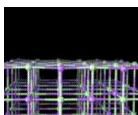


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BOUNDARIES AND BARRIERS: SURFACES AND INTERFACES

The behavior of molecules and materials is determined in many instances not by what happens in their interior, but by what happens on their surfaces. Chemical reactions often take place at surfaces - and surfaces can promote chemical reactions, as in the field of heterogeneous catalysis which contributes so much to the chemical industry and hence to our lives. Friction, the overcoming of which consumes huge amounts of energy, takes place between surfaces sliding over each other. The growth of crystals takes place at surfaces; and if we want to prevent it, we need to modify the surface. Computers are guiding and illuminating our knowledge of surface structure and behavior.



A sodium chloride (NaCl) surface. There is a slight rearrangement of the surface: sodium ions move into the surface and chloride ions relax away from the surface.

We will look first at our ability to model the structure and energies of the surfaces of crystals, which we will show leads into modeling their shape, or morphology. We will then consider the reactions at surfaces and the catalysis, before looking at the intriguing problem of the interfaces between different solid materials.

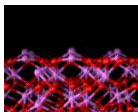
Atomic Arrangement at Surfaces

What do the structures of surfaces look like at the atomic level? This might seem an easy question to answer. Can't we simply consider a surface as being made by slicing a crystal in two? In which case, is not the structure of the surface just like that in a crystal? In many cases, this type of model seems to work well. For example, the surfaces of many metals are, to a good approximation, terminations of the structure of the crystal, as illustrated.

But the approximation is in many cases inaccurate and in some cases completely wrong. We will start with the undramatic but significant changes in surface structure manifested by that simple, classical crystal structure, sodium chloride. In understanding the subtle changes that occur on the surface of the material, the computer can again come to our aid. The image above shows a simulated structure of the surface of NaCl (obtained using energy minimization methods of the type described in elsewhere on this site).

Note that both the Na and Cl ions are slightly displaced perpendicularly to the surface: the Na⁺ ions move slightly into the surface and the Cl⁻ ions move slightly away from the surface. Clearly the atoms on the surface layer are subjected to different forces from those in the bulk of the crystal; and they respond by making these small but significant displacements.

Here are further examples where there are far more substantial rearrangements:



Rearrangement in the surface of Al₂O₃.

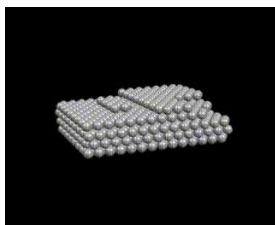


The surface of silicon exhibits rings of silicon atoms.

In the first corundum, Al₂O₃, we see that there are very substantial changes in the separation between the layers of atoms at the surface compared with corresponding ones in the bulk crystal.

Perhaps the most dramatically 'different' surface structures are found with the reconstructed surfaces of semiconductors such as silicon. The bond breaking which accompanies the formation of the surface is followed by an extensive re-bonding process leading to fascinating new, complex surface structures, one of which is shown.

Once again computational methods have proved of great value both in helping to elucidate the details of these structures and in giving guidance as to the factors controlling their stability.



Steps and kinks on a metal surface.

The perfect surface structures shown here are idealized. Real surfaces contain irregularities, and some of the commonest are shown above, where we see 'steps' separating regions of 'perfect' surface (known as terraces). These steps themselves contain irregularity - the corners and kinks shown on the figure. In addition, we can have defects and irregularities at surfaces. Such sites may play important roles in chemical reaction at surfaces as discussed later.

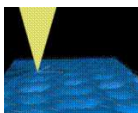
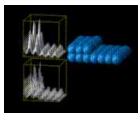


Image of a hard tip interacting with a surface.

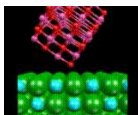
Our ability to learn about the structures of real surfaces has been revolutionized in recent years by the discovery of new types of microscopy which are all based on a very simple idea, which is that if you want to learn about the structure of an object, one strategy is to poke it with something sharp. The image above illustrates the basic mode of operation of these increasingly widely used techniques for imaging surfaces.



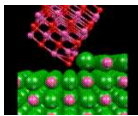
An afm tip scanning a surface.

Here an atomically sharp tip scans over the surface. And in the version of the technique we will now consider, known as Atomic Force Microscopy, as it scans the surface it is constrained to have a constant interaction force with the surface. To do this, the tip must move up and down; and these motions are in response to the structure of the surface, and can be translated into an image of the surface as shown.

But if we are to interpret these images, we need to be able to model the interaction between the surface and the tip. Recent work of Alexander Shluger, and colleagues has shown how we can simulate tip-surface interaction. The image below shows a tip model of magnesium oxide scanning over a rock salt (sodium chloride) surface maintaining a constant tip-surface force. The tip moves up and down and we can use this to produce the simulated image shown.



A model MgO AFM tip interacting with a NaCl surface.



A model MgO AFT tip interacting with a NaCl surface with a step.

These simulations show, however, that sometimes the tip can drastically perturb the surface. Here we see what happens when the tip scans over an edge. There is now major rearrangement as the tip drives into the edge. Clearly this kind of information is vital if we are to plan and interpret these experiments properly.

[Aggregates of Atoms: Order and Disorder](#)