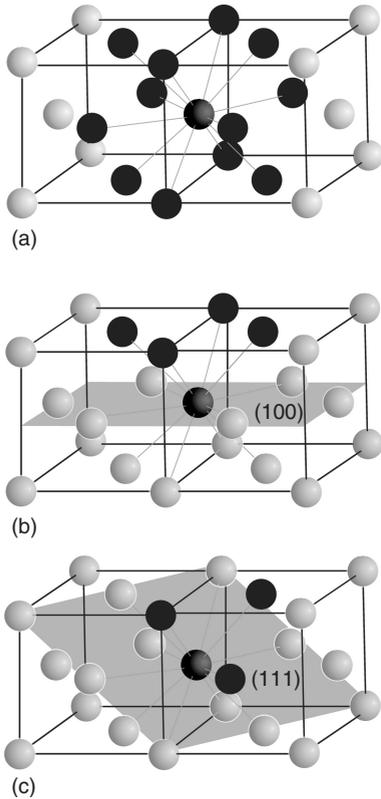
surfaces have been created (Figure 1.3), and all atoms at these two new surfaces have been bereaved of their bonds to their former neighbors (which are now at the distant opposite surface) (Figure 1.3).

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.

As a further, apparently trivial consequence of this asymmetry, 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. Third, 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).

We now discuss 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 (Figure 1.4a). 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  $E_{\text{sub}}$ , a well-known and tabulated thermodynamic quantity for 1 mol of most elements and compounds. Thus, the sublimation energy is required to break  $12N_A$  bonds,  $N_A$  being the number of atoms per mole copper (Avogadro’s number). Thus, dividing the sublimation energy by  $12N_A$  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  $1/2E_{\text{Cu-Cu}}$ . All that remains to be done is to count, on the basis of the crystal structure (Figure 1.4), the number of interrupted bonds per *surface*



**Figure 1.4** In many metals each atom is surrounded by 12 nearest neighbors (a). Cutting such crystal parallel to a plane denoted (100) (b) or a plane denoted (111) (c) leaves every *surface* atom with four or three unsaturated bonds, respectively.

atom, which is equal to 12 minus the number of remaining neighbor atoms per surface atom, and to multiply this number by  $1/2E_{\text{Cu-Cu}}$ . So, if we cut a copper crystal along the plane denoted (100) (Figure 1.4), every surface atom is left with eight neighbors, four bonds are unsaturated (between the central atom and the four black atoms in Figure 1.4b). These unsaturated bonds are called “*dangling bonds*.” Thus, the *excess* energy per surface Cu atom in the (100) plane is  $2E_{\text{Cu-Cu}}$ . 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 (Figure 1.4c), and the excess energy per Cu atom in the (111) plane is  $3/2E_{\text{Cu-Cu}}$ .

As a general rule, every physical system prefers to assume a state of minimum total energy, which under equilibrium conditions, of course, depends on the external conditions. 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 (which proves that there are attractive forces between the copper atoms). Thus, 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 (and has reached its own lowest energy state). 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 copper crystal lattice. Compared to the hypothetical lowest energy state in which *all* copper atoms of the crystal would have 12 neighbors, the mere 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  $1/2E_{\text{Cu-Cu}}$ . Given the chance, the copper crystal would try to reduce this surface excess energy by either reducing the number of “dangling bonds” or by reducing the energy per dangling bond. And there are, indeed, ways by which a crystal can achieve this.

As emphasized before, 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. As a logical consequence, we expect the surface atoms to be pulled downward, that is, closer to the next layer underneath. This reduction of distance between the first and second atomic layer, and, thus, reduction of Cu–Cu bond lengths, can nowadays easily be verified experimentally as described in Chapters 3.2.1 and 3.3, and 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 (otherwise it would not occur), and, since the atomic arrangement *parallel* to the surface remains unchanged, to a decrease of the energy per surface atom. We anticipate that the degree of surface relaxation, that is, gain of “relaxation energy,” depends on the number of bonding partners per surface atom in the second layer, that is, on the crystallographic orientation of the surface plane, for example, (100) or (111) (see Figure 1.4).

This observation that the crystal can reduce the excess energy per surface atom (as above by surface relaxation) can also be realized in a different way. 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. Our simple energetic arguments, put forward here, lead to the following correct and 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 (and/or, for the sake of completeness, the atomic radii; see Chapter 11) of the components are different.

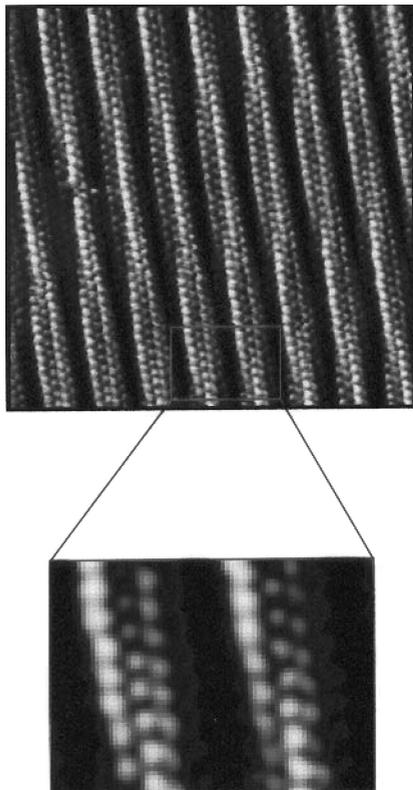
Yet another obvious strategy to reduce the surface excess energy of a given system is to reduce the total number of dangling bonds, which can be achieved in two ways, either by a reduction of the number ratio of surface-to-bulk atoms at

constant total number of atoms, for example,  $N_A$ , or by a reduction of the number of dangling bonds per surface atom. 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. Instead, if we could, without melting, 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. For instance, if a platinum (100)-terminated crystal with a quadratic arrangement of the surface atoms is annealed at sufficiently high temperature, the surface “reconstructs” and assumes a hexagonal atom arrangement like a (111) surface. This reduces the number of dangling bonds per surface atom from four to three. Of course, a layer of hexagonally packed atoms does not fit on a (still) quadratic symmetry of the second (100) layer of atoms underneath. As a consequence, this should lead to an extra “superstructure” at the surface, because not all surface atoms sit in fourfold hollow sites between second-layer atoms anymore. Only some may happen to sit in a fourfold hollow site, while others will come to sit on bridge sites between two or even on top of only one second-layer atom. Thus, we anticipate a periodic long-range height modulation of surface atoms. Figure 1.5 shows images of a reconstructed Pt(100) surface. These images were taken with a scanning tunneling microscope (STM) whose fascinating capabilities are described in Chapter 3.5. Note the wavy height (brightness) modulation of the atoms. Zooming into this structure shows, unlike the normal Pt(100) plane as sketched in Figure 1.4b, a hexagonal arrangement of the atoms (Figure 1.5). The most spectacular case of surface reconstruction is that of the silicon(111) surface, which instead of a simple hexagonal structure shows one with protruding atoms and even holes (see Chapter 3.5 and Chapter 9). The driving force for these “reconstructions” is the lowering of the surface excess energy. And even though a (111) surface is already hexagonally densely packed with the lowest number of dangling bonds among the simple crystallographic surface planes, an even further “reconstruction” is observed for gold(111) (see Chapter 3.5 and the cover of volume 2).

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. In both cases, bond lengths between atoms change; relaxation changes the lengths of bonds that point into the crystal, and reconstruction causes such changes not only perpendicular but also parallel to the surface.

It is obvious that these structural changes are manifestation of altered bonding forces between the surface-near atoms. And since interatomic bonds are “caused” by the valence electrons of the involved atoms, it is logic to anticipate that the



**Figure 1.5** Scanning tunneling microscopic (STM) images of a “reconstructed” platinum(100) surface (see text).

electronic properties at the very surface are also different from those of the bulk. Moreover, different bond strengths between atoms will change their easiness to move, that is, to vibrate (at finite temperatures). As a consequence of all this, we may, and indeed we *must*, expect that all typical solid state properties of a given piece of solid matter are different at its surface compared to its bulk.

The surface-specific electronic structure may be accompanied by different, surface-confined magnetic properties. The surface-specific vibrational properties should be the cause of not only a different molar heat capacity at the surface compared to that of the bulk but also a different ease of atom displacement in terms of diffusion and, ultimately, melting. All these expectations have been verified during the past decades of surface science. Surface-specific electronic properties, magnetism, vibrations (phonons), diffusion coefficients, melting temperatures, and so on, have been experimentally proven. It is justified to say that surfaces need to be described by physical properties that hold only for a few surface-near atomic/molecular layers, and that are different from those of the bulk, that is, by a two-dimensional surface physics. Most such investigations have been carried out over the past four decades with solid surfaces under UHV conditions. However, more recently, such investigations are extended to soft matter and liquid surfaces

as well as to solid surfaces in realistic, gas, and liquid environment. As a general result we may state: *surfaces are a new state of matter.*

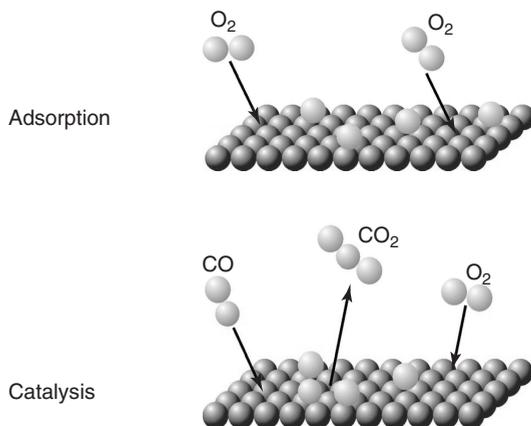
This result is a consequence of the parallel development of an impressive arsenal of methods, which are particularly sensitive to distinguish between surface and bulk properties. Undoubtedly, the most fascinating among these techniques are the STM and atomic force microscopy (AFM), which not only enable to visualize the atomic structure of surfaces but also permit to determine the other physical surface properties mentioned above *atom-by-atom*. Last but not least, these scanning probe techniques make possible the manipulation of individual atoms at surfaces (see Figure 1.1).

It is one obvious circumstance that to a great extent facilitated the investigations of surfaces: At least in UHV, surfaces are freely accessible, the atoms are openly “visible,” unlike bulk atoms or atoms at “buried” interfaces between two more or less condensed phases. This, for instance, enabled the use of particle (electron, ion, atom) beams to study surface properties. In turn, this reduced the number of available methods to look at “buried” interfaces, and it is one challenge for the future to develop new and improve existing methods to study the specific properties of surfaces in contact with other phases, that is, interfaces.

## 1.2 Importance of Surfaces and Interfaces

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 (Figure 1.6). If this oxygen uptake process proceeds into the interior of the metal, we are faced with oxidation and corrosion. If the oxide formation is limited to a thin, impermeable oxide film as it may be the case with aluminum, the surface oxide “passivates” the aluminum against further reactive attack. Steel may be protected against corrosion by a thin chromium coating. Chromium is passivated by oxidation, whereas iron is not. Copper exposed to wet air is eventually passivated by the so-called patina. 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), a consequence of the “desire” of surface atoms to saturate their dangling bonds and of the whole system to lower its total energy.

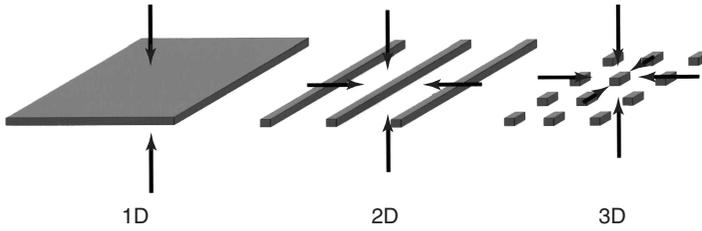
Adsorption is a fundamental *surface process* of enormous economic relevance.



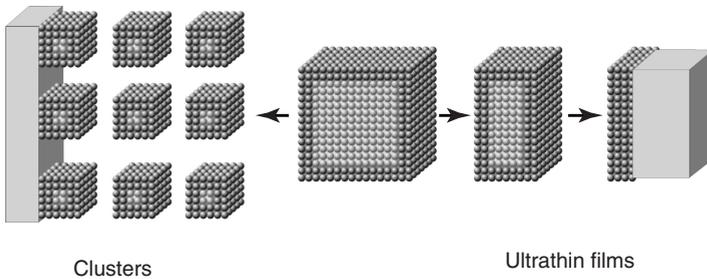
**Figure 1.6** Adsorption of molecules at surfaces may change their properties (e.g., dissociate oxygen molecules) and enhance their reactivity with other molecules, the basis of heterogeneous catalysis.

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 (Figure 1.6) 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 this way, the catalysts in our cars convert poisonous into (more or less) harmless exhaust gases. More than 90% of all industrially important chemical reactions include at least one heterogeneously catalyzed reaction step. Fuel cells, promising alternative energy sources for the future, are based on similar catalytic reactions at solid/liquid interfaces. Flotation, the process with the largest mass turnover to separate precious ore from ore gangue, is based on the choice of appropriate adsorbates at a three-phase solid/liquid/gas interface. As mentioned earlier, corrosion causes gigantic economic losses; specific reactive or physical thin film coatings can substantially lower these losses.

Owing to adsorption, atoms and molecules become fixed in space. Besides, the fact that the fixation makes them actually visible to the scanning probe techniques and that the bonding to the surface alters their properties, 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 (Figure 1.7). A convenient



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



**Figure 1.8** Illustration of the change of the number ratio of surface-to-bulk atoms if a macroscopic crystal is cut into thin layers or small clusters.

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. Even though, as discussed above, these interactions may alter the properties of these nanosized entities to some extent, the genuine properties of matter must change once its dimensions shrink to nanosize. One reason for this expectation is a logical consequence of all we have discussed before about surfaces. We came to the conclusion 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 (Figure 1.7) are dominated by surfaces; there is hardly any bulk (Figure 1.8). On the basis of this, 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.

The surface of a piece of solid matter encompasses a certain number of atoms, out of which some are surface atoms and the rest are bulk atoms, and the existence of the surface also confines the otherwise itinerant valence electrons in a solid. From the quantum mechanical model of an “electron in a box,” we know that the possible energy states of the enclosed (bound) electron depend on the dimensions of this box. The smaller the box, the higher and the more separated are the

possible energy states. Vice versa, if the box becomes larger, these energy levels are concentrated the closer at low energies. Dimensional changes of a *small* box result in significant changes of the allowed electronic states, while dimensional changes of a *very large* box have hardly any influence on the energy distribution of the states. Both together, the increasing portion of surface atoms as well as the closer surface-induced confinement of valence electrons with shrinking dimensions of nanoobjects are the basis for the great interest in nanomaterials: By simple size control, it is possible to tune the physical, chemical, and catalytic properties of small particles. The well-known STM image of a “quantum coral” of 48 iron atoms, artificially assembled atom by atom on a Cu(111) surface (Figure 1.1), not only demonstrates the outstanding capabilities of modern surface methods but also illustrates that the properties of the Cu surface inside and outside the ring are different. The confinement of a surface-specific electronic state of the Cu(111) surface within the ring makes the properties of the Cu surface inside the ring different from outside (see Chapter 5 and Figure 1.1). Besides, composite architectures of nanosized materials get on with less amount of these materials, and the closeness of individual nanosized building blocks of, for instance, electronic circuits reduces the energy consumption (conservation of materials and energy resources).

### 1.3

#### Summary

By starting from the simple and obvious fact that 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, we were able to draw some intuitive conclusions about the differences between the surface and bulk properties of one and the same piece of matter. Surface science of the past four decades has experimentally verified all these conclusions – and many more, and has thereby laid the rational basis for many modern technologies which have not only shaped our life but also seem to be of vital importance for our future.

In conclusion, if the often cited statement by Wolfgang Pauli (Nobel Prize in Physics 1945) “God made the bulk; the surface was invented by the devil” is correct, we should be very grateful to the devil.