2

Gas-solid interactions

2.1 INTRODUCTION

In this chapter we focus on a series of phenomena that occur as a result of the interaction between the chaotically moving gas particles and the surrounding solid surface (e.g. the walls of the enclosure). This interaction, together with the ability of solids to bind and store gas particles, is the major obstacle for obtaining extremely low pressures. On the other hand, gas-solid interactions also form the basis for different pump principles in vacuum techniques.

When gas or vapour particles are somehow bound by solid materials we speak of *sorption*; the release of sorbed gases and vapours is called *desorption*. Sorption may occur as a result of different mechanisms. When gas particles are bound to the surface of a solid, then we speak of *adsorption*. The magnitude and type of intermolecular forces that cause adsorption, are determined by the specific gas-solid combination. Depending on the type of bonding, we distinguish between *physical adsorption* and *chemical adsorption*. The gas particles can also enter the solid matter and be captured in the interior of the material, similar to the dissolving of gas in a liquid. This process is known as *absorption*. The transport of gas particles in a solid material is called *diffusion* and is due to differences in concentration. The direction of diffusion is always from areas with a higher gas concentration to areas of lower concentration. Finally, the 1 atmosphere pressure difference across the walls of the vacuum enclosure results in a constant gas flow from atmosphere through the walls to inside. This process of gas transport is called *permeation*.

2.2 PHYSICAL ADSORPTION

We speak of physical adsorption, or physisorption for short, when gas particles are bound to the surface by physical forces, such as the 'van der Waals' forces. These are in general weak electrostatic forces as a result of interactions between fluctuating, induced and sometimes permanent dipoles. A gas particle approaching a solid surface comes under the influence of the attraction forces as exerted by the outermost atomic layers of the solid. As

a consequence it is bound at the surface for a shorter or longer period before desorbing again due to thermal motion (see also § 1.4).

It should be noted that we only consider molecules with thermal energies, that do not damage the surface structure (sputtering) and/or penetrate into the solid (implantation). Even at very high temperatures thermal energies are too low for these effects to occur.

The period of time during which the adsorbed particles remain bound to the solid surface is called the *residence time*. Residence times range from very short (approximately 10^{-13} s) to quite long and depend on the heat of adsorption and surface temperature. By *heat of adsorption* we mean the energy released during bonding and needed to break the bond again for desorption. The higher the heat of adsorption and the lower the temperature, all the longer the residence time will be. For physisorption of atmospheric gases at metal surfaces, the heat of adsorption ranges roughly from 8 to 60 kJ/mol, corresponding to residence times of 10^{-11} up to 10^{-2} s at room temperature (~ 300 K). An important exception is water vapour, for which the heat of adsorption on metal surfaces is in the order of 100 kJ/mol and the residence time at room temperature amounts to several hours. Table 2.1 gives some guide values of the heat of adsorption for physical bond.

Table 2.1 Heat of adsorption for physical bond

Gas	Surface	Heat of adsorption [kJ/mol]
H_2	activated charcoal	8
Ar	tungsten	8
Ar, N_2, CO	platinum, silver	14
N_2	stainless steel	15
O_2	activated charcoal	21
CO_2	activated charcoal	34
H_2O	zeolite 5A	63

Usually, physisorption at a surface is restricted to at most one monolayer of gas or vapour, i.e. one layer covering the whole surface and having a thickness corresponding to the diameter of the adsorbed particles. However, in some situations the adsorbed layer may consist of several monolayers. Especially for polar molecules (molecules with a permanent dipole moment) and condensable gases (vapours), the adsorbed layer can reach thicknesses of several monolayers.

At constant pressures and temperature the gas and adsorbed phases are always in dynamic equilibrium, i.e. the number of adsorbing and desorbing particles are equal. If we change the temperature, this balance is disturbed. Increase of the temperature leads to a shorter residence time and a higher desorption rate. As a consequence the number of

molecules in the gas phase increases and a higher pressure is measured. When on the other hand the temperature is lowered, the desorption rate decreases, the adsorbed amount of gas increases and the pressure drops.

The bonding forces of the adsorbed first monolayer are denoted as adhesive forces; the second and further monolayers are bound by so-called cohesive forces, meaning that molecules bind to molecules of the same kind. Strictly speaking, one has in this situation to deal with a first step towards condensation (see also § 1.7). If we let the pressure of the considered gas increase, massive condensation begins when the gas pressure (p) reaches the saturated vapour pressure (p_s) at ambient temperature. For $p > p_s$ equilibrium between adsorption (condensation) and desorption (evaporation) is disturbed and the condensed layer (liquid or even solid) may grow to large thicknesses. This condensation effect is used in a cryopump (see § 4.10.4).

2.3   WHY NO MIRROR REFLECTION AT A SOLID SURFACE?

In the derivation of expression (1.23) for the pressure of a gas, we deliberately did not assume simple mirror reflection for gas particles colliding with the vacuum wall. This assumption indeed would have greatly simplified the derivation of (1.23), but in most cases is not correct. Support for this statement is obtained by considering a molecular flow ($Kn \gg$ 1) through a tube. In the case of mirror reflection each molecule entering a tube at one side would leave the tube at the other side. This would mean that the resistance of tubes for molecular gas flow would be independent of its length. In practice, however, the resistance does positively depend on the length as well as the specific shape of a tube.

A geometrical reason of why mirror reflection does not occur, has to do with the roughness of the surface at an atomic scale. To understand this, we first look at the condition for mirror reflection of light on a wall. This condition says that mirror reflection occurs only as long as the size of surface roughness, measured in the direction of the incident light beam, is smaller than its wavelength λ. Let the roughness as measured perpendicularly to the geometric surface be l and the angle between the incident beam and the normal θ. The aforementioned condition is then expressed by

$$l \cos \theta < \lambda \tag{2.1}$$

We can also assign a wavelength λ to a molecule with mass m and average velocity $\bar{v}$:

$$\lambda = \frac{h}{m\bar{v}}$$

where h is Planck's constant ($h = 6.62 \times 10^{-34}$ Js). Substitution in eq. (2.1) yields

$$\cos\theta < \frac{h}{l\,m\,\overline{v}} \qquad\qquad (2.2)$$

It follows from this expression that the number of specularly reflected molecules in a collision with a wall increases as the mass and the velocity of the molecules decrease and the wall surface flattens. Table 2.2 gives the minimum incidence angle θ above which hydrogen (H_2) and helium (He) are specularly reflected at a highly polished surface with a roughness of 0.1 µm at two different temperatures. We conclude that in practice mirror reflection does not occur for gas particles incident on any solid surface, regardless of whether or not these are polished.

Table 2.2 Interval of incidence angles θ at two different temperatures, for which hydrogen and helium specularly reflect at a highly polished surface (roughness 0.1 µm)

Gas	$10^{27}m$ [kg]	T [K]	$10^{-2}\,\overline{v}$ [m/s]	$\cos\theta \le$	$90 \ge \theta \ge$
H_2	3.32	300	17.8	1.12×10^{-3}	89°56'
H_2	3.32	4.2	2.11	9.5×10^{-3}	89°27'
He	6.64	300	12.6	7.95×10^{-4}	89°57'
He	6.64	4.2	1.49	6.7×10^{-3}	89°38'

The same conclusion may be drawn in a different way with the help of figure 2.1, showing a cross-sectional outline of a surface with incident molecules. Compared with the molecular dimensions, the surface looks like a mountain landscape. The sketch clearly shows that even if mirror reflection would occur on a micro scale (i.e. in each individual collision between a molecule and the local surface), all collisions together by no means lead to mirror reflection on a macro scale (i.e. with respect to the geometrical surface).
Very flat surfaces are obtained by cleaving single crystals (e.g. salt crystals) under vacuum. The then remaining surface roughness is in the order of 0.01 nm (at room temperature) and caused by thermal vibrations of the surface atoms. From eq. (2.2) it follows that mirror reflection may occur in this particular case and indeed is observed experimentally for certain gas-solid combinations. Yet, even here mirror reflection is more exception than rule.
The fundamental reason for the absence of mirror reflection has to do with the fact that molecules incident on a solid surface are oftentimes not immediately reflected but bound by *adsorption* (or even absorption) for a certain length of time. The outcome is that molecules 'forget' their direction of incidence onto the surface and consequently, the connection between the incidence angle and the angle at which they leave the surface after desorption is lost. The direction distribution of the desorbing molecules is *isotropic*