Static Contact Angles for Liquids at Heterogeneous Rigid Solid Surfaces

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The contact angles for liquids at heterogeneous rigid surfaces are discussed based on concepts that have recently been established for wetting and spreading phenomena at these surfaces. The discrete nature of the region in the vicinity of the three-phase contact line is critically reviewed and the excess energy associated with this region is analyzed. Also, the problem of classification of the surface heterogeneity with regard to the size of heterogeneous domains and their effects on contact angles is emphasized in this contribution.

The size, shape, and distribution of the heterogeneous pattern affect the advancing, receding, and equilibrium contact angles. There is, however, no universal theoretical model which describes all possible cases. It seems that the equilibrium contact angle for a liquid at a heterogeneous surface composed of macroscopic- and microscopic-sized patterns can be predicted based on the Cassie equation and the modified Cassie equation (including the line tension term) respectively. However, the contribution of the linear free energy, associated with a contorted three-phase contact line, to contact angles for liquids at heterogeneous surfaces still remains unclear. This is due to the controversial nature of the magnitude of the line tension and the effect of contortion of the three-phase contact line on the macroscopic ("apparent") contact angle. Also, both thermodynamic approaches, Cassie and modified Cassie equations, cannot predict contact angle hysteresis. The difference between the advancing and the receding contact angles depends on the position and contortion of the three-phase contact line at a heterogeneous surface. Although this phenomenon is well understood conceptually, an adequate model which could be easily adapted for real systems with randomly distributed heterogeneities of varying size and shape does not exist.

Further, the studies for systems with microscopic heterogeneities are almost exclusively limited to theoretical modelling. The systems with nanoscopic and molecular heterogeneities are poorly understood. There is still controversy with regard to the use of a theoretical model for describing the contact angles for liquids at these surfaces. Finally, the characteristic features of a region in the vicinity of the three-phase contact line and their effects on the macroscopic contact angle are poorly understood. Both theoretical modelling and experimental investigation of this region are in an early stage and no general rules can be made.

Key words: contact angle, contact angle hysteresis, heterogeneity, heterogeneous surface, line tension, wettability

Introduction

The importance of controlling the spread of a liquid over a solid or a liquid surface was recognized thousands of years ago, though the wetting phenomena were poorly understood, if at all. Seafaring cultures used oil to spread on storm-tossed waters and protect fragile crafts. Waterproofing of their boats was enhanced by painting with oil/tar. Ancient Egyptians lubricated great stones used for pyramids and monuments.
in order to improve their movement. In modern times, the significance of the wetting properties of solids and the control of spreading phenomena are recognized practically in every industry to stimulate and facilitate operations. The selective recovery of minerals from an ore using the flotation separation technique is a common example. Also, the flotation separation of plastics and the deinking flotation of wastepaper can be performed because of the differences in wetting properties of particulates. Successful tertiary oil recovery depends on surface chemistry control and wetting of rock minerals. The progress in applied surface chemistry is so advanced these days that the wetting properties of solid surfaces are artificially changed for appropriate hydrophobicity (waterproofing), oleophobicity, and/or compatibility with other phases. Examples include hydrophobization of fabrics (waterproofed clothes, tourist equipment, etc.), anticorrosive waterproofing, modification of solid surfaces in preparation of polymer-mineral composites and polymer-solid joints, modification of filler particles used for inks and toners. Other applications of wetting phenomena include lubrication processes, oil spill clean-ups with porous sorbents, flotation of dispersed oil, stabilization or destabilization of emulsions and foams with solid particles, etc.

There is no doubt that the understanding of wetting phenomena is of paramount importance to improve and develop surface chemistry related processes. The formal studies of wetting and capillary phenomena (wetting and capillary phenomena directly relate to each other in all three-phase systems) probably began sometime in the 18th century and first reports appeared in the early 19th century. It was Laplace [1] and Poisson [2] who established the fundamental background for capillarity. Importantly, for the surface science of wetting phenomena, Young [3] described the relationship between contact angle and surface energies for a liquid at a solid surface on the basis of mechanical considerations. This concept was next thermodynamically proved on a more rigorous basis by Gibbs [4]. From that time it has been known that the behavior of liquid on a solid surface is controlled by competition between the interfacial energies of the liquid-vapor ($\gamma_{LV}$), solid-liquid ($\gamma_{SL}$) and solid-vapor ($\gamma_{SV}$) interfaces. A spontaneous and complete spreading of liquid occurs over the solid surface when the spreading coefficient ($S_{SV}$) is positive or at least zero*. The spreading coefficient is expressed as follows [5]:

* The spreading coefficient is a time-dependent property of many systems. An initial spreading coefficient is calculated by using the interfacial tensions determined for two phase systems; liquid and vapor, solid and vapor, and solid and liquid; without the presence of the third phase. In this regard, this value describes the initial conditions of the system at the first moment of contact between the three phases. Usually, interfacial tensions undergo changes in the presence of the third phase. This is the effect of mutual saturation of the phases and preferential adsorption of selected components at the interface. In such a case, the final spreading coefficient (as calculated based on interfacial tensions for a saturated three-phase system) will differ, in some cases significantly, from the initial spreading coefficient [5,6]. Although the initial spreading coefficient (non-equilibrium) can be positive the final spreading coefficient (equilibrium value) is assumed to always be negative [6]. This statement is difficult to prove experimentally for the three-phase systems involving solids due to difficulties in the determination of the interfacial energies for solids. Nevertheless, it has been observed to be correct for similar three-phase systems only involving fluids [6–8].
Static contact angles for liquids...

\[ S_{SLV} = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \]  

(1)

On the other hand, the liquid forms a finite contact angle (\( \theta \)) at a solid surface when the spreading coefficient is negative. The value of this contact angle is established by the competition of interfacial energetics and is well defined by Young’s equation [3–5]:

\[ \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \]  

(2)

\[ \cos \theta = 1 + \frac{S_{SLV}}{\gamma_{LV}} \]  

(3)

where the superscript "\( \gamma \)" indicates that the contact angle is described by Young’s equation (2) and corresponds to thermodynamically defined equilibrium conditions*.

Equations (1)–(3), derived on the basis of thermodynamics, have limited practical significance. They can be applied for solids whose surfaces are homogeneous, isotropic, smooth, rigid, and which are not attacked by the probing liquid or liquid components (chemical reaction, dissolution, swelling). Real solids always deviate from such an ideal state, even when special precaution is undertaken in their preparation, preservation, and handling. Real solid surfaces can be rough, heterogeneous, anisotropic, elastic, deformable, and react with surrounded fluids or their components. Although all of these parameters affect the contact angle value, the discussion in this contribution is limited to smooth, rigid, and inert but heterogeneous surfaces. The contact angle value depends on solid surface heterogeneity but there is no simple relationship between these two parameters for most of the systems to be discussed in this paper. The size, shape, and distribution of surface heterogeneities affect the contact angles and there is no universal theoretical relationship which describes all possible cases. Several theoretical relationships describing the contact angle for a liquid at a heterogeneous solid surface have been developed in this century. Selected theoretical models are reviewed in this contribution with special emphasis on recent advances. Particularly, the problem of classification of surface heterogeneity with regard to the size of the heterogeneous domains and their effects on contact angle is discussed herein. This review is limited to the static systems.

Solid Surface Heterogeneity

Nearly all solid samples which may be examined in the laboratory exhibit surface heterogeneity. Solid surface characteristics are established by the nature and history of the solid sample, its procedure of preparation, preservation and handling, and

* It follows from this equation that the contact angle can reach a value from 0° to 180°. Although a zero contact angle is frequently observed in practice the contact angle of 180° is not realistic. There is no such system in nature, or created by man, which exhibits no interaction. A contact angle of 180° appears in two-liquid systems when one liquid preferentially and completely wets the contact solid surface. Such a situation is referred to as a zero contact angle for the wetting liquid.
finally by its environment. Natural heterogeneity, at least at an atomic level, is a
typical feature of heteroatom compounds. Only metals and solidified monoatomic
inert gases, such as helium, are exemptions. But even these surfaces are difficult to
protect against chemical (corrosion reactions) and physical (adsorption of the gas
components) interactions with the atmosphere during surface preparation, storage,
and handling. High-energy solid surfaces (surface free energy, $\gamma_{SV}$, larger than 100
mg/m$^2$) such as mineral and metal surfaces are energetically less stable than low-energy
surfaces ($\gamma_{SV} < 100$ mg/m$^2$) such as polymers, and thus they are sensitive to environ-
mental contamination (chemical and physical) [9,10]. In many applications, the
surface characteristics of solids are changed intentionally by the adsorption of
molecular layers or by the deposition and formation of both organic and inorganic
coatings/films. A variation in surface heterogeneity can be observed for almost any
material at different stages of its production, preparation, and use.

Our environment is full of heterogeneous systems owing to the fact that the
Universe has a natural tendency for disorganization (the entropic effect) and selects
preferentially heterogeneous structures instead of homogeneous ones (with a few
exceptions). A mineral ore deposit is a conclusive example of a naturally occurring
structure with all levels of heterogeneity, with regard to both distribution and size.
As shown in Figure 1, heterogeneity appears at all levels of scale from meter-sized
down to ångstrom-sized. Mineral deposits have been formed by stratification of
different inorganic and organic materials under different environmental conditions.
This results in the formation of layers/zones of varying composition and heteroge-
neity (from several meters down to several centimeters). Obviously, this scale of
heterogeneity is not a concern for surface chemists. The size of this heterogeneity
exceeds the range of action of capillary forces.

![Diagram of mineral deposit](image)

**Figure 1.** Heterogeneous nature of a mineral deposit and an ore.
Mineral strata (Figure 1) are composed of stones and particles with inclusions of different sizes, compositions, shapes, and contaminations. The heterogeneity of this system varies from atomic dimensions up to at least a few millimeters. The following surface heterogeneity scale can be specified in this case: macroscopic heterogeneity (tenth of a millimeter to a few millimeters), microscopic heterogeneity (tenth of a micrometer to several micrometers), and nanoscopic heterogeneity (tenth of a nanometer to a few nanometer). Also, during the exposure of the mineral particles to the environment their surfaces become modified with adsorbed inorganic and organic compounds. The pattern of the adsorbed contaminants usually forms a molecular heterogeneity with dimensions from a few ångstroms to several ångstroms. Finally, it must be recognized that most of the minerals are composed of different elements and thus the crystallographic structure of the mineral is an example for heterogeneity at the atomic level (atomic heterogeneity).

The above spectrum of mineral ore heterogeneity will change at each step of the processing sequence. After mining, crushing and grinding the system is reduced to mineral grains with surface heterogeneity varying from the atomic scale to the macroscopic level. During selective flotation, the general heterogeneity of the particle mixture is eliminated (or at least reduced), but on the other hand, the surface heterogeneity is intentionally changed by stimulating adsorption of collector(s) at the mineral particle surfaces. The flotation concentrate obtained requires a chemical and/or thermal purification in order to obtain a “pure mineral”, free of inclusions of other mineral(s), organic compounds, and water. Of course, the ideal mineral surface, composed of different elements, demonstrates only atomic heterogeneity if it is well isolated from the laboratory environment and all possible sources of contaminants are avoided.

The surface characteristics of many solids change when exposed to the environment. This is because of the adsorption of organic contaminants and water, deposition and precipitation of dust and colloid particles, and finally because of chemical reaction with oxygen, water or other gaseous components. Usually contaminants and corrosion products make a solid surface heterogeneous (heterogeneity produced in this way usually varies from molecular to microscopic size), however, contamination as a thin continuous film/layer is also frequently observed in practice. A thin uniform film of contaminants or corrosion products usually has a rough surface but “homogeneous” composition at molecular level. The problem of surface contamination was recently discussed in another contribution [10].

Rough and porous materials are sometimes considered as heterogeneous surfaces when the probing liquid is not able to penetrate the open area (porosity) [11–14]. This happens when the material demonstrates strong hydrophobic properties with a large intrinsic water contact angle, \( \theta > 90^\circ \).

Finally, it should be mentioned that there is an increasing interest in solid surfaces on which patterns are artificially produced and controlled. Model, and often well-defined, heterogeneous surfaces are fabricated in many laboratories with several different techniques including microlithography, micromachining, photopatterning, and stamping, and are used for studies in wetting and adhesion phenomena, electrochemistry, corrosion and etching, nucleation and growth of liquid films, patterned
crystallization and polymerization, adsorption and adhesion of proteins, optical diffraction, etc. [15–29].

**Cassie Equation**

Composite smooth solid surfaces with varying degrees of heterogeneity were analyzed by Cassie and Baxter [11,12] and Cassie [30]. Cassie derived an equation describing contact-angle changes for two-component surfaces as follows [30]:

\[ \cos \theta^C = f_1 \cos \theta_1 + f_2 \cos \theta_2 \]  \hspace{1cm} (4)

where \( f_1 \) is the fractional area of the surface with a contact angle \( \theta_1 \), and \( f_2 \) is the fractional area of the surface with a contact angle \( \theta_2 \) (the superscript \( C \) indicates Cassie contact angle). Equation (4), known as the Cassie equation, reduces to the Cassie-Baxter equation for a porous surface such as a mesh or screen surface [11,12]:

\[ \cos \theta = f_1 \cos \theta_1 - f_2 \]  \hspace{1cm} (5)

where in this case, \( f_2 \) is the fraction of open area in contact with the liquid.

Cassie and Baxter [11] experimentally verified Equation (5) for water drops on copper screens coated with paraffin (wire diameter in these screens were 70 and 130 \( \mu \)m). Agreement of the theory with experimentation was less satisfactory when the water drops were placed on wool yarn with fibers of 18 \( \mu \)m in diameter [12]. Crawford *et al.* [31] found that the contact angles for water drops on methylated quartz plates varied with the area fraction of trimethylsilyl groups in a manner similar to that predicted by the Cassie equation. Bain *et al.* [32] studied self-assembled monolayers of alkanethiols with different functional groups adsorbed onto gold. They found that the Cassie equation holds strictly only for systems where intermolecular forces between surface functionality and probe liquid are dispersive. When water was used as a probe liquid, on surfaces where specific hydrogen bonding effects were strong, the contact angle varied nonlinearly with the surface composition. This nonlinearity suggests a limitation of the Cassie equation for some surfaces with molecular-scale heterogeneities. A thermodynamic analysis of the Cassie equation for three-phase systems shows that this equation should be applicable for surfaces composed of macroscopically heterogeneous regions [33]. Nevertheless, the situation is less clear for molecular-scale heterogeneities. Also, the effect of conformation of the three-phase contact line, which is a common phenomenon of systems with heterogeneous surfaces, on the contact angle has been recognized recently to be an important factor in many systems, particularly with microscopic-scale heterogeneity [21,29,34,35]. Finally, it has been well established during the last few decades that for many heterogeneous surfaces the equilibrium contact angle is difficult (or even impossible) to measure. Usually, the three-phase system demonstrates metastable energetic minima and then several different contact angle values are observed instead of one value as described by Equation (4) [36–43]. All of these limitations of the Cassie equation are discussed in the following sections.
Structure and Properties of the Three-Phase Transition Region

As pointed out by de Gennes [44], the energetic parameters in Young’s equation (2) are those measured in the far field from the three-phase contact line (far away from the “core region” – how far remains unclear, particularly with regard to solid surface region). The structure and properties of the interfaces, particularly the liquid-gas (or liquid-liquid) interface, in the close vicinity of the contact line for the three phases may differ significantly from any other region of the system. This is because of the presence of the additional excess energy in this region originating from (a) local changes in the interfacial tension caused by the excess molecular interactions in the transition zone, and (b) local interfacial disturbances in this zone due to the surface forces [45]. These are schematically illustrated in Figure 2.

Gibbs [4] postulated that the line of discontinuity in the multiphase system (as a boundary for immiscible phases) should be treated in a similar way as the surface of discontinuity. In such a case, the source of the excess energy at the triple junction is, at least partially, due to unsaturation of intermolecular interactions for molecules located at the contact line; simply by analogy of the origin of the line tension with that for the surface tension (Figure 2a). Following this concept, Harkins [46] calculated the excess energy for molecules per unit length at the sharp edge of the contact line to be from \(1 \times 10^{-11} \text{ J/m}\) to \(1 \times 10^{-10} \text{ J/m}\). Sharp edges are common features of solids, particularly those being treated mechanically (grinding, breaking, etc.). These edges are, however, thermodynamically unstable and they become rounded with time. In the case of any liquid where the molecules are mobile and the surfaces are deformable, the unsaturated intermolecular interactions for the molecules located at the contact line reinforce a distortion of the liquid surface in this region (Figure 2a) in order to avoid the creation of high energy lines (minimization of energy in the system). The microscopic contact angle \(\theta_m\) may differ significantly from the macroscopic contact angle \(\theta\) (Figure 2a). The extent of the distortion of the liquid edge due to the excess energy of unsaturated molecular interactions probably does not exceed a distance equivalent to a few diameters of liquid molecules.

The second source of the excess energy in the region of the three-phase contact line is attributed to the surface forces. In the vicinity of the three-phase contact line, two interfaces, liquid-gas (or liquid-liquid in the case of the three-phase system with two immiscible liquids and solid support) and solid-liquid (Figure 2b), approach each other to a distance at which interfacial forces start to operate. All interfacial interactions, i.e., Lifshitz-van der Waals, electrostatic, solvation, steric, etc., are expected to appear in the region of triple junction. Two important consequences follow from the specific interaction between two interfaces approaching one another. First, the shape of the liquid surface in this region may be disturbed. Examples of the shape of liquid surface in the vicinity of the three-phase contact line are illustrated in Figure 2b. Second, the surface tension of liquid in the vicinity of the three-phase contact line is expected to differ from the surface tension of bulk liquid, i.e., the liquid surface which is far away from the region of the triple junction. The extent to which this may happen remains a mystery because of lack of understanding of the three-phase contact line region.
LINE TENSION
Molecular Interpretation

LINE TENSION
Microscopic Interpretation

\[ \gamma_{L(B)} \leq \gamma_{L(TPL)} \]

Figure 2. Schematic illustration of the region of the three-phase contact line and interpretation of the line tension based on (a) molecular and (b) microscopic approaches [45].
Although the transition region for the three-phase system is the subject of experimental [47] and theoretical [48–50] investigations of specific systems, no clear image of the shape of the liquid surface in this region exists. The structure of the solid surface in the vicinity of the three-phase contact line also remains unclear. There has been no literature that discusses this specific area of the solid surface till now (to the author’s knowledge). In this regard, the following paragraph is rather a hypothesis than a review of experimental or theoretical work done in the past.

The effects of unsaturated intermolecular interactions for molecules, located at the three-phase contact line and surface forces between interfaces, are probably much less pronounced for solid-liquid and solid-gas interfaces than we expect for the liquid-gas interface. There is no microscopic distortion of the solid surface under the action of surface forces and intermolecular forces*. However, we must be aware of the molecular effects. At the solid-liquid interface, in the vicinity of the three-phase contact line, the structure of the liquid with regard to molecular orientation and density may be different than for the rest of the interfacial area. Also, in the case of a system with multicomponent liquid(s), the composition and orientation of adsorbed molecules as well as the structure of the electrical double layer (with regard to concentration and activity of dissolved species) may be different for the transition region than for the bulk region. All of these effects probably cause a slight change in the solid-liquid interfacial tension in the vicinity of the three-phase contact line. A similar scenario is expected at the solid-gas interface but to a smaller extent. First, the solid-gas interface in the vicinity of the triple junction may have a different saturation state with regard to liquid molecules than the solid area beyond the three-phase region. Second, in the case of a system with a multicomponent liquid (i.e., surfactant solutions), the diffusive boundary of liquid phase in contact with a solid surface may reinforce a small change in concentration, configuration, and/or conformation of adsorbed molecules/ions. The transition region for the solid-gas interface, however, is expected to be very small; probably a few ångstroms, at most, for nearly all systems. The transition region for the solid-liquid interface might be at about an order of magnitude larger in some systems. There is, however, no direct experimental evidence to indicate this.

Effect of Line Tension on Contact Angle

Homogeneous Surface. The excess energy in the region of the three-phase contact line associated with intermolecular and surface forces (see previous section) is attributed to the linear excess energy which is called the line tension, when referred to a unit length of the three-phase contact line. This thermodynamic parameter has been extensively studied in recent years, particularly with regard to its value and significance. Several theoretical approaches showed that the line tension value should be from \( \sim 1 \times 10^{-12} \) J/m to \( \sim 1 \times 10^{-16} \) J/m [46,48,55–59]. Most previous experimental

* This should not be mistaken with the distortion of the solid surface which occurs at low-modulus solids [51,54]. The discussion in this contribution is limited to rigid solids.
results support the existence of a line tension magnitude of less than $1 \times 10^{-8} - 1 \times 10^{-9}$ J/m [34,60,65] (Ref. 45 provide a full spectrum of experimental data and a brief review of techniques which were used for the line tension determination). Even such tiny energetic effects in the region of the three-phase contact line may have a significant impact on the contact angle. To discuss this issue we need to accommodate the line tension into Young's equation as follows [66]:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta + \gamma_{SLV} \kappa_{gs}$$  \hspace{2cm} (6)

where $\kappa_{gs}$ is the geodesic curvature of the three-phase contact line; $\gamma_{SLV}$ is the line tension. To simplify our discussion, let us consider an axisymmetric liquid drop (or gas bubble), with drop (bubble) base radius of $r$, placed on a smooth, homogeneous, isotropic, rigid and horizontal solid surface for which Equation (6) reduces to the modified Young's equation as follows [66–68]:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta + \frac{\gamma_{SLV}}{r}$$  \hspace{2cm} (7)

frequently reported as:

$$\cos \theta = \cos \theta_{\infty} - \frac{\gamma_{SLV}}{r \gamma_{LV}}$$  \hspace{2cm} (8)

$$\theta = \theta_{\infty} \text{ for } r \to \infty$$

By intuition, it seems to be obvious that the linear excess energy becomes an important factor in the system when the size of curvature approaches the size of the transition region in the vicinity of the three-phase contact line (see Figure 2). According to de Gennes [44], the size of this region should be less than the screening length of double layer or less than the thickness of a liquid-gas diffusive boundary, and at the most it should not exceed 100 Å. In this regard, the line tension effects should appear in systems with microscopic curvatures; with radius less than 0.1 to 1 µm for most systems. This can be more precisely identified using the above equations. We use Equation (8) in the following form:

$$d = 2r = \frac{2\gamma_{SLV}}{(\cos \theta_{\infty} - \cos \theta)\gamma_{LV}}$$  \hspace{2cm} (9)

where $d$ is the drop (bubble) base diameter.

We further assume that the line tension is detectable if this causes a one degree change in the contact angle. The line tension values selected for this analysis vary from $1 \times 10^{-12}$ J/m to $1 \times 10^{-9}$ J/m, while the surface tension of the liquid varies from 70 mN/m to 0.1 mN/m. The results of the calculation are presented in Table 1. Again it becomes clear that for most systems the contact angles for drops (bubbles) with a size of a few micrometers and less should be analyzed in order to detect the line
tension phenomenon. This effect may, however, become more clear for the systems with a reduced liquid-gas surface tension (or liquid-liquid interfacial tension for systems with two liquids) particularly when the liquid exhibits good affinity for the solid surface (small contact angle value). This simple analysis, although based on strictly mathematical calculations, can be useful in the selection of experimental systems for examination of line tension effects.

**Heterogeneous Surface.** When a liquid is in contact with a heterogeneous surface composed of chemically distinct patches, the three-phase contact line is contorted, as illustrated in Figure 3. The radius of curvature for local deformation of the three-phase contact line depends on the size, shape, distribution, and wetting properties of the heterogeneous pattern [33,35,41,43,69–72]. In general, if this radius is less than a few micrometers, the correction for the local (microscopic) contact angle that incorporates the excess free energy associated with the three-phase contact line is required (with the same motivation which was used during our discussion on the modified Young’s equation for drops with a small base diameter – see previous section and Table 1). Using this approach and assuming that microscopic contortions of the three-phase contact line affect the apparent contact angle of the macroscopic system, a modification of the Cassie equation was proposed and derived [34,35,73].

<table>
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<th>Surface Tension $\gamma_{LV}$ [mN/m]</th>
<th>Contact Angle $\theta_{\infty}$ [deg]</th>
<th>$\gamma_{SLV}$ [J/m$^2$]</th>
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</table>
For a smooth and horizontal surface composed of two components uniformly distributed with circular curvatures of the three-phase contact line (Figure 3), the modified Cassie equation is as follows:

$$\cos \theta^{MC} = f_1 \cos \theta_1 + f_2 \cos \theta_2 - \left( \frac{1}{\gamma_{LV}} \left( \frac{f_1 \gamma_{SLV1}}{r_1} - \frac{f_2 \gamma_{SLV2}}{r_2} \right) \right)$$

(10)

where $r_i$ is the radius of the three-phase contact line at the $i$-component of the surface; the superscript $MC$ designates the modified Cassie contact angle; and the other nomenclature is the same as used in previous equations.

**Figure 3.** Model heterogeneous solid surface composed of hydrophobic and hydrophilic strips and the
The difference between $\theta^C$ and $\theta^{MC}$ is illustrated in Figure 3. In this particular system, the solid surface is composed of alternating and parallel strips differing in surface properties (surface/interfacial tension). A pure liquid at each surface strip forms an intrinsic contact angle ($\theta_1$ and $\theta_2$) which satisfies the modified Cassie equation (10). Two extremely different positions of the three-phase contact line at the model heterogeneous surface are drawn in Figure 3, for the surface strips parallel and normal to the three-phase contact line.

Only one equilibrium contact angle describes the situation for the first location of the wetting line presented in Figure 3, when the strips are normal to the three-phase contact line; i.e., the wetting line is contorted; and the corresponding contact angle is described by Equation (10). Of course, ideal strips are considered with no hysteresis in the contact angle.

For the second position the wetting line is smooth, because it is situated along a strip. Assuming that the dimensions of the strips are a few micrometers or less the contact angle as measured for a liquid with the three-phase contact line parallel to the strips should be equal to the theoretical value predicted by the Cassie equation. The analysis of the system becomes more complicated for strips of larger dimensions (macroscopic heterogeneity). The total free energy of the system may depend on the position of the three-phase contact line at a particular type of strip and the distance from the strip-strip border. Under these circumstances several different contact angles are possible (including the thermodynamic equilibrium contact angle which the Cassie equation predicts) due to metastable configurations of the system [36–41]. This is further discussed in the next section.

The difference between $\theta^{MC}$ and $\theta^C$ depends on the line tension value and the dimensions of the local deformations of the contorted three-phase contact line. If the dimensions of the heterogeneous mosaics (strips in the model being considered) are too large, the contribution of the linear free energy to the total free energy of the three-phase system is negligible and the modified Cassie equation is reduced to the original Cassie equation.

To verify the modified Cassie equation, mosaic patterns of 2 to 3 $\mu$m hydrophilic and hydrophobic strips and squares were prepared by the patterning of self-assembled monolayers of thiols at a gold surface using an elastomer stamp, and the wetting characteristics of these model surfaces were established by contact angle measurements [21,29]. It was found that the experimental contact angles are in good agreement with theory as calculated from the Cassie equation when the three-phase contact line was smooth, i.e., situated along the strips. On the other hand, when the strips were normal to the drop edge, contortion of the three-phase contact line affected the contact angles, and these contact angles were in close agreement with those calculated from the modified Cassie equation.

**Contact Angle Hysteresis**

The Cassie equation (Equation 4) and the modified Cassie equation (Equation 10) were derived on the assumption that the liquid (in the vicinity of the wetting line) always remains in contact with the same heterogeneous pattern of a particular solid
surface as defined by the fractional area, distribution, size and shape, whatever the direction and extent of liquid movement over this solid surface is. Thus, these equations predict only one value of the contact angle (equilibrium contact angle). In practice, several contact angles are frequently observed for heterogeneous surfaces. This is because their pattern is neither uniform nor symmetrical but rather have randomly distributed heterogeneities with local variation of heterogeneity size, shape, and properties. Two of these contact angles, advancing \((\theta_A)\) and receding \((\theta_R)\) contact angles, are commonly measured and reported in the literature. The advancing contact angle is measured for the liquid tending to advance (or measured shortly after the liquid advances) whereas the receding contact angle is measured for the liquid tending to retreat (or measured shortly after the liquid retreats). The contact angle hysteresis \((H)\) is the difference between these two contact angles, \(\Delta \theta = \theta_A - \theta_R\). The value of the contact angle hysteresis describes, to a certain extent, the quality of the solid surface*. The statement that the contact angle hysteresis increases with increased heterogeneity of solid surface is, in general, correct but it must be recognized that there is no universal theoretical model, so far, relating the size, shape, and distribution of heterogeneities to advancing and receding contact angles. Nevertheless, factors causing the contact angle hysteresis at heterogeneous surfaces are generally understood, at least to a certain extent, and are briefly discussed in this section based on a simplified model of a heterogeneous solid surface.

The model solid surface is illustrated in Figure 4. A smooth heterogeneous solid surface is assumed to be composed of two types of material differing in energetic properties (interfacial tension); the surface region of the primary material (the host material) with randomly distributed circular regions of the second material. We further assume that a liquid in contact with each surface region forms contact angles \(\theta_1\) (host material) and \(\theta_2\) (heterogeneity), where \(\theta_1 > \theta_2\). Many heterogeneous surfaces of practical importance have a similar pattern. For example, hydrophilic mineral surfaces are usually covered with submonolayers of a hydrophobic collector during flotation separation of mineral particles. At surface coverages far below the monolayer, aggregates/domains of adsorbed and/or precipitated organic compounds have been observed [82–88], often varying in size and randomly distributed. At surface coverages close to a complete monolayer, the adsorbed collectors form a matrix with uncovered regions of the mineral. Also, in this case the distribution is random. At any level of the surface coverage, heterogeneous regions have, however, irregular shapes instead of a circular shape which has been assumed in our model (in order to simplify the analysis of the heterogeneous system).

* There are several other factors which cause contact angle hysteresis, such as solid surface roughness, its instability in the environment of the probing liquid, solid saturation and swelling with the probing liquid, solid dissolution, reorientation and/or dissociation of surface molecules or functional groups, and deformation of the solid surface. A full discussion of factors affecting the contact angle hysteresis exceeds the scope of this contribution. The reader is referred to the review literature [44,69,74–81] for detailed discussion.
As shown in Figure 4, the three-phase contact line can cross a different number of regions depending on its position. This position depends on the wetting characteristics of the materials which compose the heterogeneous surface, the size of the circular regions, and the distribution of the regions. Also, there is the effect of the direction in which the three-phase contact line moves before an equilibrium position is attained (advancing or receding conditions). This aspect is considered in the next part of this section.

Usually, a variation in the contact angle during contact angle measurements on such heterogeneous surfaces, as drawn in Figure 4, is observed. This can be explained based on the analysis of the position of the three-phase contact line. For a situation represented by a three-phase contact line in position A (Figure 4), the modified Cassie equation (Equation 10) is as follows:

$$\cos \theta^{MC} = f_1^A \cos \theta_1 + f_2^A \cos \theta_2 - \left( \frac{1}{\gamma_{LV}} \left( \frac{f_1^a \gamma_{SLV1}}{r_1} - \frac{f_2^a \gamma_{SLV2}}{r_2} \right) \right)$$

(11)

where $f_1^A$ is the fractional area of the surface (in the vicinity of the three-phase contact line) with a contact angle of $\theta_1$; $f_1^a$ is the fractional length of the three-phase contact line crossing the material with a contact angle of $\theta_1$. Both $f_1^A$ and $f_1^a$ can be different than the average fractional area for the entire surface ($f_1$) with a contact angle of $\theta_1$. Also, in many cases $f_1^A$ will differ from $f_1^a$. 

Figure 4. Nature of the three-phase contact line for a model heterogeneous surface composed of hydrophobic material covered with randomly distributed hydrophilic circles.
In the case for the three-phase contact line situated at position B (Figure 4), there is no contact of this line with circular regions (the wetting line is noncontorted), and thus, the modified Cassie equation is reduced to the original Cassie equation (Equation 4):

$$\cos \theta^C = f_1^B \cos \theta_1 + f_2^B \cos \theta_2$$  \hspace{1cm} (12)

The fractional area parameters ($f_i^B$) in this equation may be different than the average values calculated for the entire area of the heterogeneous surface. In a special case, when the three-phase contact line is located on the primary material region at least a few micrometers at both sides from the host material-heterogeneity border (here we assume that hydrophilic regions are beyond the range of interactions with liquid, the area of the solid surface in the vicinity of the three-phase contact region which affects the contact angle), Equation (12) will be reduced to $\cos \theta^C = \cos \theta_1$, and thus, $\theta^C = \theta_1$. This is also true for the liquid edge located in the middle of the large heterogeneous regions ($\theta^C = \theta_2$) if the host material does not affect the contact angle.

At heterogeneous surfaces with a random distribution of a pattern, the three-phase contact line can also cross a smaller number of heterogeneities than should be expected from the average fractional area of these regions, and this situation is represented by the contact line in position C. The modified Cassie equation for this case where $r_1 \gg r_2$ is:

$$\cos \theta = f_1^C \cos \theta_1 + f_2^C \cos \theta_2 + \frac{f_2^C \gamma_{SLV}}{\gamma_{LV} r_2}$$  \hspace{1cm} (13)

Evidently, any heterogeneous surface with randomly distributed heterogeneities will demonstrate variations in the contact angle value. The largest contact angle in such systems will correspond to the advancing contact angle and smallest to the receding contact angle. We must be aware, however, that not each position of the three-phase contact line at a heterogeneous surface is possible and that the system will adopt only stable and metastable configurations. This can be explained with the same heterogeneous surface model composed of hydrophobic material and covered with randomly distributed hydrophilic circular regions. Now we assume that the liquid at a heterogeneous surface is reinforced to advance or retreat in order to pass from one position to another. This is shown schematically in Figure 5 for both cases, advancing and receding, and with regard to two heterogeneous surfaces whose pattern is different only due to the size of heterogeneities (microscopic heterogeneity and macroscopic heterogeneity models).

For the advancing conditions* (Figure 5a – here again, we simplify our discussion

* This corresponds to the conditions during the advancing contact angle measurements. For example, a) the volume of a liquid drop placed on the solid surface is increased in a sessile-drop contact angle measurement technique; b) the size of a gas bubble attached to the solid surface is reduced in a captive-bubble contact angle measurement technique; c) the solid plate is immersed more deeply into the liquid in a Wilhelmy
to a heterogeneous surface composed of hydrophobic and hydrophilic regions), the three-phase contact line (only a part of the wetting line is considered) moves over the hydrophobic region of the heterogeneous surface from position $a$ to $b$ smoothly and the advancing contact angle remains the same over this region. This contact angle is equal in value to the advancing contact angle for the homogeneous hydrophobic material (free of hydrophilic regions) as long as the hydrophilic regions are away from the three-phase contact line, probably at least a few micrometers. Hydrophilic regions which are close to the wetting line will affect the contact angle. The extent of this effect depends, among others, on the position of the contact line with respect to the hydrophilic regions. We will not, however, discuss this more detailed issue just now.

When the three-phase contact line reaches the hydrophilic region, the liquid spreads spontaneously over this region in order to satisfy the local equilibrium (movement from position $b$ to $c$ in Figure 5a) and approaches to reach the advancing contact angle for hydrophilic material. When this happens at a heterogeneous surface with macroscopic size features, the advancing contact angle at the hydrophilic material will be easily attained. Further, advance of the wetting line will proceed smoothly at the macroscopic region until the wetting line reaches a border line separating hydrophilic and hydrophobic materials (position $d$ in Figure 5a).

In the case of a surface with microscopic heterogeneities the behavior of liquid in the hydrophilic region is slightly different than in the case of a macroscopic region. When the wetting line reaches the hydrophilic region, the liquid spreads spontaneously over this region but the advancing contact angle as the characteristic value for the hydrophilic material is not attained (movement from position $b$ to $c$ in Figure 5a). Simply, there is not enough area of the hydrophilic region to establish this advancing contact angle. Instead, the three-phase contact line reaches the host material-heterogeneity border region. Here, the hydrophobicity of the host material will act as a barrier against further spreading and movement of the liquid. For this position of the contact line, the advancing contact angle will have a value which is intermediate between the values of the advancing contact angles for the host material and the heterogeneity. The value of this contact angle depends on the wetting properties of the hydrophobic and hydrophilic regions and the size of the hydrophilic region. As the heterogeneity pattern size decreases, the value of this advancing contact angle approaches the average value theoretically described by the Cassie (Equation 4) or modified Cassie (Equation 10) equations, depending on the contribution of the linear energy to the system.

The liquid with the three-phase contact line at position $c$ for the microscopic heterogeneity model and at position $d$ for the macroscopic heterogeneity model strongly interacts with the hydrophilic region. Further advance to the position $e$ requires the three-phase contact line to overcome a barrier associated with these interactions. This is why the contact angle increases before forward movement to the next position. Other authors [33,36,40–42] predicted such behavior of the liquid at a plate technique. Contact angle measurement techniques are well described in the literature [5,74,77,79,81,89].
Figure 5a. Nature of the advancing (a) and receding (b) wetting line at a model heterogeneous surface composed of hydrophobic material covered with randomly distributed hydrophilic circles.

heterogeneous surfaces based on theoretical considerations of energetics of model heterogeneous surfaces. Metastable energy states and step transitions of the wetting line from one position to another are typical phenomena of heterogeneous systems [33,36,40–42].
Microscopic Heterogeneity

Macrosopic Heterogeneity

Figure 5b.

For the receding conditions (Figure 5b)*, the three-phase contact line moves

* This corresponds to conditions during the receding contact angle measurements. For example, a) the volume of a liquid drop placed on the solid surface is decreased in a sessile-drop contact angle measurement
smoothly over the hydrophilic region of the heterogeneous surface from position $a$ to $b$ and the receding contact angle remains the same over this region (a reverse situation to advancing conditions). This contact angle is equal to the receding contact angle for the homogeneous hydrophobic material (free of hydrophilic inclusions) as long as the hydrophobic regions are of macroscopic size.

When the liquid edge reaches a border between the hydrophobic and hydrophilic regions, the three-phase contact line will remain there due to an energy barrier (pinning effect*) as long as the characteristic receding contact angle for hydrophilic material is attained, in order to satisfy a local equilibrium in the system. This will easily happen to surfaces with macroscopic-sized heterogeneity. For microscopic heterogeneities this might never be observed and the wetting line might jump to position $e$ before the characteristic receding contact angle is established. We, however, assume in our model in Figure 5b that the size of microscopic heterogeneities is still large enough to establish the receding contact angle for hydrophilic material.

When the energy barrier associated with interactions between liquid and hydrophilic heterogeneity is overcome (due to increased volume of the liquid in the region of the three-phase contact line), the wetting line will spontaneously jump from position $d$ to $e$ for the microscopic heterogeneity model and from position $e$ to $f$ for the macroscopic heterogeneity model (Figure 5b). Such behavior of the liquid at the heterogeneous surface was already predicted by other researchers based on the analysis of model heterogeneous surfaces [33,36,40–42].

In summary, based on this simplified conceptual analysis of heterogeneous surfaces, it is clear that the advancing contact angle for a liquid at a heterogeneous surface will approach the advancing contact angle of the hydrophobic component of the heterogeneous surface. On the other hand, the receding contact angle for liquid at the heterogeneous surface will approach the receding contact angle of hydrophilic component of the heterogeneous surface. Of course, the pattern of the heterogeneous surface, heterogeneity size and distribution, all have a significant impact on the contact angles in these systems. When the size of heterogeneous pattern decreases, the contact angle experimentally observed approaches the contact angle predictable on the basis of thermodynamics (Cassie and modified Cassie equations). These features of heterogeneous surfaces are now well understood [33,36,40–42]. The problem is, however, that this knowledge is still not transferred to real surfaces of practical significance.

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* Recently, pinning effects of liquids on hydrophilic regions of heterogeneous surfaces have received increased attention of both theorists [44,90–95] and experimentalists [96–98]. This should lead to further progress in our understanding of wetting characteristics for real heterogeneous surface. At this moment, however, there is still a poor link between our knowledge in this area and its practical use.
Nanosopic Heterogeneity

The modified Cassie equation (Equation 10) predicts the equilibrium (in the thermodynamic sense) contact angle for a liquid at a heterogeneous solid surface and should replace the Cassie equation (Equation 4) in any system for which the linear energy associated with the contorted three-phase contact line cannot be neglected [21,29,35]. We already discussed in the previous sections that the modified Cassie equation reduces to the Cassie equation for systems with macroscopic heterogeneity; \textit{i.e.}, in systems with large curvatures of the contorted wetting line. Further, it was shown after theoretical modelling of the contortion of the three-phase contact line that there is a critical size of heterogeneities for which any local distortion of the wetting line can be neglected [33,69]. In the case of the heterogeneous surface composed of parallel and alternating strips and made of different materials, Neumann and Good [33] calculated that a contortion of the wetting line can be neglected when the strip size is about 0.1 μm. However, this was calculated for a system with strips whose wetting properties differed by only ten degrees (30° and 40°). Usually, heterogeneous surfaces of practical significance demonstrate a much larger difference in the contact angle. For example, in flotation of mineral particles this difference may reach a value of 70–110°. This is because most minerals are hydrophilic with zero water contact angles and they are modified with hydrophobic collectors which might form a monolayer with a water contact angle as large as from 70° to 110°. For such systems, the limit of Neumann and Good may drop by about an order of magnitude. In another contribution, Boruvka and Neumann [71] predicted that a corrugation of the three-phase contact line can be expected for heterogeneous patches as small as 10 Å. They did not consider the contribution of the line tension to the free energy of the system, and they suggested that the heterogeneity size limit would be larger if the line tension was included.

Importantly, it seems from the modeling of the contortion of the three-phase contact line that there might be a range of heterogeneity size, particularly in the nanoscopic scale (at least for certain systems) for which the contortion of the three-phase contact line will disappear. If this is the case, the modified Cassie equation (Equation 10) can again be reduced to the Cassie equation (Equation 4). In practice, however, the situation is not so clear. A heterogeneous surface usually has a randomly distributed pattern. Although the size of an individual heterogeneity may be too small to affect the shape of the wetting line, mutual action of two or more heterogeneities in close proximity to each other, could cause a contortion of the contact line. This is what we currently observe at mineral surfaces covered with adsorbed organic compounds (for example, see the photograph of the contorted wetting line for water on a methylated quartz surface in Ref. 99). Other researchers have also recognized this phenomenon recently [96,98].

Molecular and Atomic Heterogeneity

It is well known that any macroscopic approach in surface chemistry has a limit of its application when the size of the object (the size of surface heterogeneity in our case) reaches the molecular dimensions. We expect that the interfacial tension values
for the surface with an area equivalent to several molecules and less are different from that which are currently determined instrumentally for large interfaces. This important issue was recently brought to our attention by Israelachvili and Gee [100] during a discussion on contact angle determination for heterogeneous surfaces which consist of molecular-sized patterns. They proposed that interfacial energies are not the relevant interfacial properties which should be averaged for these systems with respect to surface fractional coverages. Instead, such parameters of molecules as polarizabilities or dipole moments are more appropriate to use in the modelling of systems with molecular heterogeneities. A new formula they derived is:

\[ (1 + \cos\theta^{IG})^2 = f_1 (1 + \cos\theta_1)^2 + f_2 (1 + \cos\theta_2)^2 \]  

(14)

where superscript \( IG \) is used to distinguish the difference between the contact angle calculated from this equation with contact angles calculated based on Cassie or the modified Cassie equation; the other terminology is the same as used in previously discussed theoretical relationships.

As discussed by Ulman et al. [101], the disadvantage of this concept might be that the interactions between the surface functional groups are neglected. These interactions are expected to change with a change in the combination of functional groups at the surface. Also, we expect that there is a critical size of heterogeneity below which the surface properties are averaged and can be treated as a one phase (the discrete nature of domains disappears). This obviously is the case for systems with heterogeneity at an atomic level, but this probably also extends beyond the atomic level. Such systems are simply described by Young’s equation (Equation 2).

Several interesting papers have been published in the last few years presenting the contact angle data for liquids on adsorbed and self-assembled monolayers composed of a mixture of two compounds with different functional groups [32,101–107]. A majority of these results clearly indicate that there is no straight-line correlation between the cosine of the contact angle and the surface concentration of a functional group, as is predicted by the Cassie equation (Equation 4). Also, there is a rather poor agreement of these data with the theoretical approach expressed by Equation (14). Two reasons can cause a lack of agreement with these theoretical models. First, there can be a change in the interactions between functional groups in the system with increasing surface concentration of one functional group as compared to another (already noted during discussion on Equation (14)). These changes, at this moment, are unpredictable and a judgement of theoretical models cannot be completed. Second, for many systems adsorbed molecules do not form a uniform pattern but rather form domains (islands, clusters, etc.) of molecules with one type of a functional group distributed in a field of the other functional group. Already direct evidences for the adsorption of molecules at selected surface sites and growth of domains have been provided in the literature [28,108–111]. Also our recently presented contact angle data support a nonuniform growth of adsorbed monolayers [112].
Final Comment

Although heterogeneous solid surfaces are commonly encountered in all areas of technology, fundamentals for the wetting and spreading of liquids at these surfaces are not well established. Both modelling and experimentation with heterogeneous surfaces are still in an early stage of development. The wetting properties of heterogeneous surfaces have been studied theoretically, particularly in the recent years, but these studies were almost exclusively limited to model heterogeneous surfaces with a simple pattern. Experimental studies are even further behind the theoretical developments. In this regard, there is not too much quantitative information for the practitioner to use at this moment. There has been a little effort to correlate experimental observations with theoretical models and thus theory still remains to be tested. Particularly, there is a need to examine liquid behavior at a solid surface having microscopic, nanoscopic, and molecular heterogeneities. The effect of the heterogeneity size, distribution, and wetting characteristics on the contact angles for these systems (advancing, receding, and equilibrium contact angles) need to be tested and compared with theoretical models. Although several reports of such systems have appeared in the last few years, the characteristics of the surface heterogeneity is practically never reported. This makes the published data of a little practical use. Further effort to prepare and test model heterogeneous surfaces with well-defined microscopic and nanoscopic patterns of varying structure, dimensions, and properties is strongly recommended in order to clarify several issues associated with wetting phenomena and justify the proposed theoretical models and their limitations. Recent developments in microlithographic, micromachining, photopatterning, and stamping techniques [15–29] allow for the preparation of model heterogeneous surfaces with less than micron-sized heterogeneities. New analytical techniques, such as scanning probe microscopy [113], provide an excellent opportunity for scanning and mapping of solid surfaces at such a high resolution that individual atoms can be observed. This progress should be applied by surface chemists to provide an experimental basis for further improvements in our understanding of wetting and spreading phenomena at heterogeneous surfaces.

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