Molecules interact with surfaces with forces originating either from the “physical” Van der Waals interaction or from the “chemical” hybridization of their orbitals with those of the atoms of the substrate.

Depending on which contribution dominates we speak of physisorption or of chemisorption. These are limiting cases since hybridization is always present at small enough adsorption distances, even for adsorbed rare gases.

- **Physisorption** → absence of chemical bonds the molecule retains its gas phase electronic structure, although some distortion is still possible. The binding energy depends on the polarizability and on the number of atoms involved of the atoms and varies between few meV (light gases) and several eV (large organic molecules)

- **Chemisorption** → stronger perturbation of the molecular electronic structure with formation of chemical bonds with the substrate. Energies typically of several eV
**Physisorption**

Electrons and ion core attracted by the screened image charge

\[ q = \frac{1 - \varepsilon(\omega)}{1 + \varepsilon(\omega)} e \]

Metallic surface. \( \varepsilon \rightarrow -\infty, q = -e \).

For a H atom the interaction energy between the real charges and their images is:

\[ V = \frac{1}{2} \left[ -\frac{e^2}{2z} - \frac{e^2}{2(z-r)} + \frac{e^2}{(2z-r)} + \frac{e^2}{(2z-r)} \right] \]
The first term is proportional to the square of the oscillator displacement coordinate, i.e. to its energy, which is lowered by an amount inversely proportional to the cube of its distance from the surface, thus gaining energy. 

more precisely the \( z^{-3} \) coefficient depends on the atomic polarizability \( \alpha \) and on the screening of the dipole moments by the surface response function which needs to be integrated over all frequencies (integration is performed in imaginary space for a mathematical trick and because we are considering virtual excitations)

\[
V(z) = -\frac{C_V}{z^3} \quad C_V = \frac{\hbar}{4\pi} \int_0^\infty \alpha(i\omega) \left( \frac{\varepsilon(i\omega)}{\varepsilon(i\omega)+1} - 1 \right) d\omega
\]

not surprisingly the term in \( z^{-4} \) introduces a correction to the position of the image charge plane which is determined by \( d_\perp(\omega) \), i.e. by the position of the screening charge.

\( z_0 \) is the average over all frequencies and is about 0.5 Angstroem.

\[
V = -\frac{C_V}{(z - z_0)^3} = -\frac{C_V}{z^3} \left( 1 + \frac{3z_V}{z} + \ldots \right)
\]
The interaction potential is then given by

\[ V(z) = Kn(r) - \frac{C_V}{|z - z_0|^3} \]

\(Kn(r)\): repulsive force stemming from Pauli repulsion at short distances with \(n(r)\) surface electron density.

Typical binding energies are: \(10 \div 500\) meV while the equilibrium separation (or adsorption distance) is: \(3 \div 10\) Å.

- Physisorbed particles are thus relatively far from the surface plane and strongly mobile on the surface (thanks to the low binding energy).
- Given the weak interaction, physisorbates have low desorption temperatures.
- For large molecules the binding energy can however exceed several eV.
- Physisorbates may, however, be important in chemical reactions where they may act as precursors to chemisorption.
He atom scattering

Physisorption forces determine He atom scattering (HAS) intensities in He beam diffraction experiments, a technique which was firstly applied to the study of surfaces in Genova in the ’70 when STM was still unavailable.

He atom scattering is characterized by a very low (thermal) kinetic energy and is thus still useful for systems which may be easily perturbed by other probes such as self-assembled organic films at surfaces.

In its inelastic version it allows for sub meV resolution and is used to determine surface phonon spectra (most of the work was done in Goettingen).

Very recently the resolution limit of HAS was brought down to the neV using He$_3$ and the spin echo technique. Surface diffusion phenomena can then be studied (Heidelberg and Cambridge).

Spectroscopic signatures of physisorbates

Spectroscopically physisorbates are characterized by vibrational frequencies close to those of the molecules in the gas phase and by the absence of hybridised orbitals in photoemission.
A limiting case: Xe adsorption and PAX spectroscopy

The electronic states of Xe atoms interact with the electronic states of the substrate causing a shift in the core levels which depends on the atoms they are in contact with. This may be used to quantify the coverage and evaluate the closure of an ultrathin film.

Adsorption geometry:
The Xe atom influences the charge state of the neighboring Pt atoms. Adsorption of Xe in first nearest neighbour sites is therefore destabilized.

Difference charge density profile along AB
Chemisorption

Short range forces $\rightarrow$ due to the smaller adsorption distance there may be a stronger overlap of the atomic orbitals in analogy to the formation of covalent bonds.

\[
\psi = a\psi_1 (M^-, d^+) + b\psi_2 (M^+, d^-)
\]

\[
\Psi_1 \rightarrow e^- \text{ transferred from } d \text{ state to } M
\]

\[
\Psi_2 \rightarrow e^- \text{ transferred from } M \text{ to } d \text{ state}
\]

The eigenstates can be obtained by calculating the energy.
\[ E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \]

\[ E \langle \psi | \psi \rangle = \langle \psi | H | \psi \rangle \]

\[ \langle \psi | H | \psi \rangle = a^2 \langle \psi_1 | H | \psi_1 \rangle + b^2 \langle \psi_2 | H | \psi_2 \rangle + 2ab \langle \psi_1 | H | \psi_2 \rangle = a^2 H_1 + b^2 H_2 + 2ab H_{12} \]

\[ \langle \psi | \psi \rangle = a^2 \langle \psi_1 | \psi_1 \rangle + b^2 \langle \psi_2 | \psi_2 \rangle + 2ab \langle \psi_1 | \psi_2 \rangle = a^2 + b^2 + 2ab S \]

\[ E(a^2 + b^2 + 2ab S) = a^2 H_1 + b^2 H_2 + 2ab H_{12} \]

with S superposition integral

\[ \frac{\partial E}{\partial a} = 0 \quad \frac{\partial E}{\partial b} = 0 \]

Solving the determinant:

\[ E = \frac{1}{2} \frac{H_1 + H_2 - 2SH_{12}}{1 - S^2} \pm \left[ \frac{H_{12}^2}{4} \frac{H_1 H_2}{1 - S^2} + \frac{1}{4} \left( \frac{H_1 + H_2 - 2SH_{12}}{1 - S^2} \right)^2 \right]^{1/2} \]

Average ionic energy

\[ H_{12} > 0 \rightarrow E_+ \quad e_+ \quad E_- \] are, respectively, larger and smaller than the average ionic energy and correspond to the bonding (Md) and antibonding (Md)* orbitals
LUMO broadens and shifts below $E_F$.

$\epsilon_a$ affinity level of the molecule or LUMO (lowest unoccupied molecular orbital)
**Chemisorption**

Example: interaction of $\text{H}_2$ with $\text{Cu}_2$ or with $\text{Ni}_2$ used to describe the substrate
Chemisorption

- Small equilibrium distance $\rightarrow z_0: 1\div3\text{Å}$
- Binding energy $\rightarrow E_B: \sim10\text{ eV}$
- Rearrangement of the electronic orbitals $\rightarrow$ dissociation and formation of new adsorbed moieties

Example $\text{H}_2$/metal surface

- $z_p \rightarrow$ physisorption distance
- $E_{\text{diss}} \rightarrow$ dissociation energy in the gas-phase
- $z' \rightarrow \text{H}_2 + 2\text{H}$
- $E_{\text{act}} \rightarrow$ activation energy for chemisorption
- $E_B \rightarrow$ adsorption energy
- $E_{\text{des}} \rightarrow$ desorption energy

$E_{\text{des}} = E_B + E_{\text{act}}$
One, two and n-dimensional diagrams

Early barrier: can be overcome by kinetic energy

Late barrier: if the barrier is on the coordinate describing the distance between the atoms, it can be overcome only by excitation of an appropriate molecular vibration
higher dimensionality Potential energy surfaces (PES)

Cartwheeling \( \text{H}_2 \)

A1. Atop \( \rightarrow \) Bridge

at atop site

the molecule is strongly repelled from the surface

A2. Bridge \( \rightarrow \) Atop

At bridge site

Helicopterering \( \text{H}_2 \)

E1. Atop \( \rightarrow \) Bridge

The molecule dissociates without any barrier

E2. Bridge \( \rightarrow \) Atop

The molecule is weakly repelled from the surface

An activation barrier is present: If the initial energy is high enough dissociation may occur
CO adsorption: Blyholder model

CO binds effectively to transition metals which have a high density of states close to $E_F$. The binding energy is then of the order of 1.5 eV. Due to this bonding mechanism the molecule adsorbs in upright position. The overlap with the $5\sigma$ orbital is largest for on-top sites, the one with $2\pi^*$ orbitals for bridge sites. The adsorption site may thus change with coverage.

For noble metals the bond energy is significantly lower. At undercoordinated sites (steps) the d-bands are upshifted (move towards the Fermi level) thus increasing the bond strength.
Fig. 6.27. Electron energy loss spectrum of 2 eV electrons backscattered in specular reflection from a CO-covered Pt(111) surface [6.29]. The energy loss is given in spectroscopic units (8.065 cm$^{-1}$ = 1 meV). The mode pair 2100 cm$^{-1}$/470 cm$^{-1}$ belongs to CO in the α-top site, the pair at 1850 cm$^{-1}$/380 cm$^{-1}$ to CO in the two-fold bridge site. The spectrum corresponds to half a monolayer coverage for which the system realizes a c(4×2) structure (see insert).
The adsorbates may induce the reconstruction of the surface.
Fig. 6.29. Electron energy loss spectrum of the Pt(110) surface after deposition of molecular oxygen at 30 K (upper panel). Four different forms of O$_2$ are discernible. After heating to 300 K, the oxygen molecule dissociates and the spectrum displays the spectral features of adsorbed oxygen atoms (lower panel) [6.50].
H adsorption

Fig. 6.40. Electron energy loss spectrum of the surface vibrations of the (2×1) hydrogen and deuterium covered Ni(110) surface. The vibration features of hydrogen at 640 cm$^{-1}$ and 1070 cm$^{-1}$ are significantly broader than the corresponding features for deuterium due to the quantum nature of the hydrogen atom [6.80].

Fig. 6.41. Because of the small mass of the hydrogen atom, the excited vibration states of
Adsorption kinetics

- Adsorption velocity and coverage depend on different parameters.

- The adsorption kinetics is a thermodynamical approach describing the relationships between the adsorbed species and the gas phase.

- The adsorption velocity depends on the number of particles adsorbing on the surface per second and on the sticking coefficient.

- The number of particles hitting a unit area per second is

\[
\frac{dN}{dt} = \frac{p}{\sqrt{2\pi mkT}}
\]

- The coverage \( \theta \):

\[
\theta = \int u dt = \int S \frac{dN}{dt} dt = \int S \frac{p}{\sqrt{2\pi mkT}} dt
\]

Adsorption velocity (adsorbed particles per unit area per second)

Sticking coefficient
Langmuir isotherm

\[ r_a = k_a F (1 - \theta)^n \]

\[ F = \frac{p}{(2\pi mk_B T)^{1/2}} \]

\[ r_d = k_d \theta^n \]

Adsorption rate, \( n \) adsorption order
\( n=1 \) molecular, \( n=2 \) dissociative, ...

Incoming flux

At equilibrium \( r_a = r_d \) and for \( n=1 \)

\[ \frac{\theta}{(1 - \theta)} = \frac{k_a F}{k_d} \]

\[ \Theta = \frac{Kp}{1 + Kp} \]

\( K \propto k_a/(k_d T) \) depends on \( T \) and adsorption enthalpy
Langmuir isotherm vs $K$
These graphs justify the assumption that the technologically important catalytic reactions taking place at high temperature and high pressure in chemical reactors can be studied at low pressure (controlled ultra high vacuum conditions) by lowering the crystal temperature. The reactions will be the same except that the reaction velocity will be slowed down. Reactions may thus kinetically limited. If barrier are present along vibrational coordinates, laser pulses can help to overcome them exciting specific vibrational modes.
Adsorption kinetics

- The sticking probability $S$ can be determined from a measurement of coverage $\theta$ vs exposure
  
  $$S = \sqrt{\frac{2\pi mkT}{p}} \frac{u}{p} = \sqrt{2\pi mkT} \frac{1}{p} \int d\theta$$

- The first molecules chemisorb at dangling bonds → the more sites are occupied the more the reactivity towards further bonds decreases

- $S$ reflects the details of the microscopic adsorption process

- The main factors influencing $S$ are:
  1. An activation energy $E_{\text{act}}$ which needs to be overcome (Boltzmann term);
  2. The orbitals of the incident molecule need to have a certain orientation with respect to the dangling bonds of the surface (steric factor);
  3. During the adsorption process, the incident molecule must transfer its kinetic energy to the substrate since it will otherwise desorb; the substrate excitations (phonons, e-h pairs, plasmons) are involved;
  4. Adsorption sites need to be available for the molecule and for the possible dissociation products
Adsorption kinetics

\[ S(\theta) = \sigma f(\theta) \exp\left(-\frac{E_{\text{act}}}{kT}\right) \]

- Occupation factor: probability to find a free adsorption site
- Condensation coefficient: steric factors and efficiency of the energy transfer to the substrate

\[ f_1(\theta) = 1 - \theta \quad \text{Non-dissociative adsorption} \]

\[ f_2(\theta) = \frac{z}{z-\theta} (1-\theta) \quad \text{Dissociative adsorption} \]

\( \theta \) relative coverage (ratio between occupied and available sites in the first adsorption layer)

with \( z \) number of neighbour sites, since the second radical in which the molecule splits has to find place close to the one where the dissociation event has occurred.

For the entire adsorption process:

\[ f(\theta) = f_1(\theta) f_2(\theta) = \frac{z}{z-\theta} (1-\theta)^2 \]

\( \theta \ll 1 \) (small coverage)

\[ f(\theta) \approx (1-\theta)^2 \]
Langmuirian case

Kisliuk model considers the effect of precursor states
Kisliuk model

\[ \frac{S}{S_0} = \left[1 + K \theta (1 - \theta)\right]^{-1} \]

\[ k = \left[\frac{1}{\left(1 + r_{m}/r_d\right)\left(1 + r_m/(r_m + r_d)\right)}\right] \]

**FIGURE 1.7.** The Kisliuk model for “precursor” mediated adsorption.

**FIGURE 1.8.** The sticking coefficient for CO on Pd(1 1 1) as a function of coverage \( \theta \) [34].
BET adsorption kinetics

- Experimentally ($E_{\text{act}} = E_0 + \alpha \theta$)

$$S(\theta) \propto \exp \left( -\frac{\alpha \theta}{kT} \right)$$

Elovich equation

- It is not realistic to neglect adsorption in the second layer

BET (Brunauer, Emmett e Teller) isotherm

Each particle in the first layer may be an adsorption center for further particles

- The activation energy may depend on the layer in which adsorption takes place

![Graph showing BET adsorption kinetics](image-url)
Thermal desorption

The desorption order $n$ depends on the adsorption state on the surface:

$n=0$ there is no dependence on surface coverage, case of rare gases, the maximum shift to higher $T$ with coverage

$n=1$ case of non-dissociative adsorption, the maximum yield is independent of coverage, the desorption curve is asymmetric

$n=2$ case of dissociative adsorption, the maximum shifts to lower $T$ with coverage, the peak is symmetric

Fig. 6.21. Desorption spectra for the desorption order $n = 0, 1, 2$ calculated from (6.34) under the assumption of a constant heating rate $\alpha = 1 \text{ K/s}$, a rate constant $\nu_0 = 10^{13} \text{ s}^{-1}$, and an activation energy $E_{\text{act}} = 1.5 \text{ eV}$. The initial coverage is varied from 0.1 to 1 in steps of 0.1.
Thermal desorption

\[ r_{\text{des}} \frac{d \Theta_{\text{ad}}}{dt} = s(\Theta_{\text{ad}}, T) \left( \frac{\Theta_{\text{ad}}}{1 - \Theta_{\text{ad}}} \right)^2 v_0(T) e^{-\frac{Q - W(\Theta)}{k_B T}} \]
Thermal desorption
Fig. 6.23. Calculated desorption spectra for CO-desorption from a Pd(100) surface for coverages $\theta_{ad} = 0.1-1$ in steps of 0.1. The insert shows the assumed dependence of the heat of adsorption on the coverage. The broad appearance of the peak for high coverages is caused by the dependence of the heat of adsorption on the coverage.
What determines surface reactivity: surface structure

**FIGURE 2.2.** Variation of the relative coverage with N atoms, $y$, on different Fe single-crystal surfaces with $N_2$ exposure at 693K [1].

Adsorption is more likely hindered by an energy barrier for a more compact surface
What determines reactivity: electronic factors, adsorbate level vs d-band

Antibonding state filled for noble metals, empty for transition metals

Figure 3.11 The two-step conceptualization of chemisorption bond formation on transition metal surfaces: (a) early transition metal; (b) coinage metal. $E_F$, Fermi energy
Figure 3.12  The interaction strength of chemisorbed oxygen and the way in which it varies across a row of transition metals. In the upper panel the good agreement between experimental and theoretical results is shown. In the lower panel the linear relationship between interaction strength and the energy of the d-band centre, $\varepsilon_d$, is demonstrated. rel., relative, Exp. (polycryst.), experimental results for polycrystalline sample; DFT, density functional theory; GGA, generalized gradient approximation. Source of data for experimental results: I. Toyoshima and G. A. Somorjai, Catal. Rev.-Sci. Eng. 19 (1979) 105. Figure reproduced with permission from G. Ertl, “Dynamics of reactions at surfaces”, in Advances in Catalysis, Volume 45, eds B. C. Gates and H. Knözinger (Academic Press, Boston, MA, 2000), page 1. ©2000 Academic Press
Adsorption induced work function changes

- **Riarrangement of the electronic charge following adsorption**
  \[ e\varphi = E_{\text{vac}} - E_F \]
  \( E_{\text{vac}} \rightarrow \) vacuum energy
  \( E_F \rightarrow \) Fermi level

- **Strong chemisorption** → charge moves from substrate to adsorbate (or vice versa) → additional dipoles → \( e\Delta\varphi \)

- **Weak chemisorption and physisorption** → image charge below the surface

- **Semiconductor:**
  \[ e\varphi = \chi + eV_S + (E_C - E_F)_{\text{bulk}} \]
  \( \chi \) electronic affinity

- **Adsorption** → effect of surface dipoles → \( \Delta\chi \) e \( \Delta V_S \)

- Cu(110) exposed to H\(_2\)O at 90K
  - Decrease to 0.9eV and step-wise increments se vs T
  - Each step corresponds to a different adsorption state
Work Function change: semiconductors

- Sb on GaAs(110)
- Different dependence for n or p doping
- $n \rightarrow$ band bending towards higher energy
- $p \rightarrow$ band bending towards lower energies
- Dipole contribution to work function identical for p and n doping
- Dipole contribution decreases monotonously with coverage
- The combination of these dependences causes the step profile of $\varphi$ vs Sb coverage
2D phase transitions

- Interaction between adsorbed atoms or molecules
- Low coverage → negligible interactions:
  adsorbates randomly distributed or forming small islands. The concentration of either depends on Temperature
- High coverage → significant interactions
  ordered arrays and islands form

- Substrate - adsorbate interaction small compared to lateral interactions
  → 2D description
- Physisorption → comparable interactions
- Strong chemisorption → substrate/adsorbate >> lateral interaction
- Elevated T → strong mobility → the study of 2D phase transition is useful to understand lateral order
- Substrate adsorbate forces may influence the critical parameters
2D phase transitions

Nature of lateral interactions:

1. Van der Waals → fluctuations of charge (important at low T)
2. Dipolar forces → connected to permanent dipoles, generally repulsive
3. Superposition of orbitals → interaction mainly among nearest neighbors
4. Substrate mediated interactions → the substrate electronic structure is affected in the immediate neighbourhood of the adsorbate

\[
\pi + \frac{a\theta^2}{d} \left( \frac{1}{\theta} - f_p \right) = kT
\]

State equation of a 2D gas

- θ surface particle nd = θ (n volume particle density, d layer thickness)
- \(f_p\) area occupied by closed packed particles \(b = df_p\) (b volume of a particle)
- \(\pi\) force acting on an element of area \(\pi = Cp\) (p pressure)

Critical parameters \(T_c, \pi_c, \theta_c\) may be obtained
2D phase transitions

First order phase transitions

- T<T\(_c\) coexistence range between solid and liquid
  1. \(\Theta^{-1}\geq A\) only less dense gas phase
  2. \(\Theta^{-1}<B\) denser liquid phase
- T>T\(_c\) no distinction possible

- T<T\(_c\) liquid and gas phases separated by a coexistence region
- T>T\(_c\) continuous transition between gas and liquid phases
The critical parameters may be derived from the 2D Van der Waals equation

$$\theta^3 - \frac{1}{f_p} \theta^2 + \left( \frac{d}{af_p} kT + \frac{\pi d}{a} \right) \theta - \frac{\pi d}{af_p} = 0$$

solution when all roots coincide at $\theta_c$

$$\left( \theta - \theta_c \right)^3 = \theta^3 - \theta_c^3 - 3\theta^2 \theta_c + 3\theta \theta_c^2$$

Comparing with experiment:

$$\theta_c = \frac{1}{3 f_p}, \quad \pi_c = \frac{a}{27 d f_p^2}, \quad T_c = \frac{8}{27} \frac{a}{d k f_p}$$

$f_p$ (co-area) and lateral interaction energy can be derived from the experiment
Fig. 5.17. Phase diagram for a square lattice. All curves are normalized to their specific maximum transition temperature $T_c$ at $\Theta = 1/2$. The solid line is (5.108) obtained for the mean field model with repulsive nearest-neighbor interactions. The dotted line is obtained from a Monte Carlo simulation with the same type of interaction [5.35]. The dashed lines mark the phase boundaries for a system with additional attractive next-nearest neighbor interactions. The data points (black squares) refer to the Pd(100)c(2×2)H system of Behm
Detailed balance and microscopic reversibility

Figure 3.20 Maxwell–Boltzmann distribution and a step-function sticking coefficient: (a) energy distribution for incident flux, and the sticking function (as indicated by the arrows, the distribution relates to the left-hand axis, and the step function relates to the right-hand axis); (b) energy distribution of flux that absorbs; (c) energy distribution of flux that does not adsorb; (d) energy distribution of total flux that leaves the surface.
Examples hydrogen adsorption on Cu and Si

As we have seen in Section 3.5, $\text{H}_2$ adsorption on copper is activated. In a simple one-dimensional Lennard-Jones-type potential, we considered only the effect of energy along the reaction coordinate, which to a first approximation we take as the normal component of translational energy. Indeed, translational energy plays the most important role in determining the sticking coefficient of $\text{H}_2$ on copper; the sticking coefficient increases strongly with increasing $\text{H}_2$ normal energy [43, 176]. Therefore, microscopic reversibility demands that since fast $\text{H}_2$ molecules are the most likely to stick, they are also the most likely to desorb. This is the case, and it is found experimentally that the desorbed $\text{H}_2$ is very ‘hot’ in the translational degree of freedom. Furthermore, since molecules directed along the surface normal stick better than those incident at grazing angles, the desorbed molecules tend to be focused along the surface normal.

$\text{H}_2$ adsorption on silicon is also activated [163, 176]. However, the desorbed molecules are not translationally hot and therefore translational energy is not the primary means of promoting adsorption. The reason for this can be found in the role of surface excitations. Dissociative adsorption of $\text{H}_2$ on silicon is activated in the surface coordinates. Effectively, we need to excite the surface into preferential configurations for the $\text{H}_2$ to dissociate and stick as hydrogen atoms. Therefore, in desorption, the energy of the activation is not efficiently conveyed to the desorbing $\text{H}_2$ molecules. Instead, a large fraction of the activation energy remains in the silicon surface. The result is that molecules leave the surface not too hot, but a vibrationally excited surface is left behind.