

The phenomenon of contact angle hysteresis

Thermo Fisher Scientific, Process Instruments, Newington, USA

A great interest in surface energetics is contact angle hysteresis. Contact angle hysteresis is defined as the difference between advancing and receding contact angles. This hysteresis occurs due to the wide range of “metastable” states which can be observed as the liquid meniscus scans the surface of a solid at the solid/liquid/vapor interface. Because there are free energy barriers which exist between these metastable states, a true “equilibrium” contact angle is impossible to measure in real time. For an “ideal” surface that is wet by a pure liquid, contact angle theory predicts one and only one thermodynamically stable contact angle. In the real world, however, the “ideal” surface is rarely found. To fully characterize any surface, therefore, it is important to measure both advancing and receding contact angles and report the difference as the advancing angle hysteresis.

Thermodynamic hysteresis

There are at least six known sources of contact angle hysteresis¹. These fall into one of two group classifications thermodynamic and kinetic hysteresis. The first and most common classification is thermodynamic or “true” contact angle hysteresis (see Figure 1). To qualify as a “true” or classical thermodynamic hysteresis, both advancing and receding contact angles must be stable (i.e., reproducible) regardless of time (time independent) or number of im-

mersion cycles. There are two sources of thermodynamic hysteresis - surface roughness and surface heterogeneity. These represent the two most common of all sources of hysteresis in real world surfaces. (Table 1. below is a summary of the two primary sources of true contact angle hysteresis.

There are two thermodynamic equations which describe the effects of surface roughness and heterogeneity on contact angle hysteresis. The Wenzel equation, $\cos \theta_w = r \theta \cos \theta_y$, describes the effect of surface roughness. This equation takes into account the effect of an increased “effective” surface area on the contact angle. The roughness factor, “r”, represents the ratio of effective area to geometric area, θ_w represents the Wenzel angle (actual measured con-

tact angle on rough surface) and θ_y represents the stable or equilibrium young angle as measured on a corresponding “smooth” surface. Because “r” is always greater than or equal to 1, the effect of roughness on contact angle is to increase the contact angle if θ_y is greater than 90° (non-wettable smooth surface), and to decrease the contact angle if θ_y less than 90° (wettable smooth surface). This is an important concept to understand because it emphasizes the contrary effects roughness can have on the hysteresis of different starting sample surfaces.

The Cassie equation, $\cos \theta_c = Q_1 \cos \theta_1 + Q_2 \cos \theta_2$ describes the effect of surface heterogeneity on the contact angle. In this equation, θ_c , the Cassie angle, is the weighted average of the contact angles of two phases of the

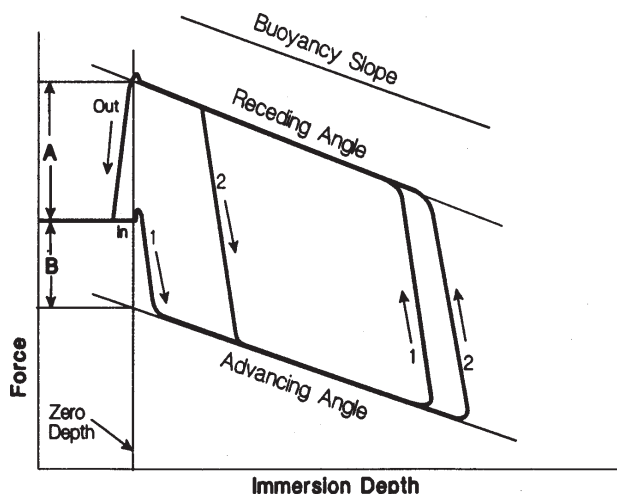


Figure 1: A typical stable reproducible two-cycle Wilhelmy plate hysteresis loop demonstrating true or thermo-dynamic hysteresis. From Reference 1.

Table 1. Sources of thermodynamic contact angle hysteresis

General assumption	Specific assumption	Effect on hysteresis	Time dependent
Surface is smooth	Surface must be smooth at the 0.1 to 0.5 μ level	$\Delta\theta$ increases with increasing roughness (θ_{adv} increases and θ_{rec} decreases with increasing roughness)	No
Surface is homogenous	Surface must be homogenous at the 0.1 μ level and above	θ_{adv} dependent on low energy phase: θ_{rec} dependent on high energy phase	No

Source: *Surface and Interfacial Aspects of Biomedical Polymers (Vol. 1)*, J. D. Andrade, editor, Ch. 7, Pp. 249-292, Plenum Press, NY, 1985.

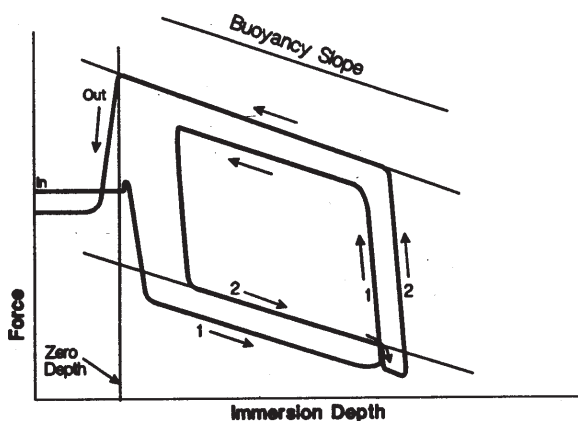


Figure 2: An example of a two-cycle contact angle hysteresis profile which is due to kinetic or time-dependent effects. From Reference 1.

surface. Q_1 and Q_2 represent the fraction of the surface covered by each phase and θ_1 and θ_2 represent the contact angle of each phase.

From these equations the surface under investigation may indeed exhibit a wide range of contact angles and thus it is impossible to measure θ_w and θ_c separate from any other θ . Nonetheless, a surface that exhibits contact angle hysteresis due to roughness or heterogeneity can be characterized by measuring the highest (advancing) and lowest (receding) contact angle values. When looking at a model of a heterogeneous surface, an important conclusion can be drawn: The advancing angle reflects the characteristics of the low-energy portion of the surface, while the receding angle reflects the characteristics of the high-energy portion of the surface.

Kinetic hysteresis

The other (secondary) classification for contact angle hysteresis is distinguished by time or cycle dependent changes in the contact angle (see Figure 2). There are four known sources of kinetic hysteresis as described in the table below:

Although far less common than thermodynamic hysteresis, surface reorientation is commonly observed in flexible polymeric materials. Polymer surface dynamics is now a well studied phenomenon, especially in the field of biomaterial engineering². According to this theory, surface groups oriented at the surface of a polymer can reorient in response to changes in the local environment to minimize the free energy at the interface. Hydrogels and other polymers such as PMMA (polymethylmethacrylate), widely used in the manufacture of contact lens and intraocular lens products, are capable of

reorienting methyl and hydroxyl groups at the surface when transferred from an aqueous to a non-aqueous environment on a very short time scale. The other three known causes of kinetic hysteresis - surface deformation, liquid penetration, and surface mobility have received less attention from the research community than surface reorientation, thus no detailed discussion on these sources is known to exist.

The dynamic contact angle technique is unique in its capacity to profile important contact angle hysteresis phenomenon in real time. Both advancing and receding contact angles are calculated, and kinetic processes such as surface reorientation are easily captured and stored for further analysis.

References:

- [1] Andrade, Joseph D. et al, *The Contact Angle and Interface Energetics. Surface and Interfacial Aspects of Biomedical Polymers. Vol 1, Plenum Press, New York, 1985.*
- [2] Andrade, J. D., *Proceedings from Eighth Rocky Mountain Regional Meeting of the ACS. June 1986. Polymer Surface Dynamics. Plenum Press, New York, 1988.*

Table 2. Sources of kinetic contact angle hysteresis

General assumption	Specific assumption	Effect on hysteresis	Time dependent
Surface is nondeformable	Modulus of elasticity in surface $> \sim 3 \times 10^5$ dyne/cm ²	Not known	Yes-due to surface deformation/relaxation effects
Wetting liquid does not penetrate surface	liquid molecular volume $> 60-70$ cc/g-mole	Increased liquid penetration lends to increased hysteresis	Yes-due mainly to diffusion
Surface does not reorient	Reorientation time at time of measurement	Increased tendency to orient lends to increased hysteresis	Yes
Surface immobile, therefore, surface entropy is constant	Configurational entropy independent of local environment	Unknown-but probably increase in hysteresis as surface mobility increases	Yes

Source:

Surface and Interfacial Aspects of Biomedical Polymers (Vol.), J.D. Andrade, editor, Ch. 7, Pp. 249-292, Plenum Press, NY, 1985.

Thermo Fisher Scientific Process Instruments

International/Germany
Dieselstr. 4,
76227 Karlsruhe
Tel. +49(0)721 40 94-444
info.mc.de@thermofisher.com

Benelux
Tel. +31 (0) 76 5 87 98 88
info.mc.nl@thermofisher.com

China
Tel. +86 (21) 68 65 45 88
info.mc.china@thermofisher.com

France
Tel. +33 (0) 1 60 92 48 00
info.mc.fr@thermofisher.com

India
Tel. +91 (22) 27 78 11 06
info.mc.in@thermofisher.com

United Kingdom
Tel. +44 (0) 1785 81 36 48
info.mc.uk@thermofisher.com

USA
Tel. 603 436 9444
info.mc.us@thermofisher.com

www.thermo.com/mc

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