In both cases $dF_s$ gives the surface excess work $dW_s$ which is stored in the surface during the deformation. In the simple case of an isotropic medium we can also write

$$dF_s = dW_s = g dA ,$$  \hspace{1cm} (2.1.17)

where $g$ is the “effective surface excess stress”.

Consequently, in an ideally plastic deformation we have

$$g_{\text{plas}} = \gamma .$$  \hspace{1cm} (2.1.18)

This relation holds for isotropic liquids: such a medium cannot sustain a shear stress so that atoms flow to the surface to restore the initial average microscopic environment as it is stretched. This is also true for solids at high temperature and for sufficiently slow deformations: at these temperatures, the atomic mobility is large enough so that, at any time, the stretched surface keeps its microscopic atomic structure. Finally (2.1.18) also applies if we cleave the crystal or let it grow, the strains before and afterwards being the same.

In an ideally elastic and isotropic deformation, the comparison of (2.1.16) with (2.1.17) yields

$$g_{\text{elas}} = \gamma + \alpha \frac{d\gamma}{da} = \sigma ,$$  \hspace{1cm} (2.1.19)

$\sigma$ being the purely elastic surface excess stress.

For a general deformation, both plastic and elastic, $g$ will take values in between $\gamma$ and $\sigma$. As a consequence, except in the ideally plastic case, $g$ cannot be identified as the surface free energy since $\sigma \neq \gamma$. This difference arises since a crystal surface, being linked to the bulk lattice, its elastic deformation implies a distortion of the crystal which does not exist in plastic deformations.

Moreover, if the solid is not isotropic, $\sigma$ (and thus $g$) becomes a tensor for an arbitrary deformation and its principal values have no necessary connection with the surface free energy.

### 2.2 Equilibrium Shape of a Crystal

The surface free energy $\gamma$ of a crystal varies with the surface crystallographic orientation. This anisotropy can be determined from a surface called the “$\gamma$-plot” which is obtained in the following way. From an arbitrarily chosen origin, $O$, we draw a vector in the direction $\mathbf{n}$ (defined by its polar and azimuthal angles $\theta$ and $\phi$) with a length equal to the surface free energy, $\gamma(\mathbf{n})$, for a surface plane perpendicular to $\mathbf{n}$. The asphericity of the $\gamma$-plot reflects the anisotropy of $\gamma$, in particular, $\gamma$ has minima in the directions $\mathbf{n}_0$ corresponding to close-packed surfaces. As we will see in Sect. 3.1.4, surfaces corresponding to neighbouring
directions (vicinal surfaces) show a periodic succession of terraces and steps. If we call the energy per unit length of a step, \( \beta \), it is easy to show that:

\[
\gamma(\mathbf{n}) = \gamma(\mathbf{n}_0) + \frac{\beta|\theta|}{d},
\]

(2.2.1)

\( \gamma(\mathbf{n}_0) \) is the surface free energy of the close-packed surface, \( \theta \) is the angle between \( \mathbf{n} \) and \( \mathbf{n}_0 \) and \( d \) is the interplanar distance along \( \mathbf{n}_0 \). Indeed, as shown in Sect. 3.1.4, \( |\theta|/d \) is the density of steps. As a consequence \( d\gamma/d\theta \) has a discontinuity at \( \theta = 0 \) and the \( \gamma \)-plot shows cusps in directions corresponding to the most close-packed surfaces (Fig. 2.2).

Let us first consider a semi-infinite crystal limited by a plane \( S \) with its normal at \( \theta = 0 \) and study its stability relative to a small polar buckling (Fig. 2.3) preserving the average orientation of the surface. The free energy of this buckled surface \( S' \) is

\[
F_{s'} = \int_S \gamma(\theta)\,dS = \int_S \gamma(\theta) \frac{dS}{\cos \theta}.
\]

(2.2.2)

An expansion up to second order in \( \theta \) gives

\[
F_{s'} = \gamma(0)S + \frac{1}{2} \int_S \theta^2 \left[ \frac{d^2\gamma}{d\theta^2} + \gamma(\theta) \right] \frac{dS}{\cos \theta}.
\]

(2.2.3)

\[\text{Fig. 2.2. An example of a } \gamma \text{-plot}\]

\[\text{Fig. 2.3. Small polar buckling of a planar surface}\]
The second term vanishes for symmetry reasons and thus the energy involved in the deformation is given by the last term. Therefore

- when \( \gamma(0) + (d^2 \gamma/d\theta^2)_{\varrho=0} > 0 \), the surface is stable (or metastable)
- when \( \gamma(0) + (d^2 \gamma/d\theta^2)_{\varrho=0} < 0 \), the surface is unstable and will minimize its energy by developing facets. This faceting phenomenon will be discussed in more detail below.

For a finite crystal limited by a surface \( S \), the equilibrium shape must minimize the excess surface free energy, i.e., the surface integral

\[
F_s = \int_S \gamma(n) dS ,
\]

subject to the constraint of fixed volume. In the simple case of a perfectly spherical \( \gamma \)-plot, the solution corresponds to the volume with a minimal surface, i.e., a sphere. More generally, the variation of \( \gamma \) with the polar and azimuthal angles of \( n \) will produce, on each surface element \( dA \), couples proportional to \( \partial \gamma / \partial \theta \) and \( \partial \gamma / \partial \phi \) which will tend to alter its direction at the same time as \( \gamma \) tends to shrink its area. Consequently, the equilibrium shape is no longer a sphere. For the sake of simplicity, let us consider the two-dimensional case. Note that all the following results have been generalized to the three-dimensional case but the derivations are more tedious; they can be found in [2.4, 5]. The "surface" \( S \) is, then, a planar closed curve \( L \) and we have to minimize the contour integral (\( \gamma \) being now the excess free energy per unit length)

\[
F_L = \oint_L \gamma(n) dl ,
\]

subject to the constraint of fixed area, \( A \). We assume that the equation of curve \( L \) is \( z = z(x) \) in cartesian coordinates and transform the above contour integral into an integral over the coordinate \( x \). The direction cosines of the normal to \( L \) at any point \( M \) (Fig. 2.4) are

\[
n_x = -z'(1 + z'^2)^{-\frac{1}{2}}, \quad n_z = (1 + z'^2)^{-\frac{1}{2}},
\]

with

\[
z' = dz/dx .
\]

Equation (2.2.5) becomes

\[
F_L = \int_{L'} \gamma(z') (1 + z'^2)^{\frac{1}{2}} dx ,
\]

where \( L' \) is the projection of \( L \) on \( O_x \). \( F_L \) must be minimized with the constraint

\[
\int_{L'} z dx = A .
\]
This problem can be solved with the help of a Lagrange multiplier, \( \lambda \). It amounts to the minimization of
\[
\int_{L'} \left[ f(z') - \lambda z \right] dx = \int_{L'} \mathcal{L}(z, z') dx ,
\]
(2.2.10a)

where
\[
f(z') = \gamma(z') (1 + z'^2)^{\frac{1}{2}} .
\]
(2.2.10b)

The function \( \mathcal{L} \) which minimizes this integral obeys the Euler equation
\[
\frac{\partial \mathcal{L}}{\partial z} - \frac{d}{dx} \left( \frac{\partial \mathcal{L}}{\partial z'} \right) = 0 ,
\]
(2.2.11)
or
\[
\frac{d}{dx} \left[ \frac{df}{dz'} \right] = - \lambda .
\]
(2.2.12)

Consequently
\[
\frac{df}{dz'} = - \lambda (x - x_0) ,
\]
(2.2.13)
and
\[
f = - \lambda \int (x - x_0) \frac{dz'}{dx^2} dx .
\]
(2.2.14)

An integration by parts gives
\[
f = - \lambda [(x - x_0)z' - (z - z_0)]
\]
(2.2.15)
where \( x_0 \) and \( z_0 \) are the integration constants and, since the origin of coordinates is arbitrary, we can always choose \( x_0 = z_0 = 0 \). Thus,
\[
f = - \lambda (xz' - z) .
\]
(2.2.16)

Suppose that \( y \) is given as a function of \( \theta_x \), \( \theta_x \) being the angle between \( Ox \) and \( n \), it is then convenient to look for the solution using parametrized cartesian coordinates, \( x(\theta_x), z(\theta_x) \). We have, see (2.2.6),
\[
z' = - \cotg \theta_x ,
\]
(2.2.17)
so that (2.2.16) becomes, see (2.2.10b),
\[
\frac{y}{\sin \theta_x} = \lambda (x \cotg \theta_x + z) .
\]
(2.2.18)
we differentiate this equation with respect to \( \theta_x \), we obtain

\[
\frac{\gamma'}{\sin \theta_x} - \frac{\gamma \cos \theta_x}{\sin^2 \theta_x} = \lambda \left[ \frac{dx}{d\theta_x} \cotg \theta_x - \frac{x}{\sin^2 \theta_x} + z' \frac{dx}{d\theta_x} \right]
\]  
(2.2.19)

where \( \gamma' = d\gamma/d\theta_x \). Using (2.2.17, 19) leads to

\[
x = \frac{1}{\lambda} (\gamma \cos \theta_x - \gamma' \sin \theta_x),
\]  
(2.2.20)

\( z \) is then derived from (2.2.18)

\[
z = \frac{1}{\lambda} (\gamma \sin \theta_x + \gamma' \cos \theta_x).
\]  
(2.2.21)

The parametric equations (2.2.20) and (2.2.21) completely define the solution. In particular, when the \( \gamma \)-plot is isotropic (\( \gamma' = 0 \)), the equilibrium shape is a circle. Moreover, from (2.2.16), we can derive a geometrical construction of the equilibrium shape, commonly called the Wulff construction [2.6]. Using (2.2.10b), (2.2.21) can be transformed into

\[
\frac{\gamma}{\lambda} = \frac{-xz' + z}{(1 + z'^2)^{1/2}} = r \cdot n = OH,
\]  
(2.2.22)

\( r \) and \( n \) being respectively the radius vector and the normal at any point of the equilibrium shape and \( H \) being the orthogonal projection of \( O \) on the tangent at \( M \) (see Fig. 2.4). Therefore, the equilibrium contour is given (to within a scaling factor determined from the area \( A \)) by the inner envelope of straight lines erected normal to, and at the tips of, the radius vectors of the \( \gamma \)-plot.

![Figure 2.4. Principle of the Wulff construction](image)
From (2.2.20 and 21) we can easily get the radius of curvature of the equilibrium shape:

\[ R = \frac{dl}{d\theta} = \left\{ \left[ \frac{dx}{d\theta} \right]^2 + \left[ \frac{dz}{d\theta} \right]^2 \right\}^{\frac{1}{2}}, \]

i.e.,

\[ R = \frac{\gamma + \gamma''}{\lambda} \quad \text{where} \quad \gamma'' = \frac{d^2\gamma}{d\theta_x^2}. \]  

(2.2.24)

In Fig. 2.5, we give two typical examples of a Wulff construction for crystals. In

![Diagram of Wulff construction](image)

(a)

![Diagram of another Wulff construction](image)

(b)

Fig. 2.5a, b. Construction of the Wulff equilibrium shape (W) from the \( \gamma \)-plot: a strongly anisotropic case, b weakly anisotropic case
the first case (Fig. 2.5a), the crystal is very anisotropic and the \(\gamma\)-plot exhibits pronounced cusps. The inner Wulff envelope, \(W\), is polyhedral, each facet being a plane perpendicular to the radius vector of the \(\gamma\)-plot at the singular points. The opposite case of weak anisotropy [2.7] is illustrated by the example of Fig. 2.5b, the \(\gamma\)-plot cusps are weakly marked and the equilibrium shape of the crystal is limited by planar facets (still normal to the radius vector of the \(\gamma\)-plot at the singular points) connected to each other by rounded parts. Note that the size of facets is proportional to the discontinuities of \(\gamma'\) at the cusps. We have already seen that when \(\gamma + \gamma''\) is negative, the planar surface with surface free energy \(\gamma\) is unstable relative to a small buckling. It can be shown easily that (in two-dimension) the stability condition \(\gamma + \gamma'' > 0\) is general since it ensures that the free energy is minimal. Indeed, the energy change associated with a small deformation, \(\delta z\), of the equilibrium shape is, using (2.2.8, 10b and 17):

\[
\delta W = \frac{1}{2} \int \frac{d^2 f}{d z^2} (\delta z')^2 dx = \frac{1}{2} \int \frac{\gamma + \gamma''}{(1 + z'^2)^{3/2}} (\delta z')^2 dx .
\]  

(2.2.25)

Assume now that, in some part of the equilibrium shape, \(\gamma + \gamma''\) is negative. Any small distortion limited to this part and conserving the area \(A\) would lead to a smaller total energy and, thus, this part would be unstable. Consequently, at any point of the equilibrium shape, the curvature is positive, see (2.2.24).

We must note that, strictly speaking, the previous derivation of the equilibrium shape, see (2.2.20, 21), only applies when \(\gamma'\) is well defined, a condition which is not satisfied near cusps. However the Wulff construction, leading to facets, does yield the correct equilibrium shape. If we replace the cusps by rounded tips the more these approach the cusps, the more \(\gamma'\) tends to a step function and \(\gamma''\) tends to infinity. Therefore from (2.2.24), the equilibrium shape is locally planar in agreement with Wulff construction.

2.3 Facetting

Let us consider a planar surface with a large surface free energy in a highly anisotropic crystal. We can ask if some energy can be gained by replacing the smooth surface by a “saw-tooth” profile with the same average orientation (Fig. 2.6), exhibiting facets corresponding to smaller surface free energies. This phenomenon occurs when \(\gamma + \gamma''\) is negative and the facets correspond to equilibrium directions. The occurrence of such a “facetting” can be discussed with the help of a geometrical construction due to *Herring* [2.5], which we will give without proof.

![Fig. 2.6. Facetting](image)
6. Adsorption Phenomena

In surface physics, the term adsorption usually means accumulation at the solid–vapour interface of atoms or molecules coming from the vapour. The most important quantity for the description of this phenomenon is the binding or adsorption energy of the adsorbate i.e., the energy released when an atom of the vapour, at rest, sticks onto the surface. Adsorption phenomena are commonly classified according to the value of this binding energy:

- the domain of physisorption corresponds to small binding energies. In this domain, the substrate–adsorbate interactions are mainly due to Van der Waals forces and involve almost no mixing between the orbitals of the adsorbate and the substrate.
- the domain of chemisorption corresponds to large binding or adsorption energies. In this case, a bond, very similar to a chemical bond, is formed between the adsorbate and the substrate. This bond can be either covalent (sharing of electrons) or ionic (electronic transfer).

The limit between these two domains is not sharp and is usually taken to be around 0.5 eV.

The adsorption theory can be tackled from three complementary points of view:

- the macroscopic or thermodynamical approach is used to derive relations between the properties of the system at equilibrium: for instance, the relation between the pressure and the amount of matter adsorbed at the surface. This will be the subject of Sect. 6.1.
- the microscopic approach in which the principles of quantum mechanics are used to compute various physical quantities describing the substrate–adsorbate interactions. We will first consider the case of physisorption (Sect. 6.3) for which the adsorption energy is small and can be treated using second order perturbation theory. Then, we will study (Sect. 6.4) strong interactions in which the electronic states of the adsorbate hybridize with the metal electron states (chemisorption). Moreover, at finite coverages, interactions between adsorbed particles come into play. These interactions, which may be attractive or repulsive, will be briefly discussed in Sect. 6.5. Finally, the case of ordered overlayers will be treated using a specific example in Sect. 6.6.
- the methods of statistical mechanics establish the connection between macroscopic and microscopic quantities and relate the two previous approaches. They
will be illustrated in Sect. 6.2 by two examples: the study of adsorption isotherms and of the order–disorder transition in an overlayer.

### 6.1 Thermodynamic Approach

For the sake of simplicity, we consider a planar surface limiting two phases, \( \alpha \) and \( \beta \), and call \( N_{\alpha}, N_{\beta} \) and \( N_i \) the number of particles of type \( i \) in the phases \( \alpha, \beta \) and the entire system, respectively. Note that in thermodynamics, which deals with macroscopic amounts of matter, it is more customary to measure this amount in number of moles. Nevertheless, in view of the comparison with microscopic theories, we will not follow this convention. Using the concept of the surface excess of a physical quantity defined in Sect. 2.1, we have

\[
N_i = N_{\alpha} + N_{\beta} + n_i \gamma A ,
\]

where \( N_i \) is the total number of \( i \) particles, \( N_{\alpha(\beta)} \) is the number of \( i \) particles in phase \( \alpha(\beta) \) and \( n_i \) is the surface density of particles \( i \) in the surface of area \( A \) (\( N_{\alpha} = \alpha n_i \)). When a single species is present in the system (solid–vapour equilibrium), we have seen, in Sect. 2.1, that it is always possible to choose the position, \( z_s \), of the surface such that \( n_s = 0 \). It is clear that when there are several species, this condition cannot be verified simultaneously for all species. It is generally chosen to satisfy this condition for the major component (the substrate) but not for the minor ones (the adsorbates).

Let us first consider a one component system. We have seen that the Kramers grand potential \( \Omega \) (2.1.5) can be written

\[
\Omega = -p_x V_x - p_\beta V_\beta + \gamma A .
\]  

At thermodynamical equilibrium \( p_x = p_\beta \), hence, from (2.1.3), the surface excess of \( \Omega \), \( \gamma \), does not depend on the choice of \( z_s \) and is given by

\[
\gamma = \frac{1}{A} \Omega_s = \frac{1}{A} (F_s - G_s) = \frac{1}{A} (F_s - \mu n_s) = f_s - \mu n_s ,
\]

where \( \mu \) is the chemical potential, \( F_s \) and \( G_s \) are the surface excess Helmholtz free energy and Gibbs free enthalpy, respectively. If \( z_s \) is chosen so that \( N_x = 0 \), we again have \( \gamma = F_s/A = f_s \) [see (2.1.8)]. For a multicomponent system, \( \gamma \) becomes [6.1, 2]

\[
\gamma = f_s - \sum_i \mu_i n_{is} ,
\]  

or

\[
F_s = \sum_i \mu_i N_{is} + \gamma A ,
\]

where \( \mu \) excess in

\[
E_s =
\]

Moreover

\[
G_s =
\]

Hence, \( \gamma \) is

\[
g_s =
\]

and the

\[
F_{si} =
\]

For each

\[
dE_{si} =
\]

and we

\[
dEs =
\]

and

\[
dF_s =
\]

Hence

\[
\mu_i =
\]

where \( \bar{i} \) per ads

\[
E_{is} =
\]
where $\mu_i$ is the chemical potential of the component $i$. Similarly, the surface excess internal energy is

$$E_s = F_s + TS_s = TS_s + \sum_i \mu_i N_{is} + \gamma A .$$

(6.1.5)

Moreover, the free enthalpy of the entire system is

$$G = \sum_i \mu_i N_{it} .$$

(6.1.6)

Hence, the surface excess free enthalpy is

$$G_s = \sum_i \mu_i N_{is} ,$$

(6.1.7a)

or

$$g_s = \sum_i \mu_i n_{is} ,$$

(6.1.7b)

and the relation $\gamma = f_s - g_s$ is still valid.

From the first and second principles of thermodynamics, we can write

$$dE = dW + dQ = -pdV + \sum_i \mu_i dN_{it} + \gamma dA + TdS .$$

(6.1.8)

For each phase, we have

$$dE_\lambda = -pdV_\lambda + \sum_i \mu_i dN_{i\lambda} + TdS_\lambda, \quad \lambda = \alpha, \beta ,$$

and we deduce immediately that

$$dE_s = TdS_s + \sum_i \mu_i dN_{is} + \gamma dA ,$$

(6.1.9)

and

$$dF_s = -S_s dT + \sum_i \mu_i dN_{is} + \gamma dA .$$

(6.1.10)

Hence:

$$\mu_i = \left( \frac{\partial F_s}{\partial N_{is}} \right)_{T,N_{js},A} = \bar{E}_{is} - T\bar{S}_{is}, \quad j \neq i ,$$

(6.1.11a)

where $\bar{E}_{is}$ and $\bar{S}_{is}$ are, respectively, the partial surface excess energy and entropy per adsorbed particle of component $i$

$$\bar{E}_{is} = \left( \frac{\partial E_s}{\partial N_{is}} \right)_{T,N_{js},A}, \quad \bar{S}_{is} = \left( \frac{\partial S_s}{\partial N_{is}} \right)_{T,N_{js},A} , \quad j \neq i .$$

(6.1.11b)
Differentiating (6.1.5) and identifying the result with (6.1.9) yields
\[ S_k \, dT + \sum_i N_{ik} \, d\mu_i + A \, dy = 0 \]

or
\[ dy = -s_i \, dT - \sum_i n_{ik} \, d\mu_i \]  \hspace{1cm} (6.1.12)

with \( s_i = S_i / A \). This equation is called the Gibbs adsorption equation.

At constant temperature, we get, from (6.1.12), the Gibbs adsorption isotherm
\[ dy = -\sum_i n_{ik} \, d\mu_i \]  \hspace{1cm} (6.1.13a)

or
\[ n_{ik} = -\left( \frac{\partial y}{\partial \mu_k} \right)_{T,\mu_j}, \quad j \neq i \]  \hspace{1cm} (6.1.13b)

which gives the surface excess of component \( i \) when \( y \) is known as a function of the chemical potential of that component.

If the vapour can be considered as an ideal gas we have
\[ \mu_i = \mu_{i0} + k_B T \ln p_i \]  \hspace{1cm} (6.1.14)

where \( p_i \) is the partial pressure of component \( i \), \( \mu_{i0} \) the chemical potential of pure vapour \( i \) at one atmosphere and \( k_B \) is the Boltzmann constant. We deduce that
\[ n_{ik} = -\frac{1}{k_B T} \left( \frac{\partial y}{\partial \ln p_i} \right)_{T,\mu_j}, \quad j \neq i \]  \hspace{1cm} (6.1.15)

This relation gives the adsorbed amount of component \( i \) in terms of its partial pressure.

To study adsorption, it is also possible to draw curves giving the pressure versus temperature, for a constant amount of adsorbates. These plots are called adsorption isotherms. From knowledge of the latter, we can define the isosteric heat of adsorption \( q_{st} \). For the sake of simplicity, let us consider a binary system made of a solid component 1, which is non volatile, and of an adsorbed species 2, in equilibrium with its vapour. Furthermore, the total number of particles of each type is fixed. We look for the relation between its pressure \( p_2 \) and the temperature needed to maintain \( n_{2s} \) at a constant value. The surface is chosen at the position such that \( n_{1s} = 0 \) and its area remains constant. We have
\[ d\mu_2 = \left( \frac{\partial \mu_2}{\partial T} \right)_{N_{2s}, A} \, dT \]  \hspace{1cm} (6.1.17)

with, from
\[ \mu_2 = \left( \right) \]
Hence, co1
\[ d\mu_2 = \]
Similarly,
\[ \mu_2 N_{2v} \]
Differenti
\[ N_{2v} \, dj \]
since \( N_{2v} \),

amount 1
\[ dE_{2v} \]
we finall
\[ d\mu_2 = \]
The ide
\[ \left( \frac{\partial p}{\partial T} \right) \]
This is per pat
\[ \frac{1}{p_2} \]
where per at equati can be
\( E_2 \)
with, from (6.1.11a)
\[ \mu_2 = \left( \frac{\partial F_s}{\partial N_{2s}} \right)_{T,A} \]

Hence, combining the above two equations, and using (6.1.10 and 11b)
\[ d\mu_2 = \frac{\partial}{\partial T} \left[ \left( \frac{\partial F_s}{\partial N_{2s}} \right)_{T,A} \right] dT + \frac{\partial}{\partial N_{2s}} \left[ \left( \frac{\partial F_s}{\partial T} \right)_{A,N_{2s}} \right] dT = -\bar{S}_{2s} dT \quad (6.1.16) \]

Similarly, in the homogeneous vapour phase
\[ \mu_2 N_{2v} = E_{2v} - T S_{2v} + p_2 V_2 \quad (6.1.17) \]

Differentiating this equation, we get
\[ N_{2v} d\mu_2 = dE_{2v} - T dS_{2v} - S_{2v} dT + p_2 dV_2 + V_2 dp_2 \]

since \( N_{2v} \) is constant, the total number of particles of type 2 and the adsorbed amount being fixed. Using
\[ dE_{2v} = T dS_{2v} - p_2 dV_2 \]

we finally get
\[ d\mu_2 = -\frac{S_{2v}}{N_{2v}} dT + \frac{V_2}{N_{2v}} dp_2 = -\bar{S}_{2v} dT + \bar{V}_2 dp_2 \quad (6.1.18) \]

The identification of (6.1.16) with (6.1.18) yields
\[ \left( \frac{\partial \mu_2}{\partial T} \right)_{n_{2s}} = -\frac{\bar{S}_{2v}}{\bar{V}_2} = -\frac{\bar{q}_{ads}}{TV_2} \quad (6.1.19) \]

This is the equation of the isoster and it defines the isosteric heat of adsorption per particle, \( \bar{q}_{ads} \). Assuming that the vapour is an ideal gas, we have
\[ \frac{1}{p_2} \left( \frac{\partial \mu_2}{\partial T} \right)_{n_{2s}} = \left( \frac{\partial \ln p_2}{\partial T} \right)_{n_{2s}} = -\frac{\bar{q}_{ads}}{p_2 \bar{V}_2 T} = -\frac{\bar{q}_{ads}}{k_B T^2} = -\frac{Q_{ads}}{k_B T^2} \quad (6.1.20) \]

where \( N \) is Avogadro's number. Consequently, the isosteric heat of adsorption per atom, \( q_{ads} \), or per mole, \( \bar{Q}_{ads} \), can be deduced from the isosters using an equation similar to the Clapeyron equation. The physical significance of \( \bar{q}_{ads} \) can be specified. Setting equal the chemical potentials given by (6.1.11) and (6.1.17), we have
\[ E_{2v} - T \bar{S}_{2v} = E_{2v} - T \bar{S}_{2v} + p_2 \bar{V}_2 \]
then, using the definition (6.1.19) of \( q_{ads} \), we get

\[
\tilde{q}_{ads} = \tilde{E}_{2s} - \tilde{E}_{2v} - p_2 \tilde{V}_2 .
\]

(6.1.21)

From the last equation, it is possible to show that \( q_{ads} \) is equal to the heat transferred between the system and the heat bath in an isothermic and isobaric transformation. Indeed:

\[
dQ = dE + pdV ,
\]

since

\[
dN_{2v} = - dN_{2s} ,
\]

\[
dE = dE_{2v} + dE_{2s} = (E_{2s} - E_{2v}) dN_{2s} ,
\]

and

\[
pdV = - p_2 \tilde{V}_2 dN_{2s} ,
\]

we get finally

\[
dQ = \tilde{q}_{ads} dN_{2s} .
\]

(6.1.22)

Other heats of adsorption can be defined that are convenient for particular experimental conditions. It is possible to show that they are simply related [6.3].

**6.2 Statistical Methods**

The aim of these approaches is to relate the macroscopic quantities, defined in the previous section, with the microscopic quantities which will be developed in the next sections. In particular, we will study some types of adsorption isotherms, i.e., the plot of the variation, at constant temperature, of the number of adsorbed particles versus the pressure of that component, for fixed values of microscopic parameters. If the interaction between adatoms is attractive, we will see that below a temperature \( T_s \), there is a region of average coverage in which a single homogeneous phase is unstable with respect to the formation of two surface phases (condensation transition). When the interaction between adatoms is repulsive, another phase transition may occur: the order–disorder transition.

These problems are, of course, extremely difficult: for instance, if one of the microscopic parameters is the binding energy of one particle, this parameter should vary with the number of particles already adsorbed, due to the interactions between them. Moreover, the substrate surface may undergo reconstruction. Nevertheless, it is instructive to treat a few cases which, although very idealized, provide a useful basis for the interpretation of experiments.
6.2.1 Adsorption Isotherms in the Absence of Lateral Interactions Between Adatoms

a) Monolayer Adsorption: Langmuir Isotherms

We consider a solid substrate (component 1) in the presence of an ideal monoatomic gas (component 2) and call, N, the number of localized sites on which an atom 2 may adsorb. We assume that all these sites are equivalent and can accommodate, at most, one adsorbed atom. The binding energy $-\epsilon_2$ of one atom 2 is considered as independent of the number of adsorbed atoms, i.e., we neglect the interactions between them. The energy of the system with $N_{2s}$ adsorbed particles is, hence, $-N_{2s}\epsilon_2$ and the number of configurations having this energy is the binomial coefficient $C^N_{N_{2s}}$. The canonical partition function is

$$\mathcal{Z}_{N_{2s}} = C^N_{N_{2s}} \exp(N_{2s} \epsilon_2 / k_B T),$$

and the grand canonical partition function can be written

$$\mathcal{Z} = \sum_{N_{2s} \geq 0} \mathcal{Z}_{N_{2s}} \exp(N_{2s} \mu_2 / k_B T).$$

Substituting (6.2.1) into this equation, we find

$$\mathcal{Z} = (1 + \exp[(\epsilon_2 + \mu_2) / k_B T])^N.$$

The probability of having $N_{2s}$ adsorbed particles is given by

$$P(N_{2s}) = \mathcal{Z}_{N_{2s}} \exp(N_{2s} \mu_2 / k_B T) / \mathcal{Z},$$

and, consequently, the average number of adsorbed particles is, using (6.2.2)

$$\langle N_{2s} \rangle = \sum_{N_{2s} \geq 0} N_{2s} P(N_{2s}) = k_B T \frac{\partial}{\partial \mu_2} \ln \langle \cdots \rangle,$$

or, using (6.2.2)

$$\langle N_{2s} \rangle = N k_B T \frac{\partial}{\partial \mu_2} \ln \{1 + \exp[(\epsilon_2 + \mu_2) / k_B T]\},$$

from which the fractional coverage $\theta$ is deduced

$$\theta = \frac{\langle N_{2s} \rangle}{N} = \frac{\exp[(\epsilon_2 + \mu_2) / k_B T]}{1 + \exp[(\epsilon_2 + \mu_2) / k_B T]}.$$

To proceed further, we must calculate the chemical potential $\mu_2$ as a function of temperature and pressure. The translation partition function for a particle of an
ideal gas is
\[ \mathcal{Z} = \frac{V}{h^3} \int_0^\infty \exp\left(-\frac{Mv^2}{2k_B T}\right)4\pi M^3 v^2 dv, \]
where \( M \) and \( v \) are the mass and velocity of the particle, respectively, and \( h \) is the Planck constant. The integration yields
\[ \mathcal{Z} = \frac{V}{h^3} \left(2\pi M k_B T\right)^{3/2}. \tag{6.2.5} \]
For \( N_2 \), indistinguishable particles, the partition function is
\[ \mathcal{Z}_{N_2} = \frac{\mathcal{Z}^{N_2}}{N_2!}, \tag{6.2.6} \]
from which we deduce the chemical potential
\[ \mu_2 = -k_B T \left(\frac{\partial \ln \mathcal{Z}_{N_2}}{\partial N_2}\right)_{v_2, T}. \]
Using (6.2.6) and the Stirling formula, we get
\[ \mu_2 = -k_B T \ln(\mathcal{Z}/N_{2v}). \]
Using (6.2.5) and the ideal gas law yields
\[ \mu_2 = k_B T \ln \left[ \frac{P_2}{k_B T} \left(\frac{h^2}{2\pi M k_B T}\right)^{3/2} \right]. \tag{6.2.7} \]
Substituting for \( \mu_2 \) from (6.2.7) into (6.2.4), we get
\[ \theta = \frac{P_2}{P_2 + P_0(T)}, \tag{6.2.8a} \]
with
\[ P_0(T) = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} k_B T \exp\left(-\frac{\epsilon_2}{k_B T}\right). \tag{6.2.8b} \]
This is the equation of the Langmuir adsorption isotherm [6.4]. It has a very simple physical meaning. The adsorption and desorption rates are proportional to \( P_2(1 - \theta) \) and \( \theta \), respectively, and are equal at equilibrium. Thus
\[ P_2(1 - \theta) = c^e \theta. \]
Solving for \( \theta \), we again obtain (6.2.8a) with the proportionality constant \( P_0(T) \). At low pressures \( \theta \) is proportional to \( P_2 \), while at high pressure it tends
asymptotically to unity (Fig. 6.1). Moreover, \( p_0 \) is the pressure for which \( \theta = 1/2 \) and, since \( p_0 \) decays exponentially when \( \epsilon_2 \) increases, it is clear that, if \( \epsilon_2 \) is too large (i.e., for chemisorbed systems), the asymptotic regime is already reached for any experimentally possible pressure.

The above formula can be generalized to take into account the vibrational degrees of freedom of the adsorbed atoms. The corresponding partition function is, for a single adatom, see (4.5.1)

\[
Z_{\text{vib}} = \prod_{i=x, y, z} \exp(-\hbar v_i/2k_B T) [1 - \exp(-\hbar v_i/k_B T)]^{-1},
\]

(6.2.9)

\( v_x, v_y, v_z \) being the vibration frequencies in the \( x, y, z \) directions. The above calculation remains valid provided that \( \exp(\epsilon_2/k_B T) \) is multiplied by \( Z_{\text{vib}} \) in (6.2.1). The form of the Langmuir adsorption isotherm is unchanged but \( p_0(T) \) is divided by \( Z_{\text{vib}} \):

\[
p_0(T) = \left( \frac{2\pi Me^2 k_B T}{\hbar^2} \right)^{3/2} Z_{\text{vib}}^{-1} k_B T \exp(-\epsilon_2/k_B T).
\]

(6.2.10)

We are now able to relate the macroscopic isosteric heat of adsorption to the microscopic binding energy \( \epsilon_2 \). Solving (6.2.8a) for \( p_2 \), we get

\[
\left( \frac{\partial \ln p_2}{\partial T} \right)_\theta = \left( \frac{\partial \ln p_0(T)}{\partial T} \right)_\theta.
\]

(6.2.11)

Assuming \( v_x = v_y = v_z = v \), \( Z_{\text{vib}} \) takes the form

\[
Z_{\text{vib}} = \left( \frac{2}{\pi} \frac{\hbar v}{2k_B T} \right)^{-3}.
\]

(6.2.12)

\[\text{Fig. 6.1. Langmuir adsorption isotherm}\]
Substituting for $\mathcal{Z}_\text{vib}$ from (6.2.12) into (6.2.10), and taking (6.2.11 and 20) into account, yields

$$Q_{\text{ads}} = \mathcal{N} \left( - e_2 - \frac{5}{2} k_B T + \frac{3}{2} h v \coth \frac{h v}{2 k_B T} \right). \quad (6.2.13a)$$

In the low temperature limit, $h v \gg k_B T$, we get

$$Q_{\text{ads}}(T \to 0) = \mathcal{N} \left( - e_2 - \frac{3}{2} k_B T + \frac{3}{2} h v \right). \quad (6.2.13b)$$

Conversely, in the high temperature limit, $h v \ll k_B T$, we obtain

$$Q_{\text{ads}}(T \to \infty) = \mathcal{N} \left( - e_2 + \frac{1}{2} k_B T \right). \quad (6.2.13c)$$

b) Multilayer Adsorption: Brunauer, Emmett and Teller (BET)

Isotherms

In the Langmuir model, it was assumed that adsorption could only occur on the unoccupied substrate adsorption sites. We will now remove this restriction. In this case, adsorption occurs by the formation of stacks of particles on each site. We want to calculate the average height of these stacks and, hence, the coverage (measured in monolayers). When a particle 2 adsorbs directly on the substrate the involved energy is still denoted by $- e_2$ while, when it adsorbs on an occupied site it is $- e'_2$. The latter quantity is taken as constant whatever the height of the stack. A reasonable estimate of $e'_2$ is the heat of sublimation of component 2.

The grand canonical partition function of a single site is

$$\mathcal{Z} = \sum_{n=0}^{\infty} \mathcal{Z}_n \exp(n \mu_2/k_B T), \quad (6.2.14)$$

where $\mathcal{Z}_n$ is the canonical partition function of a site with $n$ adsorbed particles. From the assumptions made on the binding energies, we can write

$$\mathcal{Z}_n = \mathcal{Z}_1 (\mathcal{Z}')^{n-1} \quad n \geq 2, \quad (6.2.15)$$

with

$$\mathcal{Z}_1 = \exp(e_2/k_B T), \quad (6.2.16a)$$

and

$$\mathcal{Z}' = \exp(e'_2/k_B T), \quad (6.2.16b)$$

if we neglect the vibrations. Hence

$$\mathcal{Z} = 1 + \exp(\mu_2/k_B T) \sum_{n=0}^{\infty} \mathcal{Z}'^n \exp(n \mu_2/k_B T),$$

and summing the geometric series

$$1 - \mathcal{Z}' \exp(\mu_2/k_B T) = \frac{1}{1 - \mathcal{Z}' \exp(\mu_2/k_B T)}.$$

The average occupancy of a site is given by

$$\theta = \frac{1}{\mathcal{Z}} \sum_{n=0}^{\infty} n \mathcal{Z}_n \exp(n \mu_2/k_B T).$$

It can be transformed into

$$\theta = \frac{1}{\mathcal{Z}_1} \mathcal{Z}' \exp(\mu_2/k_B T).$$

The summation can be performed

$$\sum_{n=1}^{\infty} n \chi^{-1} = \frac{1}{(1 - \chi)^2},$$

and, using (6.2.16 and 17), we get

$$\theta = \frac{\exp[\theta_2 \mu_2/k_B T]}{\exp[\theta_2 \mu_2/k_B T] + \exp[\theta_2 \mu_2/k_B T]}.$$ 

Since, when $\mathcal{Z}' = 0$, we should have

$$\frac{\exp[\theta_2 \mu_2/k_B T]}{1 + \exp[\theta_2 \mu_2/k_B T]} = \frac{p_0(T)}{1 + \exp[\theta_2 \mu_2/k_B T]} = \frac{p_0(T)}{1 + \exp[\theta_2 \mu_2/k_B T]} = p_2,$$ 

$\exp[\theta_2 \mu_2/k_B T] = p_2/p_0$. Combining (6.2.19) and (6.2.20), we get

$$\theta = \frac{p_0(T) + p_2 - p_2 \exp[\theta_2 \mu_2/k_B T]}{p_0(T) + p_2 - p_2 \exp[\theta_2 \mu_2/k_B T]}.$$

This is the equation of the BET isotherm for multilayer adsorption. The shape of this isotherm is shown in the figure. This curve shows a flat region,
G. Calculation of the Current in a Scanning Tunneling Microscope

We will follow here the treatment given by Lang [G.1], based on the Bardeen tunneling Hamiltonian formalism [G.2]. Let us consider two electrodes of the same metal, separated by a vacuum region in the z direction. We want first to calculate the tunneling current in the presence of an infinitesimal bias voltage V. The Hamiltonian for the left (right) electrode considered separately, i.e., in the absence of the other is written:

\[ H_{L(R)} = -\frac{\hbar^2}{2m} \Delta + V_{L(R)} \]  

(G.1)

\( H_{L(R)} \) has eigenfunctions \( \psi_n^L(\psi_n^R) \) and eigenvalues \( E_n^L(E_n^R) \). If we assume that the rearrangement of charges inside each electrode, due to the presence of the other, can be neglected, the Hamiltonian for the combined two-electrode system is (Fig. G.1):

\[ H = H_L + V_R = -\frac{\hbar^2}{2m} \Delta + V_L + V_R \]  

(G.2)

We consider an electron which at \( t \rightarrow -\infty \) is in the state \( \psi_n^L \) and switch on adiabatically the potential \( V_R \). The wave function of this electron, at time \( t \), can be written:

\[ \psi_n(r,t) = a(t) \psi_n^L(r) e^{-i E_n^L t/\hbar} + \sum_v b_v(t) \psi_v^R(r) e^{-i E_v^R t/\hbar} \]  

(G.3)

with

\[ a(-\infty) = 1, \quad b_v(-\infty) = 0, \]

\( \psi_n(r,t) \) satisfying the time-dependent Schrödinger equation

\[ -\frac{\hbar}{i} \frac{\partial \psi_n}{\partial t} = (H_L + V_R e^{\epsilon t}) \psi_n \]  

(G.4)

\( \epsilon \) is a small positive factor which ensures that the perturbation is applied adiabatically. We assume that the switching-on of \( V_R \) can be regarded as a small perturbation. We will discuss the validity of this approximation below. Within this assumption, the substitution of \( \psi_n \) from (G.3) into (G.4) gives

\[ \frac{da(t)}{dt} = 0 \]
and
\[
\frac{db_\nu(t) \, dt}{t} = - \frac{i}{\hbar} \langle \psi^R_\nu | V_R | \psi^L_\mu \rangle \, e^{- \frac{i}{\hbar}(E^L_\mu - E^R_\nu + i\epsilon)t}.
\]

so that
\[
a(t) = 1,
\]
\[
b_\nu(t) = \frac{1}{E^L_\mu - E^R_\nu + i\epsilon} \langle \psi^R_\nu | V_R | \psi^L_\mu \rangle \, e^{- \frac{i}{\hbar}(E^L_\mu - E^R_\nu + i\epsilon)t}.
\]

Hence, in the adiabatic limit
\[
b_\nu(t) = \left[ \mathcal{P} \left\{ \frac{1}{E^L_\mu - E^R_\nu} \right\} - i\pi \delta(E^L_\mu - E^R_\nu) \right] \langle \psi^R_\nu | V_R | \psi^L_\mu \rangle \, e^{- \frac{i}{\hbar}(E^L_\mu - E^R_\nu)t},
\]

where \( \mathcal{P} \) indicates that the principal value is to be taken. This first order perturbation treatment is thus valid if the matrix element \( \langle \psi^R_\nu | V_R | \psi^L_\mu \rangle \) is small, i.e., if the vacuum region is large enough so that, when the overlap between \( \psi^L_\mu \) and \( \psi^R_\nu \) is non zero, \( V_R \) is small.

The current density corresponding to the electron in the state \( \psi_\mu(r,t) \) is given by
\[
j_\mu(r,t) = - \frac{e\hbar}{2im} (\psi^*_\mu \nabla \psi_\mu - \psi_\mu \nabla \psi^*_\mu).
\]

To the smallest order in perturbation, and taking into account the fact that there is, of course, no current in the ground state of one electrode taken as an isolated system, we find by substituting (G.3) into (G.6)
\[
j_\mu(r,t) = - \frac{e\hbar}{2im} \sum_\nu \left\{ b_\nu(t) e^{i(E^L_\mu - E^R_\nu)t} \left( \psi^{L*}_\mu \nabla \psi^R_\nu - \psi^R_\nu \nabla \psi^{L*}_\mu \right) \right\} \text{ c.c.}
\]

We now calculate the intensity of the current, \( I_\mu \), through a planar surface \( S \), at \( z_i \) in the vacuum region (Fig. G.1), and parallel to the electrodes
\[
I_\mu = \iint_S j_\mu \cdot dS = \iint_{S'} j_\mu \cdot dS'.
\]

In the second integral, \( S' \) is the surface of a parallelepiped in the \( z \leq z_i \) region and with its edges, along the coordinate axes, of lengths tending to infinity. Equation (G.8) holds since the flux of \( j_\mu \) through the surface parallel to \( S \) cancels with \( \psi^L_\mu \) and its derivative with respect to \( z \) when \( z \to -\infty \). Moreover, the fluxes through the other faces parallel to the \( z \) axis, cancel two by two since the kinetic energy operator is hermitic relative to \( \psi^L_\mu \) and \( \psi^R_\mu \).
Using the Green–Ostrogradsky theorem, $I_\mu$ can be transformed into

$$I_\mu = \sum_v \left[ b_v(t)e^{i(E^L_v - E^R_v)t} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{e^{ch}}{2i} \right.$$

$$\times \left( \psi^{L*}_\mu \Delta \psi^R_\mu - \psi^R_\mu \Delta \psi^{L*}_\mu \right) d^3r + c.c.] \quad (G.9)$$

Let us call $J_{\mu\nu}$ the three-fold integral in (G.9). Substituting for $\Delta$ from (G.2) into (G.9) yields

$$J_{\mu\nu} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( \psi^{L*}_\mu H \psi^R_\mu - \psi^R_\mu H \psi^{L*}_\mu \right) d^3r$$

In the integration domain $V_R$ vanishes, hence $H \psi^R_\mu = H \psi^{L*}_\mu = E^R_\mu \psi^R_\mu$ and $J_{\mu\nu}$ becomes:

$$J_{\mu\nu} = - \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^{L*}_\mu (H - E^L_\mu) \psi^R_\mu d^3r$$

or

$$J_{\mu\nu} = - \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^{L*}_\mu (H - E^L_\mu) \psi^R_\mu d^3r$$
which can be transformed into

$$J_{\mu\nu} = -i e \frac{\hbar}{h} \left[ \langle \psi_{\mu}^L | V_R | \psi_{\nu}^R \rangle \left( E_{\mu}^R - E_{\mu}^L \right) \int \int \int \psi_{\mu}^L \psi_{\nu}^R \, d^3r \right] \right] \quad (G.10)$$

Substituting $J_{\mu\nu}$ and $b_v(t)$, given by (G.5b), into (G.9) leads to

$$I_\mu = \sum_v \left\{ -i e \left[ \mathcal{P} \left\{ \frac{1}{E_{\mu}^L - E_{\nu}^R} \right\} - i\pi \delta(E_{\mu}^L - E_{\nu}^R) \right] \left[ \left| \langle \psi_{\nu}^R | V_R | \psi_{\mu}^L \rangle \right|^2 - \langle \psi_{\nu}^R | V_R | \psi_{\mu}^L \rangle \left( E_{\mu}^R - E_{\mu}^L \right) \right] \int \int \int \psi_{\mu}^L \psi_{\nu}^R \, d^3r \right\} + c.c. \right\} \right) \quad (G.11)$$

In presence of the positive small bias voltage, $V = V_{+} - V_{-}$, the total current can be written (taking spin degeneracy into account)

$$I = 2eV n_L(E_F) I_\mu (E^L_{\mu} = E_F) \quad (G.12a)$$

where $n_L(E_F)$ is the density of states of the left electrode at the Fermi level, or

$$I = 2eV \sum_{\mu} \delta(E_{\mu}^L - E_F) I_\mu \quad (G.12b)$$

Substituting for $I_\mu$ from (G.11) into (G.12b), we find

$$I = -\frac{4\pi e^2}{\hbar} V \sum_{\nu, \mu} |\langle \psi_{\nu}^R | V_R | \psi_{\mu}^L \rangle|^2 \delta(E_{\mu}^L - E_{\nu}^R) \delta(E_{\mu}^L - E_F)$$

$$+ 2e V \sum_{\mu} \delta(E_{\mu}^L - E_F) \sum_{\nu} \left[ i e \left[ \mathcal{P} \left\{ \frac{1}{E_{\mu}^L - E_{\nu}^R} \right\} \langle \psi_{\nu}^R | V_R | \psi_{\mu}^L \rangle \left( E_{\nu}^R - E_{\mu}^L \right) \right] \right] \int \int \int \psi_{\mu}^L \psi_{\nu}^R \, d^3r + c.c. \right\} \right.$$ 

If the functions $\psi_{\nu}^R$ and $\psi_{\mu}^L$ are real, the expression between square brackets vanishes. In the general case, if we note that $\psi_{\nu}^L$ and $\psi_{\mu}^L$ are different eigenfunctions of $H_L$ corresponding to the same energy $E_{\mu}^L$ (and, similarly, for $\psi_{\nu}^R$ and $\psi_{\mu}^R$) and perform the summation over $\mu$ and $\nu$, it is rather easy to show that the second term vanishes. Consequently, the expression for the tunneling current is given by

$$I = -\frac{4\pi e^2}{\hbar} V \sum_{\nu, \mu} |\langle \psi_{\nu}^R | V_R | \psi_{\mu}^L \rangle|^2 \delta(E_{\mu}^L - E_{\nu}^R) \delta(E_{\mu}^L - E_F) \quad (G.13)$$

the summation being performed on orbital states. Equivalent formulae can be found in the literature. For instance, using (G.10), (G.13) can be rewritten

$$I = -4\pi h V \sum_{\nu, \mu} |J_{\mu\nu}|^2 \delta(E_{\mu}^L - E_{\nu}^R) \delta(E_{\mu}^L - E_F) \quad (G.14)$$
or, if we introduce the matrix element

\[ M_{\mu\nu} = \frac{\hbar^2}{2m} \int \sum_S \left( \psi_{\mu}^L \nabla \psi_{\nu}^R - \psi_{\nu}^L \nabla \psi_{\mu}^R \right), \tag{G.15} \]

\[ = -i\frac{\hbar}{e} J_{\mu\nu}, \tag{G.16} \]

we find

\[ I = -\frac{4\pi e^2}{h} \gamma' \sum_{\mu,\nu} |M_{\mu\nu}|^2 \delta(E_{\mu}^L - E_{\nu}^R) \delta(E_{\mu}^L - E_F). \tag{G.17} \]

the total

\[ I = -\frac{4\pi e^2}{h} \gamma' V_0^L(r_0) \sum_{\mu} \delta(E_{\mu}^L - E_F) \sum_{\nu} |\psi_{\nu}^R(r_0)|^2 \delta(E_{\nu}^R - E_F), \tag{G.12b} \]

\[ = -\frac{4\pi e^2}{h} \gamma' V_0^L(r_0) n_L(E_F) n_R(r_0, E_F), \tag{G.12b} \]

where \( n_L(r_0, E_F) \) is the local density of states of the sample at the tip position \( r_0 \) and at the Fermi level. Thus

\[ I \propto n_R(r_0, E_F). \tag{G.18} \]

Tersoff and Hamann [G.3] have shown that the same result is obtained when the tip is replaced by a sphere of radius \( R \), centered at \( r_0 \), and when only s-like wave functions \( \psi_{\mu}^L \) are taken into account.

We will consider now a finite positive bias potential, \( \gamma' \), although relatively small on the scale of the work function. The potential of the total system is shown in Fig. G.2c, taking the origin of energies at the mid-point between the two electrodes; it can be still decomposed into \( V_0^L \) and \( V_0^R \) (Fig. G.2a and b) and the preceding calculation remains valid; in particular (G.11) can still be used but all quantities appearing in this formula must be calculated in the presence of \( \gamma' \). The states which contribute to the tunneling current must be occupied on the left electrode and unoccupied on the right electrode. Consequently, the total current is given by

\[ I = \sum_{\mu,\nu} \left[ \delta(E_{\nu}^R - E_{\mu}^F) - \delta(E_{\mu}^L - E_{\nu}^F) \right] I'_{\mu}. \tag{G.19} \]

The primed quantities refer to the system with the bias voltage and \( I'_{\mu} \) is given, mutatis mutandis, by (G.11). The same reasoning as done previously on (G.11) shows that the second term of the second bracket gives no contribution when
The expression for the current is given by
\[ I = -\frac{4\pi e}{\hbar} \sum_{\mu,\nu} \left[ \theta(E_v^R - E_F^R) - \theta(E_\mu^L - E_F^L) \right] |\langle \psi_v^R | V_R | \psi_\mu^L \rangle|^2 \delta(E_\mu^L - E_v^R) , \]
(G.20)
where the summation is performed over orbital states. Taking (G.10) into account, (G.20) can be transformed into
\[ I = -\frac{4\pi e}{\hbar} \sum_{\mu,\nu} \left[ \theta(E_v^R - E_F^R) - \theta(E_\mu^L - E_F^L) \right] |\langle \psi_\mu^L | V_L | \psi_v^R \rangle|^2 \delta(E_\mu^L - E_v^R) . \]
(G.21)

The eigenenergies in the presence of the bias voltage are related to those corresponding to the zero voltage by the following relations
\[ E_\mu^L = E_\mu^L + eV/2 , \]
(G.22a)
\[ E_v^R = E_v^R - eV/2 . \]
(G.22b)
The expression (G.21) of the total current can thus be rewritten

\[
I = -\frac{4\pi \hbar}{e} \sum_{\mu, \nu} \left[ \theta(E^R_\nu - E_F) - \theta(E^L_\mu - E_F) \right] |J_{\mu\nu}|^2 \delta(\varepsilon_{\mu\nu}^L - E^R_\nu + e\gamma^\nu)
\]

or

\[
I = -\frac{4\pi \hbar}{e} \sum_{\mu, \nu} \left[ \theta(E^R_\nu - E_F) - \theta(E^R_\nu - e\gamma^\nu - E_F) \right] |J_{\mu\nu}|^2 \delta(\varepsilon_{\mu\nu}^L - E^R_\nu + e\gamma^\nu).
\]  

(G.23)

If we assume that \( J_{\mu\nu} \) is nearly independent of \( \gamma^\nu \), and use, as before, the point probe approximation for the left electrode (tip), we have

\[
|J_{\mu\nu}|^2 \approx |J_{\mu\nu}|^2 \propto |\psi^R_\mu(r_0)|^2,
\]

the current \( I \) becomes:

\[
I \propto \sum_{\nu} \left[ \theta(E^R_\nu - E_F) - \theta(E^R_\nu - e\gamma^\nu - E_F) \right] |\psi^R_\nu(r_0)|^2 \sum_{\mu} \delta(\varepsilon_{\mu\nu}^L - E^R_\nu + e\gamma^\nu),
\]

\[
\propto \sum_{\nu} \left[ \theta(E^R_\nu - E_F) - \theta(E^R_\nu - e\gamma^\nu - E_F) \right] |\psi^R_\nu(r_0)|^2 n_L(E^R_\nu - e\gamma^\nu).
\]

If we assume that the tip density of states is constant, we get by differentiating with respect to \( \gamma^\nu \)

\[
\frac{dI}{d\gamma^\nu} \propto \sum_{\nu} \delta(\varepsilon^R_\nu - e\gamma^\nu - E_F)|\psi^R_\nu(r_0)|^2 \propto n_0(r_0, E_F + e\gamma^\nu).
\]  

(G.24)

When \( \gamma^\nu \) is positive (Fig. G.1b), the study of \( dI/d\gamma^\nu \) gives the local density of states of unoccupied states of the sample. The same calculation can be carried out, mutatis mutandis, if we assume that the sample is at a negative potential relative to the tip. It shows that the local density of occupied states of the sample is now investigated.

However, the assumption \( J_{\mu\nu} = J_{\nu\mu} \) breaks down when \( |e\gamma^\nu| \) becomes an appreciable fraction of the work function. In this last case, (G.24) can somewhat be corrected by multiplying the right-hand side by a factor \( T(\gamma^\nu) \) approximated using a WKB (Wentzel-Kramers-Brillouin) treatment of the one-dimensional jellium model [G.4]. Thus, the determination of \( n_0(r_0, E_F + e\gamma^\nu) \) from the measurement of \( dI/d\gamma^\nu \) may become rather inaccurate.

From the assumptions made at the beginning, the above calculations are valid when the two electrodes are of the same chemical species. When they are not, there is a charge rearrangement as the electrodes are brought closer together (with no bias voltage) which produces a dipole layer at the electrode surfaces ensuring the equality of the Fermi levels on both sides. As a result the potential of the system can no longer be considered as the superposition of the

\[
- E^R_\nu,
\]

(G.20)

10) into

(G.21)

to those

(G.22a)

(G.22b)
two potentials of each electrode taken separately. However, this total potential can always be split into a left and a right part. Consequently, (G.15) and (G.17) still hold but \( \psi^L_z \) and \( \psi^R_z \) are not strictly the eigenfunctions of the isolated electrodes. Nevertheless, we can hope that (G.18) remains approximately valid.

As a conclusion, this approach is only approximate in the general case. Furthermore, the use of a first order perturbation theory has been questioned by some authors [G.5]. More accurate treatments can be found in the literature [G.6]. However, a practical calculation on a specific tip-sample system is still to come.

**H. Calculation of the Atomic Dynamic Polarizability**

For simplicity, we consider the case of an hydrogen atom in an oscillating electric field directed along the z axis applied adiabatically from \( t = -\infty \), i.e.

\[
E_z = E(e^{-i\omega t} + c.c.) e^{it},
\]

where \( \eta \) is a small positive parameter. If \( \mathbf{p} \) is the dipole moment of the hydrogen atom, the classical interaction energy is given by

\[
V(z, t) = -\mathbf{p} \cdot \mathbf{E} = e_z E_z.
\]

From time-dependent perturbation theory, the perturbed ground-state wave function of the electron is, to first order

\[
|\psi\rangle = e^{-i\frac{\epsilon_1}{\hbar}} |100\rangle + \sum_{|nlm\rangle \neq |100\rangle} a_{nlm}(t) e^{-i\frac{\epsilon_{nl}}{\hbar}} |nlm\rangle,
\]

\( |nlm\rangle \) is the unperturbed wave function of quantum numbers \( n, l, m \) and \( a_{nlm} \) is given by

\[
a_{nlm}(t) = \frac{1}{i\hbar} \int_{-\infty}^{100} \langle nlm | V(z, t) |100\rangle \exp(i\omega_{n,1} t) dt \tag{H.4a}
\]

with

\[
\hbar \omega_{n,1} = (\epsilon_n - \epsilon_1).
\]

Substituting (H.2) into (H.4a) yields

\[
a_{nlm}(t) = -\frac{eE}{\hbar} \langle nlm | z |100\rangle \left( \frac{e^{i(\omega_{n,1} + \omega - i\eta)t}}{(\omega_{n,1} + \omega - i\eta)} + \frac{e^{i(\omega_{n,1} - \omega - i\eta)t}}{(\omega_{n,1} - \omega - i\eta)} \right)
\]

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Let \( u \)

\[
H = \mathbf{f}_{10}\alpha(\omega)
\]

or

\[
\mathbf{a}(\alpha)
\]

or intr

\[
f_{10}\alpha
\]

we get

\[
\alpha(\alpha)
\]

Since th