

Contact angles and wettability: towards common and accurate terminology

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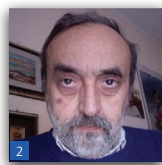
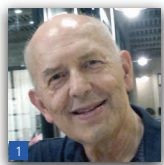
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Much interest has recently been focused on contact angles, wetting and non-wettable surfaces as is evidenced by the rapid pace and sheer number of papers published in recent years. However, in many cases there exist misconceptions and misuses of terminology, leading to misinterpretation of experimental contact angles, measurements of which deceptively appear to be simple. Terms describing contact angles, wettability, superhydrophobicity and similar other terminology are loosely used. In this contribution, key terms used in relation to contact angles are defined precisely based on the accumulative knowledge from the surface chemistry community over the last decades. The definitions provided are scientifically rigorous to avoid any ambiguity and confusion. The theoretical considerations underlying these definitions are only briefly mentioned, with references to the relevant papers. Interpretation and meaning of the measured contact angles can be made simpler if the basic concepts are clearly understood and theory-based indications are applied. The clarity of definitions should make data interpretation and comparison easier for future contributions to journals, including this journal.

1. Introduction

Contact angle, as a thermodynamic property that characterises the wettability of solid surfaces, is of utmost importance in modern technological applications and materials science. Despite its ostensible, conceptual simplicity and a long history of investigations, contact angle measurement and interpretation still suffer from deficient experimental and theoretical protocols.^{1–5} Simplistic measurement methodology, associated with incomplete understanding of wetting phenomena, has led to publications presenting contact angles that are either not well defined or not properly interpreted. Contact angles are sensitive to many factors, such as surface geometry, roughness, contamination and deformation. Such sensitivity enables detecting very small-scale effects by this rather macroscopic measurement. However, this sensitivity has also made it difficult to find an accepted collection of contact angle data for common materials to serve as the reference source at the handbook level for researchers, students and technicians.

A naive view of the contact angle simply considers this thermodynamic property as the observed angle between the tangent

to the solid surface and the tangent to the liquid–fluid interface at the contact line between the three phases (note that the contact angle is always measured through the denser fluid). In fact, the contact angle observed for a system is not necessarily a unique value and a few contact angles need to be considered carefully. Ignoring this fundamental fact, many works have contributed to the misconceptions related to contact angle measurement and its interpretation in terms of wetting. The other issue is the misuses of terminology that is seen when analysing the wetting behaviour of a liquid on a substrate. As a result, there is a misunderstanding and confusion among researchers working in different laboratories, and the challenge is in comparing the wetting characteristics of the same materials. Another complicating factor in the literature is the recent prominence and use of the contact angle concept in areas other than surface chemistry (e.g. mechanical engineering, materials science, electrical engineering and physics) due to the interdisciplinary work and miniaturisation of various systems. Obviously, confusion among surface chemists reflects on these additional fields as well or becomes enhanced as a result of the naive use of terminology and interpretation of contact angle data by researchers new to the field.

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For the mentioned reasons, the authors consider it necessary to ensure a common ‘language’ that will enable unequivocal communication between various researchers and laboratories and make the comparison of experimental data meaningful. Here, a glossary of terms and definitions related to contact angles and wettability is provided. Many of these have been accepted and used within the past decades by the surface chemistry research community. However, some are either forgotten or ignored by people that are new to the field or by those who have become confused by the contradictions seen in the literature. In addition, some new terms are required to describe phenomena that have been recently studied more in depth, such as superhydrophobicity and related properties.

To aid the scientific community and overcome the problems described above, the authors decided to provide clear and refined definitions for wetting and contact angle terminology. This was done by discussions among co-authors, drawing from combined experience of nearly 100 years of research in this field, and by consultation with other experts in the field. These rigorous definitions are founded on scientific grounds and should help to make data interpretation and comparison easier for all researchers.

Table 1 presents the glossary of prefixes that have been used in the literature to form the contact angle and wettability terminology. These prefixes are listed according to their language of origin. In the following, the set of prefixes that are proper and coherent is discussed. Since the emphasis is on terminology, the physical explanations are only briefly mentioned. Prefixes not discussed in this contribution are either inappropriate or used for specific and often narrow cases. They will not be discussed here and should be avoided and, if possible, be replaced with the terms listed in the following sections. The reader is encouraged to find more complete explanations given earlier by one of the co-authors³ and in the references that are cited in the following sections.

2. Terminology for defining surface

It should be recognized that definitions provided in this section apply to wetting studies. Some of the terms could be defined differently in different disciplines or subdisciplines.

Table 1. Prefixes used in surface chemistry literature

Greek		Latin		English	
Term	Meaning	Term	Meaning	Term	Meaning
Amphi-	Both, around	Oleo-	Oil	Super	Above, supreme
Hydro-	Water	Omni-	All		
Hygro-	Liquid (used also with regard to humidity)	Quasi-	As if		
Lipo-	Fat, fatty	Ultra-	Extreme		
Lyo-	Dispersion, dissolution				
Meta-	At a later stage of development				
Para-	Beyond				
-Philic	Loving				
-Phobic	Fearing				

Smooth surface – A surface that is free of topographic features. A smooth surface may be heterogeneous and, therefore, its surface energy does not need to be uniform over the entire area. A smooth surface does not have porosity, which is either penetrable by the liquid or causes the formation of air pockets.

Homogeneous surface – A surface of uniform composition (i.e. free of inclusions and islands of different materials/surface chemistry (physisorbed or chemisorbed), phases and their orientations). A surface may be made of similar molecules – for example, a self-assembled monolayer of alkane thiols – but they may not be considered as homogeneous at all scales because of different orientations of tail groups or underlying domains/grains.

Isotropic surface – A surface that exhibits uniformity in properties in all directions.

Rigid surface – A surface that does not deform under the weight and/or pressure of a liquid droplet or a liquid meniscus in contact with the surface to a degree that could influence the value of the contact angle. Deformation of a substrate during contact angle measurements is typically detected for soft polymers, hydrocarbon-based products and gels.

Ideal surface – A smooth surface that is rigid and chemically homogeneous and does not chemically interact with the probe liquid.

Real surface – A solid surface that is not ideal, regardless of type(s) of its deviation from the ideality of surface defined earlier. Real surfaces form the majority of surfaces that are used and tested; they require the most attention for contact angle measurements and data interpretation. Many of the aforementioned misconceptions and misinterpretations in the literature stem from the confusion of such surfaces for one of the previously defined surfaces.

3. Terminology for defining contact angles

Contact angle – An angle experimentally observed on the liquid side (denser liquid side in case that there are two liquids) between the tangent to the solid surface and the tangent to the liquid–fluid interface at the contact line among the three phases (see Figure 1). The point of intersection between tangent lines is known as the contact point (see Figure 1).

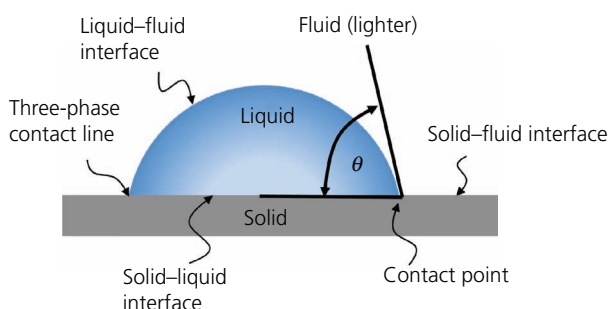


Figure 1. The contact angle θ is shown for a sessile drop. The contact line in this case is the outline of the contact circle between the solid and the liquid (note that the drop is assumed to be axisymmetric with its profile shown)

The preceding definition is general in the sense that it applies to all equilibrium and non-equilibrium situations. As such, it is of little use without an adjective that describes the specific situation. This information is complemented in the following.

Young contact angle – The contact angle that is calculated from the description of the Young equation (1805).⁶

This contact angle is a thermodynamic property of the three-phase system that corresponds to the lowest state of the energy for the system.

Ideal contact angle – The contact angle on an ideal surface.

For drops with radii of curvature larger than nanometric size, this contact angle equals the Young contact angle and represents the single equilibrium state that a drop may have on an ideal solid. For drops with smaller radii of curvature, a correction term that is related to the concept of ‘line tension’ needs to be applied.^{7–10} The ideal contact angle is typically not accessible experimentally due to difficulties associated with the preparation of an ideal solid surface and maintaining equilibrium conditions during measurements. It needs to be assessed from measurable contact angles, using proper correlations.

Actual (local) contact angle – The contact angle that exists locally at any point along the contact line (Figure 2). The actual contact angle was theoretically proven to be equal at equilibrium to the ideal contact angle.¹¹ However, the actual (or local) contact angle cannot be easily measured; therefore, it is considered to be inaccessible.

Apparent (global) contact angle – The contact angle measured experimentally on the macroscopic scale (Figure 2). The apparent contact angle is the only one that can be routinely measured. This contact angle describes an ‘average’ contact angle for the entire three-phase contact line. There are a few types of apparent contact angles that are related in different ways to the Young contact angle, depending on the specific nature of the real solid surface. Apparent contact angles may represent either metastable equilibrium states of the system (local minimum in the Gibbs energy curve) or a stable equilibrium state (lowest minimum in the Gibbs energy curve) (Figure 3). The various kinds of the apparent contact angles are described in the following.

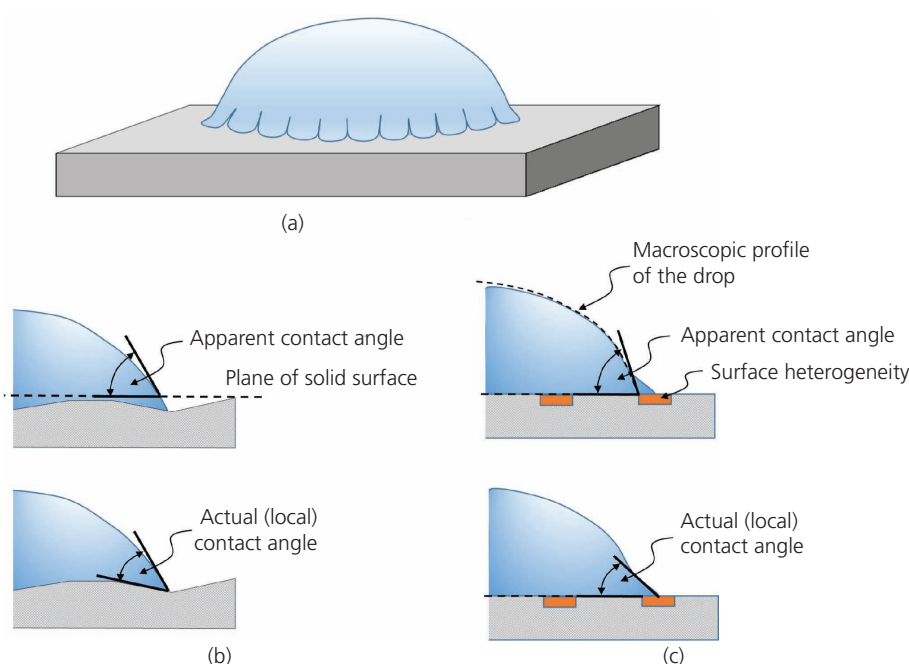


Figure 2. A hypothetical liquid drop on real solid surface: (a) corrugated drop base; (b) apparent and actual contact angles on a rough surface; (c) apparent and actual contact angles on a heterogeneous surface

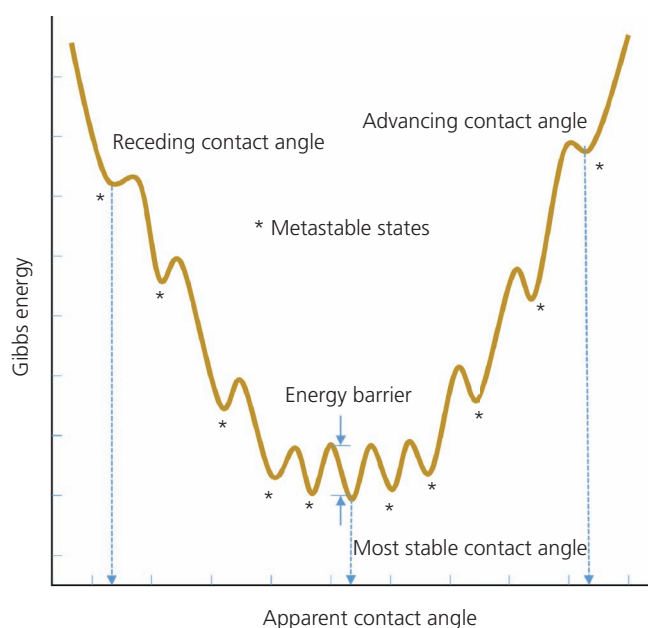


Figure 3. The Gibbs energy for a liquid on a rough or heterogeneous solid surface

- **Most stable contact angle** – The *apparent* contact angle associated with the state of the lowest Gibbs energy for a system. There may be a few ways that may lead to this state. One method that has been applied in a few studies is vibrating the solid surface.¹² However, the exact measurement of this contact angle is still under study.

The most stable contact angle on a rough but chemically homogeneous solid surface is predicted by the Wenzel equation.¹³ This equation applies if the liquid completely penetrates into the grooves of a rough surface and if the drop is sufficiently large compared to the roughness scale.¹⁴ The most stable contact angle on a chemically heterogeneous but smooth solid surface is predicted by the Cassie equation¹⁵ if the drop is sufficiently large compared to the heterogeneity scale.¹⁶ An extended version of the Wenzel and Cassie equations exist for cases that deal with wetting of a rough surface, when the liquid incompletely penetrates (or does not penetrate at all) into the roughness grooves. As such, the surface is ‘seen’ by the liquid as a rough and heterogeneous surface that is composed of the solid and ‘air’. This case is covered by the Cassie–Baxter equation.¹⁵

- **Advancing contact angle** – The highest metastable apparent contact angle that can be measured (e.g. by increasing the volume of the drop) (Figure 3).
- **Receding contact angle** – The lowest metastable contact angle that can be measured (e.g. by decreasing the volume of the drop) (Figure 3).

The advancing and receding contact angles may depend on the method of measurement¹⁷ and on the parameters of the system. Their measurements with a sessile-drop method are schematically illustrated in Figure 4 and described in detail in

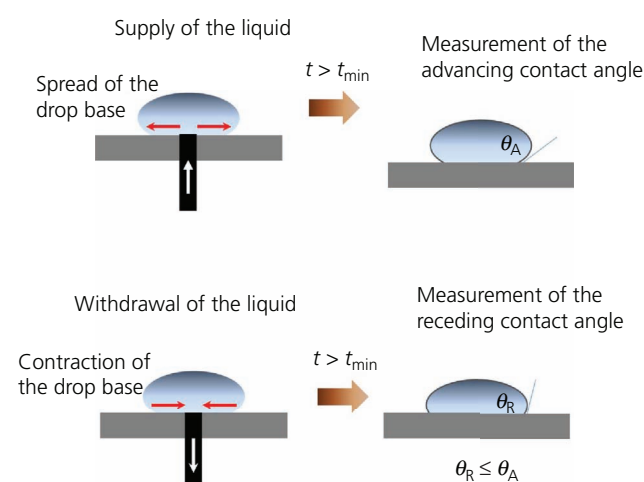


Figure 4. Principles of advancing and receding contact angle measurements using a sessile-drop method

another reference.² For example, in the case of a system that consists of a drop on a solid surface, these contact angles may depend on the drop volume.^{18,19} It has to be noted that independently of the experimental method, the values of advancing and receding contact angles may be affected by random noise – for example, vibrations of a building.²⁰

- **Contact angle hysteresis** – The difference between advancing and receding contact angles. The advancing and receding contact angles (thus also the contact angle hysteresis) cannot be correlated with the ideal contact angle based on current knowledge. For example, using the Wenzel equation for the advancing or receding angle is a misleading mistake. However, measurement of these angles is extremely important since contact angle hysteresis is a measure of the non-ideality of the solid surface. Also, contact angle hysteresis may be thought of as a rough indication of the degree of drop adhesion onto a solid surface, since in many cases the larger the contact angle hysteresis, the stronger is drop adhesion. It was demonstrated that nanometric holes in a monolayer can be detected through measurements of contact angle hysteresis.²¹

In addition, a common misconception needs to be clarified. It is quite common to call the advancing and receding contact angles ‘dynamic’. It is true that the transition between metastable contact angles is indeed a dynamic process; however, these contact angles by themselves represent equilibrium states (although metastable).

- **Dynamic contact angle** – A contact angle measured under dynamic flow conditions that is affected by the velocity of the flow due to viscous effects. Thus, it cannot characterise the equilibrium wettability. The deviation of the dynamic contact angle from the equilibrium contact angles depends on the capillary number.
- **Static contact angle** – A misleading term that refers to measuring the contact angle ‘as is’ – namely, as the drop

happens to land on the solid surface. Unfortunately, this is a meaningless measurement, since there is a random element involved in the process of drop landing – that is, the contact can be any value within the range of advancing and receding contact angles; therefore, this contact angle is not useful for any analysis.

4. Terminology for describing solid surface wettability

4.1 Smooth surface

Hydrophilic surface – Characterised by Young contact angle for water that is smaller than 90° (Figure 5).

Hygrophilic surface – Characterised by Young contact angle for any liquid that is smaller than 90° .

Liquids other than water, commonly used in contact angle measurements, have a surface tension smaller than that of water. Therefore, their Young contact angle on a smooth solid surface is usually lower than that of water. Therefore, hydrophilic surfaces are also usually hygrophilic.

Hydrophobic surface – Characterised by Young contact angle for water that is larger than or equal to 90° (Figure 5).

Hygrophobic surface – Characterised by Young contact angle for any liquid that is larger than or equal to 90° .

In contrast to the case of hygrophilic surfaces, not every hydrophobic surface is also hygrophobic. Also, not all surfaces will be hygrophobic to all liquids. Thus, there may be a need to limit the definition to a certain group of liquids.

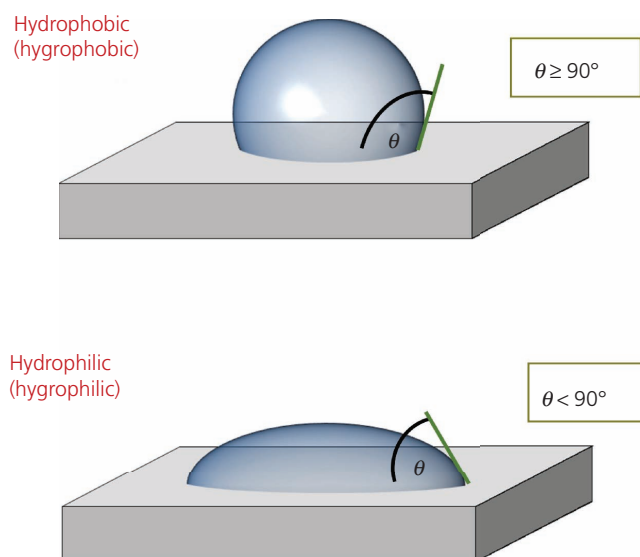


Figure 5. Liquid drop on a hydrophobic (hygrophobic) surface and a hydrophilic (hygrophilic) surface

In previous cases the prefix ‘lyo-’ was used with the same meaning as ‘hygro-’. However, it is important to note that this usage of ‘lyo-’ seems to result from some misunderstanding, since its meaning, as shown in Table 1, is different from the meaning that was intended.

4.2 Rough surfaces

As mentioned earlier, two regimes of wetting exist on rough surfaces: the liquid either completely or partially penetrates into the grooves of a rough surface (Figure 6). In the former case, the Wenzel equation predicts that the most stable contact angle on a roughened hydrophilic surface is lower than the corresponding ideal contact angle. On roughened hydrophobic surfaces, this equation predicts that the most stable contact angle is higher than on the ideal one. In the case of partial penetration, the most stable contact angle may further increase, since part of the surface that is in contact with the liquid consists of air. This, however, may reduce hysteresis and enable easy roll-off of a drop from the solid surface. The following definitions help to distinguish clearly between these states.

Parahydrophilic (or hydrophilic) surface – A roughened surface on which the most stable contact angle of a liquid in general (or water in particular) is reduced by the roughness beyond (= *para*) its ideal contact angle.

Parahydrophobic (or hydrophobic) surface – A roughened surface on which the most stable contact angle of a liquid in general (or water in particular) is increased by the roughness beyond (= *para*) its ideal contact angle.

Superhydrophilic (or hydrophilic) surface – A solid surface on which a liquid in general (or water in particular) spreads completely to a zero contact angle.

As in the case of hydrophilic surfaces, a superhydrophilic surface is usually also a superhydrophilic one.

Superhydrophobic (hydrophobic) surface – A parahydrophobic (hydrophobic) surface that is also characterised by a low roll-off angle (the inclination angle at which the drop starts rolling). A low value of the roll-off angle stems from low-contact angle hysteresis. These properties make the surface ‘non-wettable’. The commonly accepted quantitative definition (advancing contact

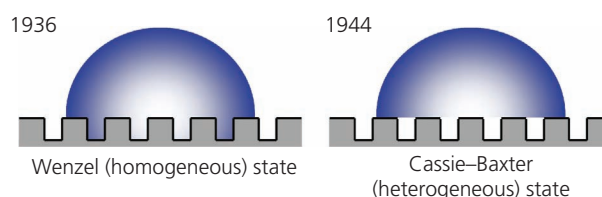


Figure 6. Illustration of homogeneous and heterogeneous states for a liquid drop sitting on a rough surface

angle larger than $\sim 150^\circ$ and contact angle hysteresis of less than $\sim 10^\circ$, or roll-off angle of less than $\sim 5^\circ$) is still empirical.

As an example of the usage of these definitions, the story of the so-called petal effect may be discussed. This effect was first introduced in 2008 to describe structured surfaces, such as rose petals, which exhibit a very high water contact angle but also strong adhesion to water that prevents the water droplets from rolling off the surface.²² Because of the high contact angle, the petal effect was associated with ‘superhydrophobicity’; however, because of the high adhesion, the term ‘superhydrophobicity combined with high hysteresis’ was used. This term actually contradicts the definition of superhydrophobicity as describing cases with high water contact angles and very low roll-off angle. It is simpler and better to describe this surface as parahydrophobic.

5. Concluding remarks

To advance both the characterisation of material surfaces and the science of wetting phenomena, it is necessary to achieve reproducibility in contact angle measurements and ensure their unambiguous interpretation among research laboratories. In order to succeed in this effort, the meaning of contact angles and terms describing wetting must be clarified and broadly adopted by the research community. Here, the authors collected and defined basic terms describing contact angles as well as surfaces on which such measurements take place. It is their expectation that this collection of terms will help many researchers to avoid past mistakes in contact angle measurements and eliminate misinterpretations of contact angles that appear in modern literature at accelerated and alarming rate.

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