1

Wettability of an Ideal Surface: Overview

1.1. Wetting angle

Young's relationship and definition of the work of adhesion.

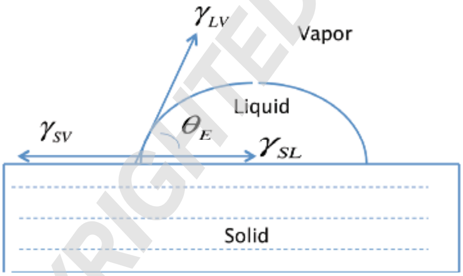

Figure 1.1. *Equilibrium of a liquid droplet on an ideal solid substrate*

When a liquid droplet is placed in a solid, it takes on a given configuration according to the interactions which take place between the solid and the liquid.

The system evolves toward a configuration of minimum free energy characterized by an angle of equilibrium θ_E.

If there is no chemical reaction at the solid–liquid interface, the geometry is simple, as shown in Figure 1.1.

Young's relationship [YOU 05] provides the equilibrium of forces at the triple line. Interfacial tensions are described as forces per unit of triple line length [DEF 66, DE 03]

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta_E \qquad [1.1]$$

where θ_E is the wetting angle and γ is the interfacial tension of solid–vapor, liquid–vapor and solid–liquid, respectively.

COMMENT 1.1.– γ_{SV} is the interfacial tension of the solid in equilibrium with the vapor phase. This value is generally different from the surface tension of the solid in equilibrium with vacuum or a neutral gas, denoted as γ_S. This difference is known as spreading pressure: π_e

$$\pi_e = \gamma_S - \gamma_{SV} \qquad [1.2]$$

Young's equation can therefore be written as follows:

$$\gamma_S = \gamma_{SL} + \gamma_{LV} \cos\theta_E + \pi_e \qquad [1.3]$$

The same result as Young's equation can be deduced from a virtual thermodynamic cycle (there are a number of different variations of this demonstration):

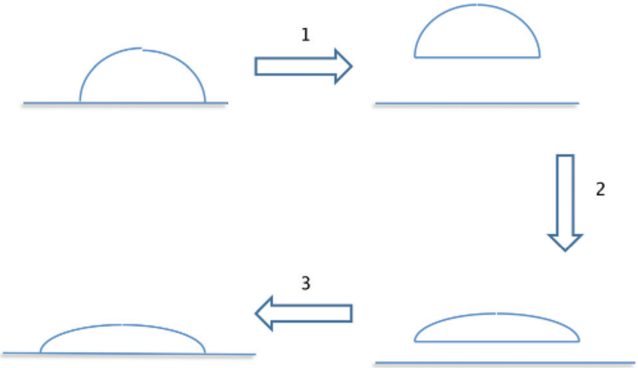

Figure 1.2. *Virtual thermodynamic cycle for the equilibrium of a liquid droplet*

Using a droplet with the interfacial area Ω placed on the solid, it can be assumed first that the droplet can be separated from the substrate without changing its shape.

$$\Delta G_1 = -\gamma_{SL}\Omega + \gamma_{SV}\Omega + \gamma_{LV}\Omega$$

Subsequently, the raised droplet undergoes a variation in contact area dΩ corresponding to the equilibrium situation. As a result, there is a variation in the area of the droplet cap: dΩ cosθ (Figure 1.3).

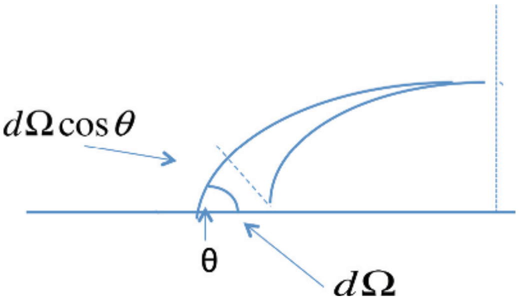

Figure 1.3. *Area variation of the liquid droplet when it reaches the state of equilibrium*

Hence: $\Delta G_2 = \gamma_{LV} d\Omega + \gamma_{LV} d\Omega \cos\theta.$

In the third stage, the droplet is placed back onto the solid:

$$\Delta G_3 = \left(\gamma_{SL} - \gamma_{SV} - \gamma_{SL}\right)\left(\Omega + d\Omega\right)$$

The overall outcome is: $\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3$.

Hence: $\Delta G = \left(\gamma_{SL} - \gamma_{SV} + \gamma_{LV}\cos\theta_E\right) d\Omega.$

At equilibrium, this gives: $d\Delta G / d\Omega = O.$

Hence: $\gamma_{SL} - \gamma_{SV} + \gamma_{LV}\cos\theta_E = 0.$

This does indeed bring us back to Young’s equation.

1.2. Adhesion effect

Dupré definition, spreading coefficient.

The work of adhesion W_{SL} is the variation of free energy per unit area involved in the following transformation shown in the diagram in Figure 1.4.

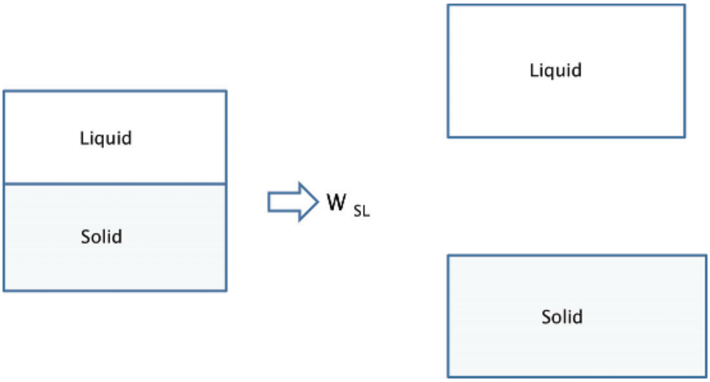

Figure 1.4. *Definition of work of adhesion*

The Dupré relationship is written as follows [DEF 66]:

$$W_{SL} = \gamma_S + \gamma_{LV} - \gamma_{SL} \qquad [1.4]$$

In this definition, γ_S corresponds to a flat surface without vapor adsorption. The solid and liquid phases are very far away from each other.

The introduction of Young's relationship thus leads to the following expression:

$$W_{SL} = \gamma_{LV}\left(1+\cos\theta_E\right)+\pi_e$$

This expression is too often reduced to the following one which ignores the spreading pressure without truly considering its relevance (see Chapter 3):

$$W_{SL} = \gamma_{LV}\left(1+\cos\theta_E\right) \qquad [1.5]$$

Indeed, the difference $\pi_e = \gamma_S - \gamma_{SV}$ can only be ignored in the case of a solid with low surface energy or if the vapor (water) adsorption only has a minor influence: polymers or oxides with a largely contaminated surface.

The ability of a solid for wetting by a liquid is shown by a strong adhesion effect and a low wetting angle.

Another parameter is also used to calculate wetting, which is the spreading coefficient S_e popularized by de Gennes [DE 03]:

$$S_e = \gamma_S - \gamma_{LV} - \gamma_{SL} \qquad [1.6]$$

Using previous relationships, the spreading coefficient can be written as follows:

$$S_e = \pi_e - \gamma_{LV}\left(1 - \cos\theta_E\right) = W_{SL} - 2\gamma_{LV}$$

Extensive spreading of the liquid over the solid is obtained for positive spreading coefficients.

COMMENT 1.2.– Free energy of adhesion ΔF_a which is equal, apart from the sign, to the adhesion effect is a concept which is also widely used in the scientific literature.

1.3. Surface tension and free surface energy

Simplified analysis of surface tension and stresses for a solid or liquid surface. Relation with specific free surface energy.

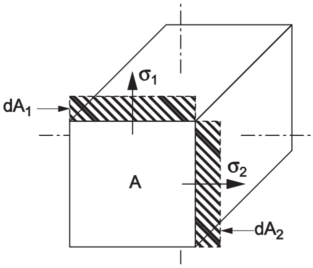

Figure 1.5. *Reversible deformation of a face of a solid crystal*

For the solid surface of a crystal, Figure 1.5 shows the reversible deformation at a constant temperature of the face of the crystal, slightly deformed by quantities dA_1 and dA_2 due to surface stresses σ_1 and σ_2 and in the absence of volume deformation:

$$\sigma_1 dA_1 + \sigma_2 dA_2 = d\left(A.F_A\right)$$

where F_A is the specific free energy of the surface

with $F_A = U_A - TS_A$ (U_A: specific energy of the surface and S_A specific entropy of the surface).

For a symmetrical crystal or an isotropic solid, Shuttleworth shows that [SHU 50]:

$$\sigma_1 = \sigma_2 = \gamma_A$$

$$\gamma_A (dA_1 + dA_2) = \gamma_A dA = d(AF_A)$$

Hence:

$$\gamma_A = F_A + A\left(\frac{dF_A}{dA}\right) \qquad [1.7]$$

For a liquid substrate which undergoes isothermal deformation at a constant volume, the second term of the previous equation is zero. Indeed, the atoms of the liquid are transferred to the surface and the number of atoms per unit area remains constant.

At low temperatures in the case of a solid, atoms are relatively immobile. After deformation, the number of atoms per unit area at a surface layer varies and dF_A/dA is not zero.

However, at high temperatures where diffusion is sufficient, it can be assumed that the number of atoms per unit area in the surface layer will remain relatively constant and therefore $dF_A/dA \approx 0$.

Hence:

$$\gamma_A \approx F_A \qquad [1.8]$$

The complete thermodynamic analysis as proposed by Defay and Prigogine [DEF 66] helps to rigorously establish the useful relationships between the characteristic quantities of the surface.

We refer back to these simply by using their analogy with the thermodynamic relationships of the bulk phase, which are supposedly more familiar.

The definition of free enthalpy G is written as:

$G = F + PV = \Sigma_i n_i \mu_i$ or by volume unit: $G_V = F_V + P = \Sigma_i c_i \mu_i$

F_v represents the free energy per volume unit, c_i is the bulk concentration of the element i and μ_i its chemical potential.

This relation is written as: $-P = F_V - \Sigma_i c_i \mu_i$

By analogy, we obtain the following for the surface phase:

$$\gamma = F_A - \Sigma_i \Gamma_i \mu_i \qquad [1.9]$$

Gibbs adsorptions are given by the expression $\Gamma_i = n_i^A / \Omega$ where n_i^A represents the excess in the number of moles of the constituent I on the uppermost surface compared to the bulk composition $n_i^A = n_i^s - n_i^b$ (rigorously for a division surface placed above the surface layer covering the homogeneous bulk phase) and Ω is the area of the surface.

The surface tension γ, similar, apart from the sign, to the bulk pressure, is expressed according to the specific free energy of the surface F_A, chemical potentials and Gibbs adsorptions Γ_i.

This relation shows that the surface tension γ is only reduced to the specific free energy of the surface F_A for a pure body or systems for which the adsorption Γ_i can be cancelled out by a suitable choice of the position of the division surface.

For multi-component systems where the temperature is such that diffusion can take place, there may be a segregation of one or more surfactant agents toward the surface or interface, causing an enrichment of the interface in surfactant elements and a reduction in the surface tension [DEF 66].

The variation in the free enthalpy G of a bulk phase can generally be written as follows:

$$dG = VdP - SdT + \Sigma_i \mu_i dn_i = d(\Sigma_i n_i \mu_i)$$

After simplification, this relation leads to the generalized Gibbs Duhem relationship, hence per volume unit:

$$dP_V = S_V dT + \Sigma_i c_i d\mu_i$$

By analogy, we can obtain the Gibbs adsorption equation:

$$d\gamma = -S_A dT - \Sigma_i \Gamma_i d\mu_i \qquad [1.10]$$

This relationship will be used during the study of the solid–electrolyte interface in Chapter 7.

To conclude this short introduction, we predict that wettability studies will be important in various domains of application in material science.

At high temperatures, studies of this type will be necessary to address the issue of adhesion of different assemblies, such as, for example, ceramic–metal solder joints or the manufacturing of composite materials such as Al/SiC or Al/C.

At lower temperatures (close to ambient temperature), wettability studies help to establish the energy of solid surfaces, which can show structural defects and/or can be coated with a contamination layer (real case). It would therefore be possible to characterize the acid-base properties of the material studied, which is a quantity which guides in particular the adhesion of the now widely-used metal-polymer assemblies.