

Functional Surfaces

Summary on Surface Science

- Useful Website:

<http://www.uksaf.org/tutorials.html>

What is a surface?

Solid-vacuum interface

- Surface reactions
- Heterogeneous catalysis
- Semiconductor technology
- Corrosion
- Nanotechnology

Heterogeneous catalysis

Heterogeneous catalytic reactions are the basis of the chemical industry: a large fraction of the chemicals of industrial and practical interest are produced by heterogeneous catalytic reactions.

Heterogeneous reactions occur typically on a liquid-solid or gas-solid interface. The surface of a solid gives the possibility to block in a fixed geometry some of the reactants, or the catalytic species if the catalyst is not the surface itself.

Surface science and the real world

- Pressure gap (UHV to atmospheric pressure or higher)
- Temperature gap (liquid helium or liquid nitrogen temperature to hundreds or thousands of K)
- Material gap (single crystals versus highly inhomogeneous surfaces)

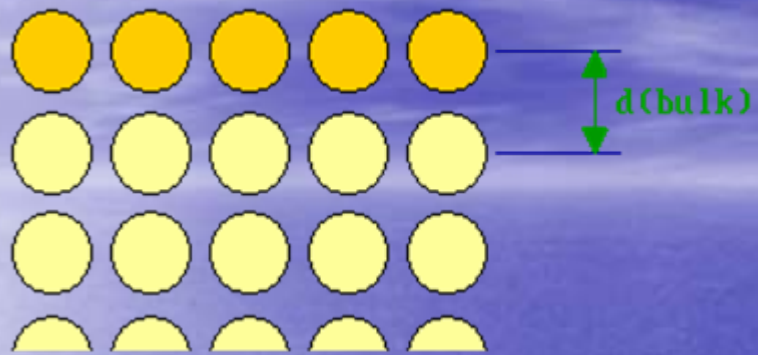
Why surface science then?

- Model systems with few controllable parameters and reproducible properties
- Studying electronic and geometric structure in great detail
- Monitoring adsorption, desorption, decomposition and reaction processes on surfaces with powerful techniques

Single-crystal surfaces

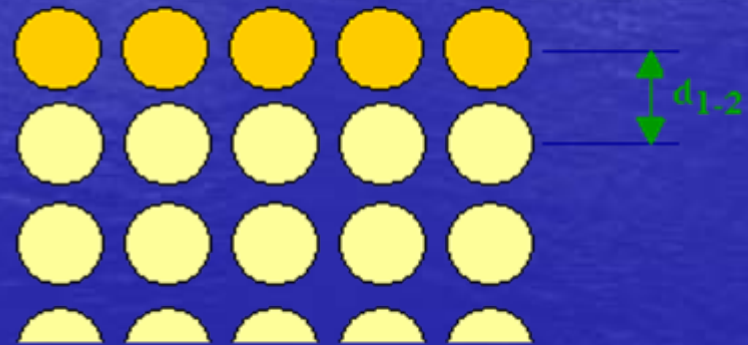
- A surface is formed ideally by removing a plane of bulk atoms. Surfaces are composed of atoms which do not have the same coordination number as in the bulk, but a lower one.
- The effect of having unbalanced forces at the surface is that the whole surface region is at relatively high energy compared to the bulk. We can compare it to the surface tension in a liquid.

Vacuum \ Gas Phase



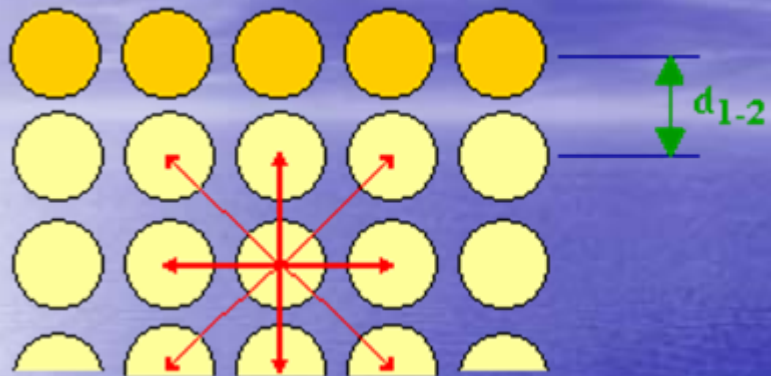
Bulk Solid

Vacuum \ Gas Phase



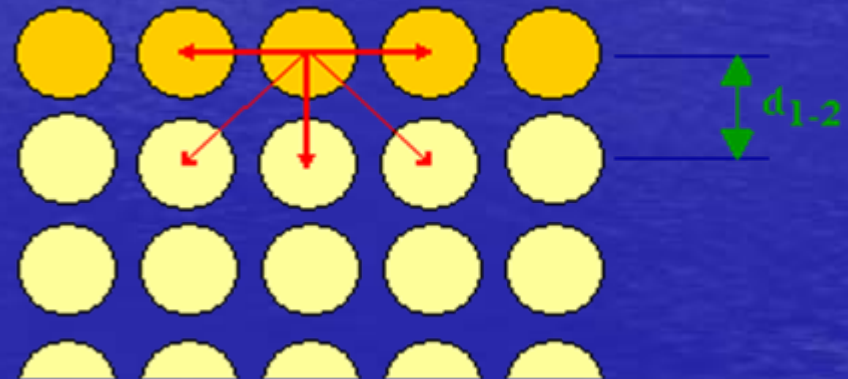
Bulk Solid

Vacuum \ Gas Phase

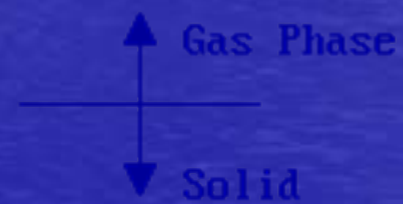
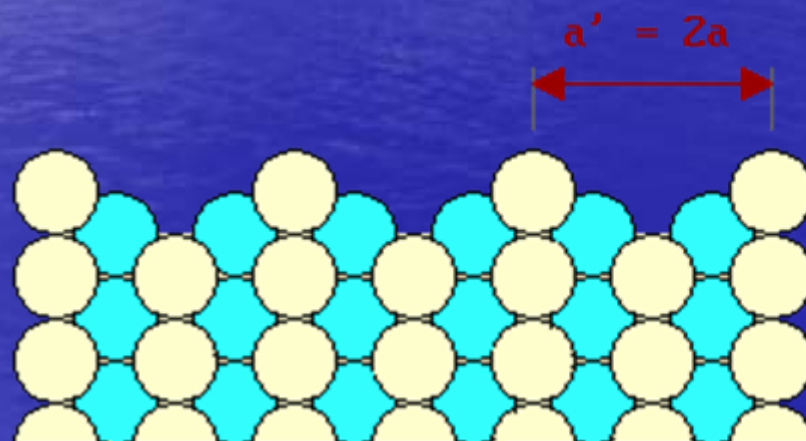
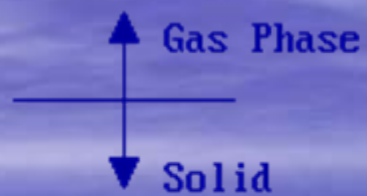
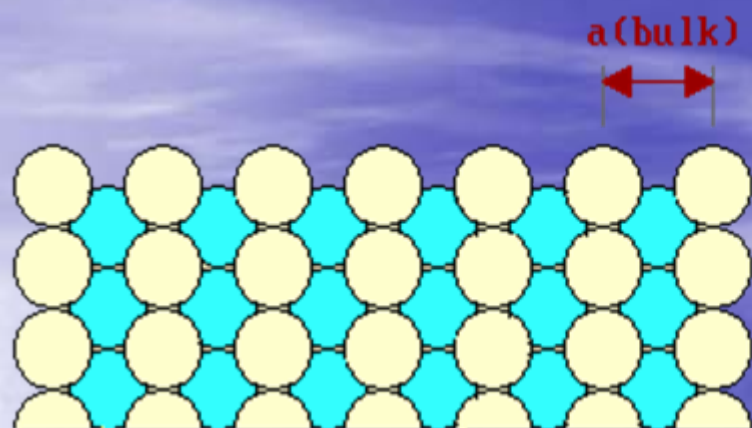


Bulk Solid

Vacuum \ Gas Phase



Bulk Solid



- The electronic structure of the surface is different from that one of the bulk
- The crystallographic structure of the surface is not simply the truncation of the bulk, because the surface atoms may move to minimize the surface energy ("surface reconstruction")
- The adsorption of gases is strongly favoured at the surface, either by formation of chemical bonds (chemisorption) or by van der Waals-type of interaction (physisorption)

Studying Surfaces: UHV

- Ultra high vacuum is required for most surface science experiments for two principal reasons :
- To enable atomically clean surfaces to be prepared for study, and such surfaces to be maintained in a contamination-free state for the duration of the experiment.
- To permit the use of low energy electron and ion-based experimental techniques without undue interference from gas phase scattering.

What is Ultra High Vacuum (UHV) ?

- The SI unit of pressure is the Pascal ($1 \text{ Pa} = 1 \text{ N m}^{-2}$)
- Normal atmospheric pressure (1 atm.) is 101325 Pa or 1013 mbar ($1 \text{ bar} = 10^5 \text{ Pa}$).
- An older unit of pressure is the Torr ($1 \text{ Torr} = 1 \text{ mmHg}$). One atmosphere is ca. 760 Torr (i.e. $1 \text{ Torr} = 133.3 \text{ Pa}$).
- Whilst the mbar is often used as a unit of pressure for describing the level of vacuum, the most commonly employed unit is still the Torr. (The SI unit, the Pa , is almost never used !)

Rough (low) vacuum : $1 - 10^{-3}$ Torr

Medium vacuum : $10^{-3} - 10^{-5}$ Torr

High vacuum (HV) : $10^{-6} - 10^{-8}$ Torr

Ultrahigh vacuum (UHV) : $< 10^{-9}$ Torr

Gas Exposure - the "Langmuir"

The *gas exposure* is a measure of the amount of gas which a surface has been subjected to. It is numerically quantified by taking the product of the pressure of the gas above the surface and the time of exposure (if the pressure is constant, or more generally by calculating the integral of pressure over the period of time of concern).

Although the exposure may be given in the SI units of Pa s (Pascal seconds), the normal and far more convenient unit for exposure is the *Langmuir*, where $1 \text{ L} = 10^{-6} \text{ Torr s}$. i.e.

$$(\text{Exposure/L}) = 10^6 \cdot (\text{Pressure/Torr}) \cdot (\text{Time/s})$$

Sticking Coefficient & Surface Coverage

The *sticking coefficient*, S , is a measure of the fraction of incident molecules which adsorb upon the surface i.e. it is a probability and lies in the range 0 - 1, where the limits correspond to no adsorption and complete adsorption of all incident molecules respectively.

In general, S depends upon many variables i.e.

$$S = f(\text{surface coverage, temperature, crystal face})$$

The *surface coverage* of an adsorbed species may itself, however, be specified in a number of ways :

as the number of adsorbed species per unit area of surface (e.g. in molecules cm^{-2}).

as a fraction of the maximum attainable surface coverage
i.e.

$$\theta = \frac{\text{Actual surface coverage}}{\text{Saturation surface coverage}}$$

How long will it take for a clean surface to become covered with a complete monolayer of adsorbate ? This is dependent upon the flux of gas phase molecules incident upon the surface, the actual coverage corresponding to the monolayer and the coverage-dependent sticking probability ... however , it is possible to get a minimum estimate of the time required by assuming a unit sticking probability (i.e. $S = 1$) and noting that monolayer coverages are generally of the order of 10^{15} per cm^2 or 10^{19} per m^2 . Then

$$\text{Time / ML} \sim (10^{19} / F) \quad [\text{s}]$$

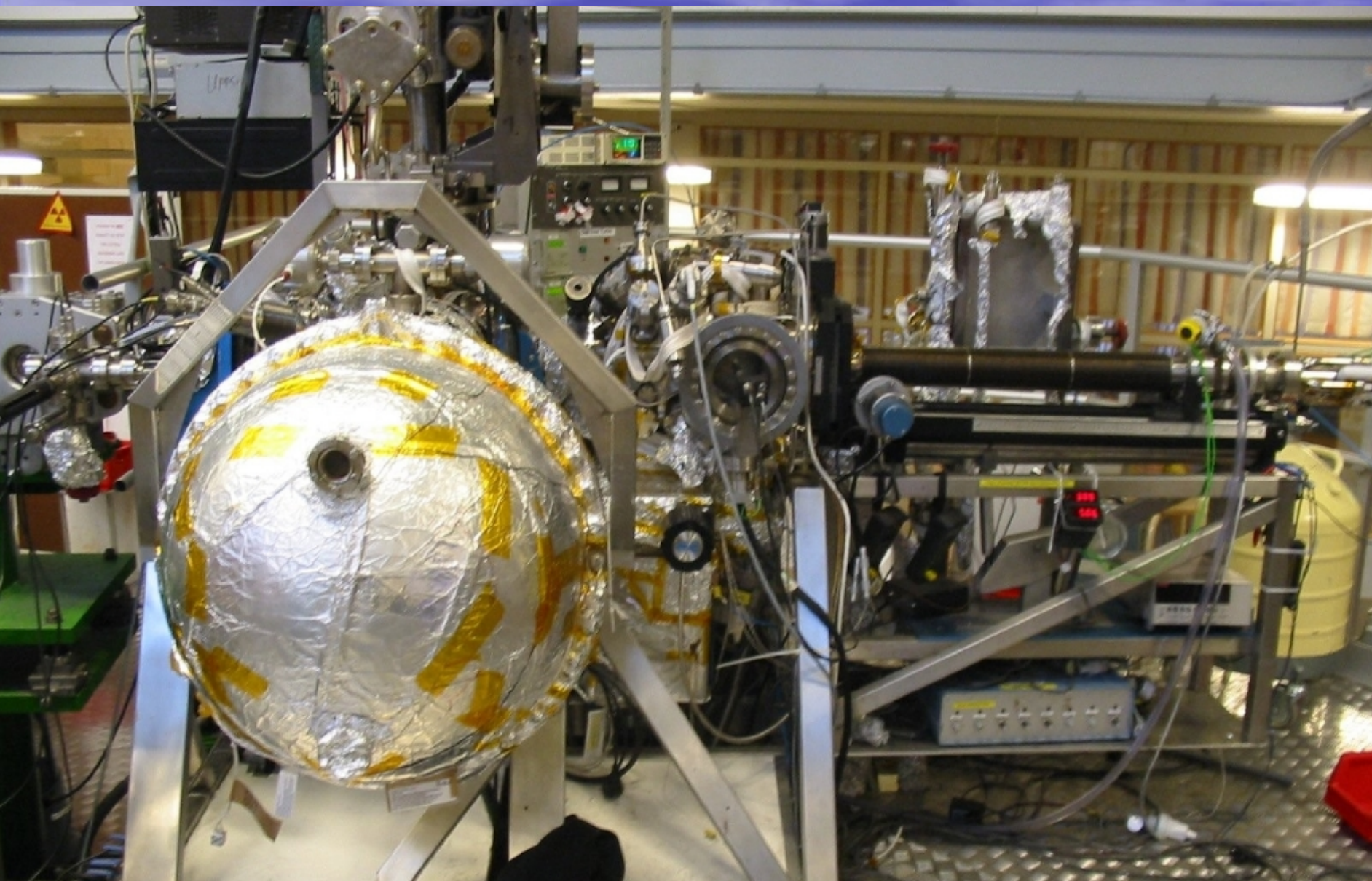
For surface spectroscopy, the mean free path of probe and detected particles (ions, atoms, electrons) in the vacuum environment must be significantly greater than the dimensions of the apparatus in order that these particles may travel to the surface and from the surface to detector without undergoing any interaction with residual gas phase molecules. This requires pressures better than 10^{-4} Torr.

(On a practical level, it is also the case that the lifetime of channeltron and multiplier detectors used to detect charged particles is substantially reduced by operation at pressures above 10^{-6} Torr).

Most spectroscopic techniques are also capable of detecting molecules in the gas phase; in these cases it is preferable that the number of species present on the surface substantially exceeds those present in the gas phase immediately above the surface - to achieve a surface/gas phase discrimination of better than 10:1 when analysing ca. 1% of a monolayer on a flat surface this requires that the gas phase concentration is less than ca. 10^{12} molecules cm^{-3} ($= 10^{18}$ molecules m^{-3}), i.e. that the (partial) pressure is of the order of 10^{-4} Torr or lower.

Components of a vacuum chamber

- Stainless steel vessel
- Pumping system
- Sample insertion system
- Sample manipulator
- Gas inlet system
- Mass spectrometer



Surface Preparation and Cleaning Procedures: In-situ Experiments

- A. Evacuation (e^{-t}) - removal of gas volume
- B. Surface desorption ($1/t$) - adsorbed water on inner surfaces
- C. Wall diffusion ($1/t^{1/2}$) - gases dissolved in walls
- D. Permeation limit (ultimate pressure) - gas diffusion through walls

Pump Down

typically follows a well-defined sequence according to the types of pumps on the vacuum system

for UHV systems, typically requires a few hours to reach a medium vacuum after a vent to air

for low vacuum systems, typically requires within an hour to reach operating conditions after a vent to air

Bake Out

heats the chamber to temperatures between 100 °C to 200 °C for an extended period of time (1 - 2 days)

rapidly removes adsorbed gases from the chamber walls at high temperatures in order to lower the outgassing rates at room temperature

Experimental procedures

Degassing components during and after bakeout. This may apply to masks for deposition, evaporation sources, gauge and TSP pump filaments. The main point is that such equipment will degas during use, worsening the pressure, often directly in the neighborhood of the sample.

Cleaning the sample and characterising it for cleanliness, typically with AES and/or by LEED

Perform the treatment or experiment: deposit/anneal, react with gases, bend the sample.

Examine the sample with the techniques at your disposal.

Sample cleaning procedures

The various possibilities for sample cleaning include the following: heating, either resistive, using electron bombardment or laser annealing; ion bombardment; cleaving; oxidation; in-situ deposition and growth. These may be applied singly, or more often in combination or in various cycles. Typically, the first time a sample is cleaned, the procedure is more lengthy, or more cycles are required. Thereafter, relatively simple procedures are needed to restore a once-cleaned surface.