

What is Contact Angle ?

SEO (Surface Electro Optics)

The contact angle is a tangent angle between the interfaces formed when a phase contacts to the other immiscible phase. As the interfaces are equilibrated, the contact angle is called to the equilibrated (or static) contact angle. The contact angle is applied to adhesive materials, coating technology, polymer area, thin film technology, and surface treatment as well as the interface science and technology.

Contact angle measurement is easily performed by a direct observation using the Goniometer, tilting method, Neuman method, capillary method, Wesburn method, and sessile drop technology.

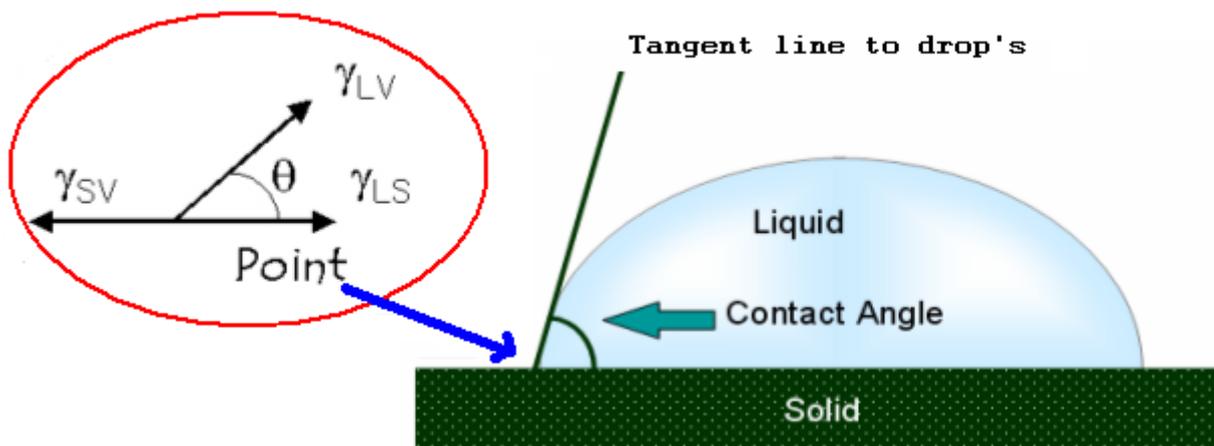


Figure 1. Schematic of a sessile-drop contact angle system

As shown in Figure 1, when a liquid drop is settled on a solid surface, the contact angle of the drop on the solid surface is defined by the mechanical equilibrium, of the drop under the action of three interfacial tensions. The equilibrium relation is known as Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta_Y$$

where θ_Y is the Young contact angle, which is suited in the Young's equation. The Young's equation represents that the contact angle measured in the field should be Young contact angle if one used the Young equation or any other equation connect to the Young equation.

In practice, however, the contact angle measured in the laboratory or any related field could not be the Young contact angle because of the following experimental errors:

- (1) Any gravitational effect during the drop is set on the solid surface
- (2) Any volume reduction of the drop when the syringe tip is detached from the liquid drop after the drop is set on the solid surface
- (3) Heterogeneity of the solid surface
- (4) Any absorption of the liquid phase of the drop by the solid
- (5) Any reaction between the liquid phase of the drop and the solid or any variation of the liquid surface tension due to the adsorption of a surface active materials or impurities when the liquid phase is not pure
- (6) Effect of the line tension produced at the solid/liquid/gas contact line (Drop size effect)
- (7) Any experimental errors on the drop profile observation during the measurement

In order to assure that the experimentally measured contact angles do not violate due to the above problems, one requires careful experimentations and suitable methodology. However, usually the contact angles are typically measured simply by depositing a drop of liquid on a given solid surface and by manually placing a tangent to the drop at its base using a so-called goniometric-sessile drop technique.

Currently, to obtain an accurate and thermodynamically stable state contact angle, which is Young's contact angle, many researchers have studied according to the measuring technique. The Young's angle could be measured by a 'low-rate expanding drop technique' (similar to the captive drop technique). The method is that the drop formed at the solid surface is expanded very slowly by adding a continuous drop liquid coming from the syringe needle tip and the drop profile is captured and the advancing contact angle is measured. It is known that the low-rate advancing contact angle is essentially identical to the static contact angle for relatively smooth surface. The goniometric technique which is currently used for a long time, however, cannot be identical to the Young's contact angle because some experimental errors in the measurements. Automated devices for the contact angle measurement recently developed can perform the measurement of the low-rate advancing contact angle. To obtain the Young's contact angle, the advancing velocity of the three-phase contact angle is in the range from 0.1 to 1.5 mm/min.

Generally, there are two types of contact angle multiple-value phenomena: the contact angle hysteresis and the drop size dependence of contact angles. For a system with a non-ideal (real) solid surface, the largest and smallest of the angles are recorded and termed the advancing contact angle θ_a and receding contact angle θ_r , respectively.

The θ_a is the contact angle of the liquid tending to advance across a solid surface and the receding contact angle is the contact angle of the liquid tending to recede from a solid surface. The difference between the advancing and receding contact angles is called 'contact angle hysteresis'. Generally, the major causes for the contact angle hysteresis included the roughness and the heterogeneity of the solid surfaces. Therefore, the contact angle hysteresis also can be used to characterize the solid surface heterogeneity. The second type of multiple-value contact angle

phenomena is called the drop size dependence of contact angles. Usually, this phenomenon is explained in terms of the so-called line tension, or the tension of the three-phase contact line.

This line tension is defined as the specific free energy of the three-phase contact line as a force operating in the three-phase line. The mechanical equilibrium condition for any point at the three-phase contact line can be given as:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta + \frac{\sigma}{R}$$

where R is the radius of the three-phase contact circle.

To avoid the line tension effect, the radius of the circle formed between the drop and the solid surface usually should be larger than 3mm.

II. Interfacial energy

At present there are many static methods suitable for measuring interfacial tensions for oil/water and gas/liquid interfaces. In drop shape analysis method, two examples are the sessile drop method and the pendent drop method. Unfortunately, each requires difficult measurements of high precision.

The shape of a liquid drop being acted upon solely by gravitational and surface energy forces is given by equation:

$$\frac{d\Phi}{dS} = \frac{2}{B - Z} - \frac{\sin \Phi}{X} \tag{3}$$

$$\frac{dZ}{dS} = \frac{\sin \Phi}{dX} = \cos \Phi \tag{4}$$

$$B = b \sqrt{c} = b \left(\frac{\Delta \rho g}{\gamma} \right)^{1/2} \tag{5}$$

In this equation, P is the radius of curvature at the point (X,Z), Φ is the angle made by the tangent at the point (X,Z) and the X coordinate axis, and β is the shape parameter. By taking the drop shape, the interfacial tension can be calculated. Also the change of the drop size enables one to expand and compress the interface. The dynamic interfacial tension, i.e. a tension when the interface is expanded or compressed, can be obtained by using axisymmetric drop shape analysis (ADSA) as a function of surface area.

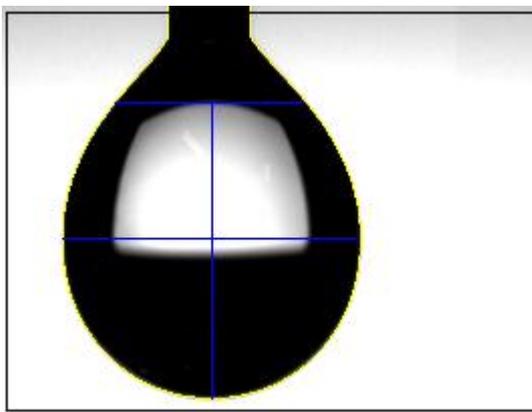


Fig 3. Pendent Drop

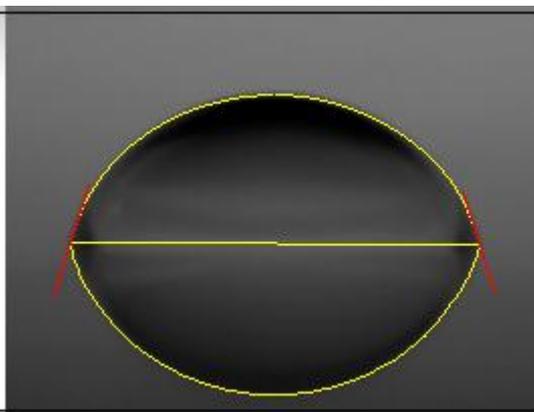


Fig 4. Sessile Drop

III. Surface energy of the solid surface

The contact angle measurements are also used to calculate the surface energy of the solid surface. As previously noted, the contact angle complexities are present in the measurement, which prevent use of the measurements for energetic calculations. Therefore, to measure the exact surface energy of the solid surface, the following criterion must be satisfied in the contact angle measurement.

1. The Young's equation must be satisfied in the values of three interfacial energies, γ_{LV} , γ_{LS} , and γ_{SV} . So, the three-phase contact angle must be Young's contact angle.
2. Pure liquids are always used in contact angle measurement. Also, the γ_{LV} remains constant during the measurement.
3. There is no chemical reaction (including desolving) between L/V, S/L, and S/V interfaces.
4. The liquid surface tension (γ_{LV}) of the testing liquids should be higher than that of solid surface tension. So one needs an appropriate choice of the liquids.

There are two categories in the surface energy calculation using the contact angle data: 1) surface tension component approach, and 2) equation of state approach.

The approach of the surface tension components was pioneered by Fowkes. He postulated that surface tension can be expressed as a sum of different surface tension component, each of which arises due to a specific type of intermolecular forces (hydrogen and dipole-dipole bonding). With the Young's equation, the surface energy of the solid surface can be calculated with the liquid surface tension component.

Similar equations have been developed as mentioned above. Owens-Wendt-Kaelble approach has a similar result by assuming that the liquid surface tension components are dispersed force and hydrogen bonding energy. The hydrogen bonding component is due to both hydrogen bonding and dipole-dipole interactions.

Lifshitz-van der Waals / acid-base approach was claimed to be a generalization of the Fowkes approach. Van Oss et. Al. divided the surface tension into different perceived components, i.e. the so-called Lifshitz-van der Waals (LW), acid(+), and base (-) components. Currently this method is used to measure the surface energies because simple and relatively accurate technique. To do this experiment, one needs two of polar liquid and one of non-polar liquid.

Equation of state approach is based on Antonow's rule and Berthelot's rule. By combination of the state equation and the Young's equation, the following equation is obtained:

$$W_{sl} = \sqrt{\gamma_{lv}\gamma_{sv}} e^{-\beta(\gamma_{lv} - \gamma_{sv})^2}$$

The solid surface tension can be determined from the experimental (Young) contact angles and liquid surface tensions. With pair data of the contact angle and the liquid surface tension, the solid surface energy (γ_{sv}) and constant (β) can be determined by a regression.

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