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Review

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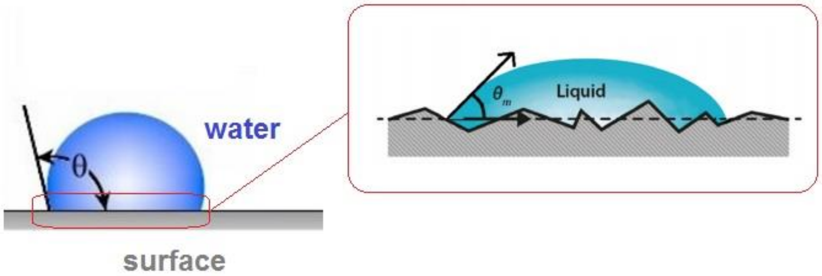
Graphical abstract

$$\frac{(1+\cos\theta)\gamma_l}{2}=\sqrt{\gamma_s^{LW}\gamma_l^{LW}}+\sqrt{\gamma_s^{+}\gamma_l^{-}}+\sqrt{\gamma_s^{-}\gamma_l^{+}}$$



Surface free energy of solids by contact angle measurements

Abstract
Surface energy is very important concept in the materials science and engineering. For solids, this can be calculated from contact angle measurements and different theoretical approximations; however, when a membrane is the object of study, porosity can be considered to be the main factor affecting the measures of contact angle and, in consequence, the results of surface energy. The objectives of this article is the performing of the theoretical description for the determination of surface energy from contact angle measures and to give key points for physical interpretation of data and illustrate its application for characterization of polymeric materials.

Keywords
Contact angle
Surface energy
Acid-base interactions
van der Waals forces

Energía superficial de sólidos mediante medidas de ángulo de contacto

Resumen

La energía superficial es un concepto muy importante en la ciencia de materiales y en ingeniería. Para sólidos, esta puede calcularse a partir de medidas de ángulo de contacto y diferentes aproximaciones teóricas; sin embargo, para membranas como objeto de estudio, la porosidad puede ser considerada como el principal factor que afecta las medidas de ángulo de contacto y, en consecuencia, afecta los resultados de energía superficial. Los objetivos de este artículo es la realización de la descripción teórica para la determinación de las energías superficiales desde medidas de ángulo de contacto y dar puntos claves para la interpretación física de los datos e ilustrar su aplicación para la caracterización de materiales poliméricos.

Palabras claves
Ángulo de contacto
Energía superficial
Interacciones ácido-base
Fuerzas de van der Waals

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Research Article

Surface free energy of solids by contact angle measurements

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Abstract

Surface energy is very important concept in the materials science and engineering. For solids, this can be calculated from contact angle measurements and different theoretical approximations; however, when a membrane is the object of study, porosity can be considered to be the main factor affecting the measures of contact angle and, in consequence, the results of surface energy. The objectives of this article is the performing of the theoretical description for the determination of surface energy from contact angle measures and to give key points for physical interpretation of data and illustrate its application for characterization of polymeric materials.

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Content

1. Introduction

Surface energy is very important concept in the materials science and engineering. For example, surface tension is the driving force for sintering of metals, ceramic materials and polymers made from powders. Also, it is the driving force the growth of particles dispersed in gases, liquids or solids; and to determine the distribution of size and shapes of solids and liquids in multiphase systems and phase transformations [1]. It is widely accepted that knowledge of interactions associated with surface free energy is necessary for understanding and modeling many surface and interface processes which involve such wetting phenomena as preparation of suspensions and emulsions, flotation of minerals, detergency, adhesive joints, painting, drug preparation, and others. In addition, in biological science, the free surface energy of solid is used for the thermodynamic description of adsorption of microorganisms on surface. From this parameter is obtained information about mechanism of aggregation, biofouling and biofilms [2-4].

To carry out the characterization of surface there are different techniques which must be selected depending on objective of characterization. Among the most widely used methods are: For the study of composition, X-ray diffraction, photoelectron spectroscopy, Fourier transform infrared spectroscopy usually by attenuated total reflectance; whereas for the study of morphology, scanning electron microscopy and atomic force microscopy. These methods require relatively expensive equipment, skilled technicians and sophisticated techniques to interpret data. However, measurement of surface energy of the solid can also provide a good understanding of the surface properties of a solid using relatively a very simple approach. In addition, the surface energy of a solid can be determined from the measurement of contact angle of one pure liquid drop, or systems of liquids, deposited on that solid [5-6]. Different works have been performed for membranes systems; however, though these measurements are useful to analyze relative changes of membranes, information associated with structural characterization of the phase cannot be obtained because a magnitude of porous effects is not considered [7-8].

The objective of this article is the performing of the theoretical description for the determination of surface energy from contact angle measures, to give key points for physical interpretation of data and illustrate its application for characterization of polymeric materials.

2. Theory

2.1 Surface free energy of solids

In thermodynamic, free energy is the amount of work that a system can perform. From a more interpretative point of view, the free energy is the internal energy of a system minus the amount of energy that cannot be used to perform work. On the other hand, for a closed system with two components *a* and *b*, at constant temperature and pressure, the surface energy, also called "Gibbs surface energy" or most commonly surface tension (γ) is easily defined to be the partial derivate of Gibbs energy (G) respect to surface (A) at pressure (P), temperature (T) and composition to be constants. Thus:

$$\gamma = -\left(\frac{\partial G}{\partial A}\right)_{P,T,n} \tag{1}$$

Note that units of γ are N/m or force per unit length (see Appendix A). The term "surface free energy" (γ) implies only that work required to form a new surface, *i.e.*, the work required to bring molecules from the interior of the phase to the surface; in consequence, γ is associated with the force per unit of length requires to carry out the surface work and/or the variation of Gibb energy respect to changes of surface. Details are given by D. Readey (2017) [1, 9-10].

Two important concepts are: work of cohesion (w_{11}) and work of adhesion (w_{12}). In the first case, w_{11} is the free energy change to separate a material from contact condition (ΔG_{11}); whereas, w_{12} is the free energy change to separate two different materials from contact condition (ΔG_{12}). For non-polar and polar systems, the ΔG_{11} of a condensed phase material may be expressed by equation of Dupré,

$$\Delta G_{11} = w_{11} = -2\gamma_1 \tag{2}$$

where γ_1 is the surface tension of material corresponding to condensed phase 1. But also, for apolar materials,

$$\Delta G_{11} = \frac{-A_{11}}{12\pi\, l_0^2} \tag{3}$$

where A_{11} is the Hamaker's constant and l_0 is the minimum equilibrium distance between two parallel layers of material 1. When Hamaker's constant is greater than zero the interaction is attractive and when it is less than zero the interaction is repulsive [11]. A comprehensive review about Hamaker's constant see Bergström (1997) [12].

For adhesive forces, when two different materials are in contact through common interface, equation 2 can be written to be

$$\Delta G_{12} = w_{12} = \gamma_{12} - \gamma_1 - \gamma_2 \qquad (4)$$

where γ_{12} is the interfacial tension of material corresponding to interface between the phases 1 and 2. The amount γ_{12} is one of the most important concepts in colloid and surface science. By its description, a quantitative expression for the free energy of interparticle or intermolecular interaction in condensed phase systems can be obtained. Since interfacial tensions between solids and liquids and between solids and solids cannot be determined directly, commonly this interfacial tensions γ_{12} are obtained by theoretical treatments from surface tensions γ_1 and γ_2 of interacting materials [l].

2.2. Components of surface energy

Surface energy components control much of the interfacial interactions and describe the surface characteristics of the studied material and it is known that the adhesive and cohesive forces are resulting of interaction forces a molecular level; this forces can be grouped to be interactions of Lifshitz-van der Waals and polar interactions (or acid-base interactions). The main difference between Lifshitz-van der Waals interactions and acid-base interacttions is that electron donor-acceptor reactions are not symmetrical while van der Waals interactions are. These are shortly described below:

2.2.1. Interactions of Lifshitz-van der Waals

The Lifshitz-van der Waals component is a grouping of three different interactions named as Keesom (dipole-dipole), Debye (dipole-induced dipole) and London forces (induced dipole- induced dipole); these three forces are additive and therefore,

$$\gamma_d^s = \gamma_d^{LW} = \gamma_d^L + \gamma_d^D + \gamma_d^K \qquad (5)$$

where the superscripts *s, LW, L, D and K* denote “solid”, Lifshitz-van der Waals, London, Debye and Keesom, respectively. The subscript *d* denotes “dispersive contribution” [10, 11]. The Lifshitz-van der Waals forces are symmetrical interactions because these are resulting of factors which have place in both interacting entities through an interface (*i.e.*, direct contact). Thus, the molecular polarizabilities and the ionization energies are factor determining of dispersion force [1].

2.2.2. Polar or acid-base interactions

The acid-base components include two components named to be the electron donor (γ^-), and the electron acceptor components (γ^+). These interactions are mainly hydrogen donor and electron acceptor/donor interactions. Thus, for an electron acceptor-donor interaction, symmetry does not exist because in a strict sense a basic functional group, such as a carboxylic acid, will not interact as a base with another basic entity. One must act as an electron donor and the other must act as an electron acceptor [1, 10, 13]. It is widely accepted that non-dispersive forces only occur when there are complimentary groups interacting (*i.e.*, an electron acceptor and an electron donor in a Lewis sense).

Surface tension can be described by two additive components: Lifshitz-van der Waals (γ^{LW}) and acid-base (γ^{AB}) interactions. However, γ^{LW} is constituted by additive components whereas components of γ^{AB} include two non-additive parameters. As in the acid-base interaction between polar condensed phases 1 and 2, the electron-acceptor of 1 interacts with the electron-donor of 2, and the electron-donor of 1 interacts with the electron-acceptor of 2, therefore, acid-base contributions resulting are $(\gamma_1^+\gamma_2^-)^{1/2}$ and $(\gamma_1^-\gamma_2^+)^{1/2}$ [10].

2.3. Contact angle and Young’s equation

Contact angle (θ) is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface [1, 10]. By geometrical criteria, contact angle can be obtained by applying a tangent line from the contact point along the liquid-vapor interface in the droplet profile, which can be obtained by photographic image by depositing of liquid drop on the surface (see Figure 1).

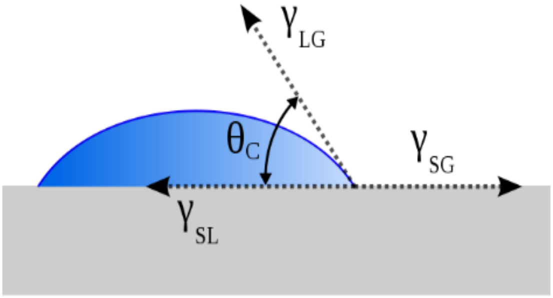

Figure 1. Contact angle and interface energies

A small contact angle is observed when the liquid spreads on the surface, while a large contact angle is observed when the liquid beads on the surface. More specifically, a contact angle less than 90° indicates that wetting of the surface is favorable, and the fluid will spread over a large area on the surface; while contact angles greater than 90° generally means that wetting of the surface is unfavorable so the fluid will minimize its contact with the surface and form a compact liquid droplet [14].

Measurements of contact angle have been used in the study of surface energy, wettability and adhesion properties. In addition, the contact angle using one liquid, a hydrophilic or hydrophobic liquid, permits a quantitative description of polar nature of surface, as well as, wetting of a solid by a liquid and the surface changes which can occur and alter the previous feature [14]. Thus, for example, when water is used as test liquid and polypropylene as target surface, high values of θ are expected because water is hydrophilic in nature whereas polypropylene surface is hydrophobic in nature. If by chemical reaction polypropylene surface is modified and polar groups are inserted on the surface, then a decrease of values of θ are expected; this decrease will be different for different polar functional groups. In addition, the change on value of θ can be monitored throughout surface using a 2D-point distribution and thus to obtain information of surface anisotropy resulting of chemical modification. Figure 2 shown the representation of contact angle.

Ideally, the shape of a liquid droplet is determined by γ of liquid. In a pure liquid, each molecule in the bulk is pulled equally in every direction by neighboring liquid molecules, resulting in a net force of zero. However, the molecules exposed at the surface do not have neighboring molecules in all directions to provide a balanced net force. Instead, they are pulled inward by the neighboring molecules, creating an internal pressure (see Fig. 3) [14].

The contact angle of a liquid drop on an ideal solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions,

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{6}$$

where γ_{lv}, γ_{sv}, and γ_{sl} represent the liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively (see Appendix B).

On the other hand, by geometrical criteria, the shape of drop can be associated with contact angle (see Figure 4). Respective equation, assuming a spherical shape, is given by

$$\tan\left(\frac{\theta}{2}\right) = \frac{h}{d} \tag{7}$$

where h and d are the height and radius of the drop, respectively. Equation 7 is only valid for small drops because gravitational effects are negligible.

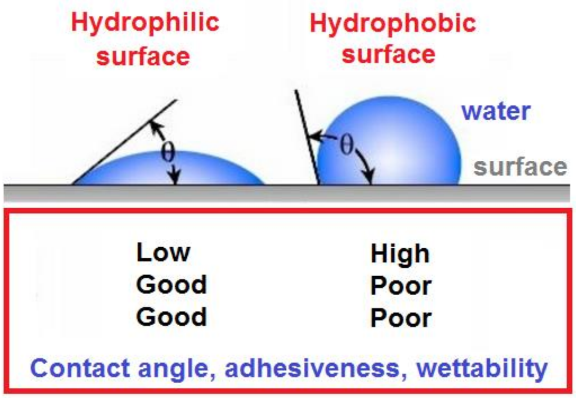

Figure 2. Illustration of expected contact angle for water on different surfaces

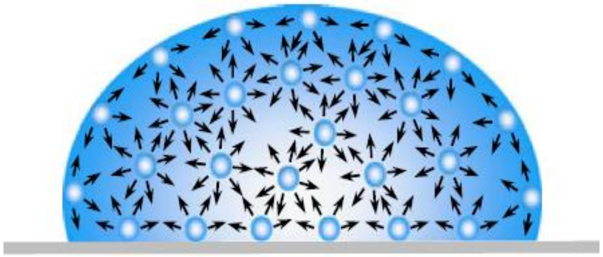

Figure 3. Illustration of force balance in the liquid on liquid-gas and solid-liquid interfaces.

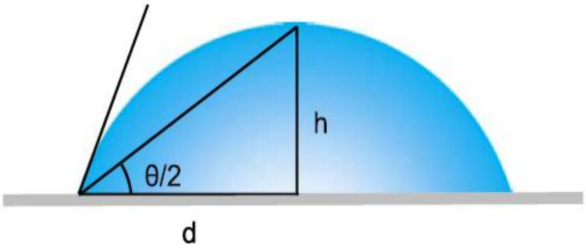

Figure 4. Geometrical description of drop

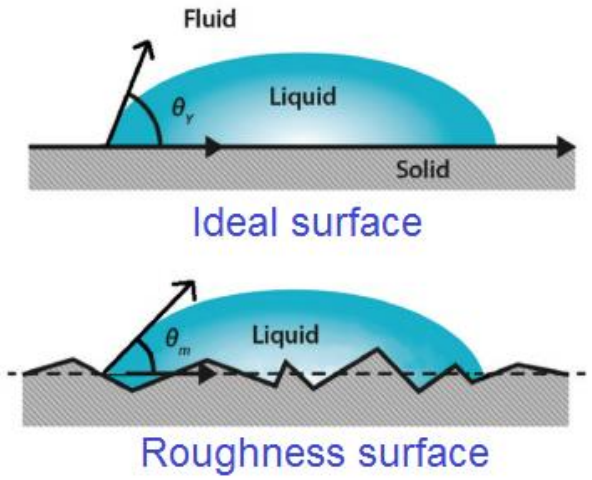

Figure 5. Illustration of ideal and non-ideal surface.

Young equation is valid only for ideal surfaces (*i.e.*, roughness equal to zero) (Figure 5). For this reason, the contact angle can be named as observed contact angle (θ_{obs}) and intrinsic contact angle or Young contact angle (θ_Y). Observed contact angle is the contact angle measured on a non-ideal surface or with roughness and it is the experimental contact angle, also it is named as apparent contact angle. On the other hand, θ_Y is the contact angle non-affected by surface roughness. To correct the effect of roughness, the Wenzel equation is used. This is given by

$$\cos\theta_{obs} = R\cos\theta_Y \tag{8}$$

where R is the average roughness ratio defined as the factor because roughness increases the solid-liquid interfacial area. R is the ratio of the area of the rough surface to the area of the effective planar surface [15, 16].

In cases where the liquid does not penetrate into the channels, the Wenzel equation does not apply and, in this case, the Cassie equation is used instead. The Cassie equation was first developed to describe chemically heterogeneous surfaces, with two different chemical natures, and is given by

$$\cos\theta_{obs} = f_1\cos\theta_1 + f_2\cos\theta_2 \tag{9}$$

where θ_1 is the contact angle for component 1 with area fraction f_1, and θ_2 is the contact angle for component 2 with area fraction f_2 present in the composite material [17-19]. This equation takes on special meaning when in a 2-component system one component is air with a contact angle of 180°. With $\cos(180) = -1$, the equation reduces to:

$$\cos\theta_{obs} = f_1(\cos\theta_1 + 1) - 1 \tag{10}$$

From Young's equation is expected only one value of contact angle for specific solid-liquid-gas system; However, from experimental results, even in static conditions, at least two different contact angles can be measured on the same solid surface and for the same liquid. These angles are defined as advancing and receding contact angles (θ_a and θ_r, respectively).

It is important to remember that Young's contact angle is defined for ideal surface (*i.e.*, zero roughness). Thus, advancing and receding contact angles are commonly explained for surface roughness, microscopic chemical heterogeneity, drop size effect, molecular reorientation, and the penetration of the liquid molecules into the solid surface. An equilibrium angle (θ_{eq}) has been defined to be

$$2\cos\theta_{eq} = \cos\theta_a + \cos\theta_{.r} \tag{11}$$

It has been demonstrated that average of cosine gives improve results in comparison with arithmetic average (Good's approximation). Several papers have published a new interpretation of the contact angle hysteresis and its relation with surface free energy [20]:

$$\gamma_s^{tot} = \frac{\gamma_l(1+\cos\theta_a)^2}{(2+\cos\theta_r+\cos\theta_a)} \tag{12}$$

2.4. Determination surface free energy of solids

From Fowkes's theory [11, 13-14], contact angle concept and surface energy concepts (all these aspects are grouped usually as van Oss-Chaudhury-Good theory), it can be concluded the Young-Dupre equation, which stablishes:

$$(1+\cos\theta)\gamma_l = -\Delta G_{sl} \tag{13}$$

where the subscript l denotes the liquid used in the drop for contact angle measurement and s indicates the solid [21, 22].

$$(1+\cos\theta)\gamma_l = -\Delta G_{sl} \tag{14}$$

Table 1. Surface tension components at 20 °C in mN/m [1, 5, 3,10].

Liquid	γ_l	γ_l^{LW}	γ_l^{AB}	γ_l^{+}	γ_l^{-}
Decane	23.83	23.83	0	0	0
Dodecane	25.35	-	0	0	0
Tetradecane	26.6	26.6	0	0	0
Hexadecane	27.47	-	0	0	0
cis-Decalin	32.2	32.2	0	0	0
α-Bromonaphthalene	44.4	44.4	~0	~0	0
Diiodomethane	50.8	50.8	~0	~0	0
Hexane	18.40	18.40	0	0	0
Carbon tetrachloride	27.0	27.0	0	0	0
Methylene iodide	50.8	50.8	0	0	0
Benzene	28.85	28.85	0	0	2.7
Chloroform	27.15	27.15	0	3.8	0
Ethanol	22.4	18.8	2.6	0.019	68
Ethylene glycol	48.0	29.0	19.0	1.92	47.0
Glycerol	64.0	34.0	30.0	3.92	57.4
Formamide	58.0	39.0	19.0	2.28	39.6
Water	72.8	21.8	51.0	25.5	25.5

The complete Young equation, comprising both the apolar and polar interactions, becomes

$$\frac{(1+\cos\theta)\gamma_l}{2} = \sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^{+}\gamma_l^{-}} + \sqrt{\gamma_s^{-}\gamma_l^{+}} \qquad (15)$$

Note that, using three different liquids and one same solid surface is possible to obtain three different contact angles. In addition, parameters associated to surface tension of liquids are known, therefore, resolving a 3x3 equation system is possible to obtain the values associated to solid surface. Thus,

$$\gamma_s = \gamma_s^{LW} + 2\sqrt{\gamma_s^{+}\gamma_s^{-}} \qquad (16)$$

Values of surface tension and their components for different liquids are shown in the Table 1. For correct application of Eqs. 13 and 14, analysis must be carry out using a minimum of 5 data per liquid, with a small coefficient of variation. It is very important minimize the mistake in the parameter of equation in order to avoid the error propagation.

2.5. Interpretation

Interpretation of values of contact angle must be careful performed. Researcher must consider the nature of surface and specify the suppositions used to offer comparable information (Young contact angle, Wenzel, ideal surface, etc.). Tips for interpretation of data are shown below, these are based in the information previously cited [1-23].

In relation with the magnitude of data, a high surface energy is related with a strong cohesion and, in consequence, a high boiling point (it is important to remember that surface energy correlates with evaporation enthalpy), being in many cases an adequate approximation. But also, the formation of a new surface is associated with different surface processes; thus, for example, a material with high surface energy tends to reduce the energy via adsorption of "contaminants" from surroundings.

Liquids can interact with two main types of solid surfaces. Traditionally, solid surfaces have been divided into high-energy solids and low-energy types. The relative energy of a solid has to do with the bulk nature of the solid itself. Solids such as metals, glasses, and ceramics are known as 'hard solids' because the chemical bonds that hold them together (*e.g.*, covalent, ionic, or metallic) are very strong. Thus, it takes a large input of energy to break these solids (alternatively large amount of energy is required to cut the bulk and make two separate surfaces so high surface energy), so they are termed "high energy". Most molecular liquids achieve complete wetting with high-energy surfaces. The other type of solids is weak molecular crystals (*e.g.*, fluorocarbons, hydrocarbons, etc.) where the molecules are held together essentially by physical forces (*e.g.*, van der Waals and hydrogen bonds). Since these solids are held together by weak forces, a very low input of energy is required to break them, thus they are termed “low energy”. Depending on the type of liquid chosen, low-energy surfaces can permit either complete or partial wetting.

In addition, it is proper uses an experimental system to contrast the results; thus, for example, it is useful to remember that "pure" non-polar liquids (*e.g.*, alkanes) and "pure" non-polar solids (*e.g.*, teflon, polyethylene, polypropylene) have only dispersive components. In consequence, $\gamma = \gamma^{LW}$.

3. Conclusions

Measurements of contact angle are a easy, fast and versatile method to determine the solid surface energies and their components. This is an indirect determination based on theoretical approximations described by van Oss-Chaudhury-Good theory. In addition, it is possible the interpretation of surface energy and dispersive and acid-base contributions in terms of interaction forces, being a good alternative for the description and characterization of materials.

Finally, depending of features of solid surface, different approximations have been developed and these need to be considered. It is suggested the performing of this methodology in parallel with other techniques in order to permit an improving of interpretation of data.

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Conflict of interests

The authors declare no conflict of interest.

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Appendix A: Thermodynamic definition of γ

For a system formed by two components *a* and *b*, with capacity to perform two works: pressure-volume work ($w_{PV} = -PdV$, which is associated to changes of volume as a result to apply a force per unit of surface) and surface work ($w_{sur} = \gamma dA$, which is associated to changes of the surface as a result to apply a force per unit of length), the first law can be expressed by

$$dU = dQ + dw_{PV} + dw_{sur} \qquad \text{(A1)}$$

where dU and dQ are the variation of internal energy and heat, respectively. Combining dU, $dH = dU + d(PV)$, $dQ = TdS$ and $dG = dH - d(TS)$ is obtained:

$$dG = -TdS + VdP + \mu_a dn_a + \mu_b dn_b - \gamma dA \qquad \text{(A2)}$$

Considering T, P, n_a and n_b to be constants,

$$dG = -\gamma dA \qquad \text{(A3)}$$

In consequence, it is concluded the Equation 1.

Appendix B: Young's equation

When a drop is deposited on the solid surface and static equilibrium is achieved (see Figure B1, red lines), on point of convergence of three interfaces (liquid-vapor, solid-vapor, and solid-liquid) is possible, from concepts of mechanical equilibrium, to link θ with the different interface tensions. For that, the first one is to understand that $dw = Fdx$, but also, $F = dw/dx = \gamma$. According to the Newton Laws,

$$-\gamma_{sl} + \gamma_{sv} + \gamma_{lv,y} = 0 \qquad \text{(B1)}$$

In addition,

$$\gamma_{lv,y} = \gamma_{lv} \cos\theta \qquad \text{(B2)}$$

Combining the above equations,

$$\cos\theta = \frac{\gamma_{sl} - \gamma_{sv}}{\gamma_{lv}} \qquad \text{(B3)}$$

Note that depending if analysis is done using the contact angle of the right side the sign in the numerator change respect to contact angle of the left side (Compare B3 with Eq. 6).

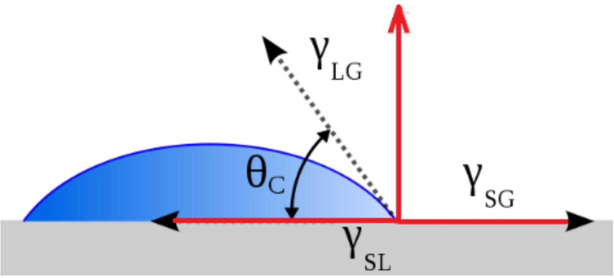

Figure B1. Illustration of vectors of force considred in the description of Eq. B3