

4.2: Why is UHV required for surface studies ?

Ultra high vacuum is required for most surface science experiments for two principal reasons:

1. 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.
2. To permit the use of low energy electron and ion-based experimental techniques without undue interference from gas phase scattering.

To put these points in context we shall now look at the variation of various parameters with pressure

Gas Density

The gas density ρ is easily estimated from the [ideal gas law](#):

$$\rho = \frac{N}{V} = \frac{P}{kT} \quad (4.2.1)$$

with

- ρ is the gas density [molecules/ m⁻³]
- P is the pressure [N m⁻²]
- k is Boltzmann constant, which is $\frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J K}^{-1}$)
- T is absolute temperature [K]

Mean Free Path of Particles in the Gas Phase

The average distance that a particle (atom, electron, molecule ..) travels in the gas phase between collisions can be determined from a simple hard-sphere collision model - this quantity is known as the *mean free path* of the particle, here denoted by λ , and for neutral molecules is given by the equation:

$$\lambda = \frac{kT}{\sqrt{2}P\sigma} \quad (4.2.2)$$

with

- λ is the mean free path [m]
- P - pressure [N m⁻²]
- k - Boltzmann constant (= 1.38 x 10⁻²³ J K⁻¹)
- T - temperature [K]
- σ - collision cross section [m²]

Incident Molecular Flux on Surfaces

One of the crucial factors in determining how long a surface can be maintained clean (or, alternatively, how long it takes to build-up a certain surface concentration of adsorbed species) is the number of gas molecules impacting on the surface from the gas phase. The incident *flux* is the number of incident molecules per unit time per unit area of surface.

The flux takes no account of the angle of incidence, it is merely a summation of all the arriving molecules over all possible incident angles

For a given set of conditions (P, T etc.) the flux is readily calculated using a combination of the ideas of statistical physics, the ideal gas equation and the [Maxwell-Boltzmann gas velocity distribution](#).

Step 1:

It can be readily shown that the incident flux, F , is related to the gas density above the surface by

$$F = \frac{1}{2} n \bar{c} \quad (4.2.3)$$

with

- n is the molecular gas density [molecules m^{-3}]
- F is the flux [molecules $\text{m}^{-2} \text{s}^{-1}$]
- \bar{c} is the average molecular speed [m s^{-1}]

Step 2: the molecular gas density is given by the ideal gas equation, namely

$$n = \frac{N}{V} = \frac{P}{kT} \quad (\text{molecules } \text{m}^{-3}) \quad (4.2.4)$$

Step 3: the mean molecular speed is obtained from the Maxwell-Boltzmann distribution of gas velocities by integration, yielding

$$\bar{c} = \sqrt{\frac{8kT}{m\pi}} \quad (\text{m s}^{-1}) \quad (4.2.5)$$

where

- m - molecular mass [kg]
- k - Boltzmann constant (= $1.38 \times 10^{-23} \text{ J K}^{-1}$)
- T - temperature [K]
- $\pi = 3.1416$

Step 4: combining the equations from the first three steps gives the Hertz-Knudsen formula for the incident flux

$$F = \frac{P}{\sqrt{2\pi mkT}} \quad [\text{molecules } \text{m}^{-2} \text{s}^{-1}] \quad (4.2.6)$$

Note

1. all quantities in the above equation need to be expressed in SI units
2. the molecular flux is directly proportional to the pressure

Gas Exposure: The "Langmuir"

The *gas exposure* is 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.

$$(\text{Exposure}/\text{L}) = 10^6 \times (\text{Pressure}/\text{Torr}) \times (\text{Time}/\text{s}) \quad (4.2.7)$$

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.

$$S = f(\text{surface coverage}, \text{temperature}, \text{crystal face} \dots) \quad (4.2.8)$$

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

1. as the number of adsorbed species per unit area of surface (e.g. in molecules cm^{-2}).
2. as a fraction of the maximum attainable surface coverage i.e.

$$\theta = \frac{\text{actual surface coverage}}{\text{saturation surface coverage}} \quad (4.2.9)$$

3. - in which case θ lies in the range 0 - 1 .
4. relative to the atom density in the topmost atomic layer of the substrate i.e.

$$\theta = \frac{\text{No. of adsorbed species per unit area of surface}}{\text{No. of surface substrate atoms per unit area}} \quad (4.2.10)$$

where θ_{max} is usually less than one, but can for an adsorbate such as H occasionally exceed one.

Note:

1. whichever definition is used, the surface coverage is normally denoted by the Greek θ
2. the second means of specifying the surface coverage is only usually employed for adsorption isotherms (e.g. the Langmuir isotherm). The third method is the most generally accepted way of defining the surface coverage.
3. a *monolayer* (1 ML) of adsorbate is taken to correspond to the maximum attainable surface concentration of adsorbed species bound to the substrate.

✓ Example 4.2.1:

How long will it take for a clean surface to become covered with a complete monolayer of adsorbate?

Solution

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 and other aspect. 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

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

Variation of Parameters with Pressure

All values given below are approximate and are generally dependent on factors such as temperature and molecular mass.

Degree of Vacuum	Pressure (Torr)	Gas Density (molecules m^{-3})	Mean Free Path (m)	Time / ML (s)
Atmospheric	760	2×10^{25}	7×10^{-8}	10^{-9}
Low	1	3×10^{22}	5×10^{-5}	10^{-6}
Medium	10^{-3}	3×10^{19}	5×10^{-2}	10^{-3}
High	10^{-6}	3×10^{16}	50	1
UltraHigh	10^{-10}	3×10^{12}	5×10^5	10^4

We can therefore conclude that the following requirements exist for:

Collision Free Conditions	\Rightarrow	$P < 10^{-4}$ Torr
Maintenance of a Clean Surface	\Rightarrow	$P < 10^{-9}$ Torr

Summary

For most surface science experiments there are a number of factors necessitating a high vacuum environment:

1. 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. There are, however, some techniques, such as IR spectroscopy, which are "photon-in/photon-out" techniques and do not suffer from this requirement.
(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).
2. 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.

To begin experiments with a reproducibly clean surface, and to ensure that significant contamination by background gases does not occur during an experiment, the background pressure must be such that the time required for contaminant build-up is substantially greater than that required to conduct the experiment i.e. of the order of hours. The implication with regard to the required pressure depends upon the nature of the surface, but for the more reactive surfaces this necessitates the use of UHV (i.e. $< 1 \times 10^{-9}$ Torr).

It is clear therefore that it is the last factor that usually determines the need for a very good vacuum in order to carry out reliable surface science experiments.

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