Wetting

Wetting is the ability of a liquid to maintain contact with a solid surface , resulting from intermolecular interactions when the two are brought together . The degree of wetting (wettability) is determined by a force balance between adhesive and cohesive forces . Wetting deals with the three phases of materials : gas , liquid , and solid . It is now a center of attention in nanotechnology and nanoscience studies due to the advent of many nanomaterials in the past two decades (e.g. graphene , carbon nanotube) .

Wetting is important in the bonding or adherence of two materials . Wetting and the surface forces that control wetting are also responsible for other related effects , including capillary effects .

There are two types of wetting : non @-@ reactive wetting and active wetting .

Explanation

Adhesive forces between a liquid and solid cause a liquid drop to spread across the surface . Cohesive forces within the liquid cause the drop to ball up and avoid contact with the surface .

The contact angle (?) , as seen in Figure 1 , is the angle at which the liquid ? vapor interface meets the solid ? liquid interface . The contact angle is determined by the result between adhesive and cohesive forces . As the tendency of a drop to spread out over a flat , solid surface increases , the contact angle decreases . Thus , the contact angle provides an inverse measure of wettability .

A contact angle less than 90 ° (low contact angle) usually indicates that wetting of the surface is very favorable , and the fluid will spread over a large area of the surface . Contact angles greater than 90 ° (high contact angle) generally means that wetting of the surface is unfavorable , so the fluid will minimize contact with the surface and form a compact liquid droplet .

For water , a wettable surface may also be termed hydrophilic and a nonwettable surface hydrophobic . Superhydrophobic surfaces have contact angles greater than 150 ° , showing almost no contact between the liquid drop and the surface . This is sometimes referred to as the " Lotus effect " . The table describes varying contact angles and their corresponding solid / liquid and liquid / liquid interactions . For nonwater liquids , the term lyophilic is used for low contact angle conditions and lyophobic is used when higher contact angles result . Similarly , the terms omniphobic and omniphilic apply to both polar and apolar liquids .

High @-@ energy vs. low @-@ energy surfaces

Liquids can interact with two main types of solid surfaces . Traditionally , solid surfaces have been divided into high @-@ energy solids and low @-@ energy types . The relative energy of a solid has to do with the bulk nature of the solid itself . Solids such as metals , glasses , and ceramics are known as ' hard solids ' because the chemical bonds that hold them together (e.g. , covalent , ionic , or metallic) are very strong . Thus , it takes a large input of energy to break these solids (alternatively large amount of energy is required to cut the bulk and make two separate surfaces so high surface energy) , so they are termed ? high energy ? . Most molecular liquids achieve complete wetting with high @-@ energy surfaces .

The other type of solids is weak molecular crystals (e.g. , fluorocarbons , hydrocarbons , etc .) where the molecules are held together essentially by physical forces (e.g. , van der Waals and hydrogen bonds) . Since these solids are held together by weak forces , a very low input of energy is required to break them , thus they are termed ? low energy ? . Depending on the type of liquid chosen , low @-@ energy surfaces can permit either complete or partial wetting .

Dynamic surfaces have been reported that undergo changes in surface energy upon the application of an appropriate stimuli . For example , a surface presenting photon @-@ driven molecular motors was shown to undergo changes in water contact angle when switched between bistable conformations of differing surface energies .

Wetting of low @-@ energy surfaces

Low @-@ energy surfaces primarily interact with liquids through dispersion (van der Waals) forces . William Zisman had several key findings in the work that he did :

Zisman observed that cos ? increases linearly as the surface tension (?LV) of the liquid decreased . Thus , he was able to establish a linear function between cos ? and the surface tension (?LV) for various organic liquids .

A surface is more wettable when ?LV and ? is low . Zisman termed the intercept of these lines when cos ? = 1 , as the critical surface tension (?c) of that surface . This critical surface tension is an important parameter because it is a characteristic of only the solid .

Knowing the critical surface tension of a solid , it is possible to predict the wettability of the surface . The wettability of a surface is determined by the outermost chemical groups of the solid . Differences in wettability between surfaces that are similar in structure are due to differences in packing of the atoms . For instance , if a surface has branched chains , it will have poorer packing than a surface with straight chains .

= = Ideal solid surfaces = =

An ideal surface is flat , rigid , perfectly smooth , and chemically homogeneous , and has zero contact angle hysteresis . Zero hysteresis implies the advancing and receding contact angles are equal . In other words , only one thermodynamically stable contact angle exists . When a drop of liquid is placed on such a surface , the characteristic contact angle is formed as depicted in Fig . 1 . Furthermore , on an ideal surface , the drop will return to its original shape if it is disturbed . The following derivations apply only to ideal solid surfaces ; they are only valid for the state in which the interfaces are not moving and the phase boundary line exists in equilibrium .

= = = Minimization of energy , three phases = = =

Figure 3 shows the line of contact where three phases meet . In equilibrium , the net force per unit length acting along the boundary line between the three phases must be zero . The components of net force in the direction along each of the interfaces are given by :
<formula>
<formula>
<formula>
where ? , ? , and ? are the angles shown and ?ij is the surface energy between the two indicated phases . These relations can also be expressed by an analog to a triangle known as Neumann ? s triangle , shown in Figure 4 . Neumann ? s triangle is consistent with the geometrical restriction that <formula> , and applying the law of sines and law of cosines to it produce relations that describe how the interfacial angles depend on the ratios of surface energies .

Because these three surface energies form the sides of a triangle , they are constrained by the triangle inequalities , ?ij < ?jk + ?ik meaning that no one of the surface tensions can exceed the sum of the other two . If three fluids with surface energies that do not follow these inequalities are brought into contact , no equilibrium configuration consistent with Figure 3 will exist .

= = = = Simplification to planar geometry , Young 's relation = = = =

If the ? phase is replaced by a flat rigid surface , as shown in Figure 5 , then ? = ? , and the second net force equation simplifies to the Young equation ,
<formula>
which relates the surface tensions between the three phases : solid , liquid and gas . Subsequently , this predicts the contact angle of a liquid droplet on a solid surface from knowledge of the three surface energies involved . This equation also applies if the " gas " phase is another liquid , immiscible with the droplet of the first " liquid " phase .

= = = = Real smooth surfaces and the Young contact angle = = = =

The Young equation assumes a perfectly flat and rigid surface often referred to as an ideal surface . In many cases , surfaces are far from this ideal situation , and two are considered here : the case of rough surfaces and the case of smooth surfaces that are still real (finitely rigid) . Even in a perfectly smooth surface , a drop will assume a wide spectrum of contact angles ranging from the so @-@ called advancing contact angle , <formula> , to the so @-@ called receding contact angle , <formula> . The equilibrium contact angle (<formula>) can be calculated from <formula> and <formula> as was shown by Tadmor as ,
<formula>
where
<formula>

= = = = The Young ? Dupré equation and spreading coefficient = = = =

The Young ? Dupré equation (Thomas Young 1805 ; Anthanase Dupré and Paul Dupré 1869) dictates that neither ?SG nor ?SL can be larger than the sum of the other two surface energies . The consequence of this restriction is the prediction of complete wetting when ?SG > ?SL + ?LG and zero wetting when ?SL > ?SG + ?LG . The lack of a solution to the Young ? Dupré equation is an indicator that there is no equilibrium configuration with a contact angle between 0 and 180 ° for those situations .
A useful parameter for gauging wetting is the spreading parameter S ,
<formula>
When S > 0 , the liquid wets the surface completely (complete wetting) . When S < 0 , partial wetting occurs .
Combining the spreading parameter definition with the Young relation yields the Young ? Dupré equation :
<formula>
which only has physical solutions for ? when S < 0 .

= = Nonideal rough solid surfaces = =

Unlike ideal surfaces , real surfaces do not have perfect smoothness , rigidity , or chemical homogeneity . Such deviations from ideality result in phenomenon called contact @-@ angle hysteresis , which is defined as the difference between the advancing (?a) and receding (?r) contact angles
<formula>
In simpler terms , contact angle hysteresis is essentially the displacement of a contact line such as the one in Figure 3 , by either expansion or retraction of the droplet . Figure 6 depicts the advancing and receding contact angles . The advancing contact angle is the maximum stable angle , whereas the receding contact angle is the minimum stable angle . Contact @-@ angle hysteresis occurs because many different thermodynamically stable contact angles are found on a nonideal solid . These varying thermodynamically stable contact angles are known as metastable states .
Such motion of a phase boundary , involving advancing and receding contact angles , is known as dynamic wetting . When a contact line advances , covering more of the surface with liquid , the contact angle is increased and generally is related to the velocity of the contact line . If the velocity of a contact line is increased without bound , the contact angle increases , and as it approaches 180 ° , the gas phase will become entrained in a thin layer between the liquid and solid . This is a kinetic nonequilibrium effect which results from the contact line moving at such a high speed that complete wetting cannot occur .
A well @-@ known departure from ideality is when the surface of interest has a rough texture . The rough texture of a surface can fall into one of two categories : homogeneous or heterogeneous . A homogeneous wetting regime is where the liquid fills in the roughness grooves of a surface . A

heterogeneous wetting regime , though , is where the surface is a composite of two types of patches . An important example of such a composite surface is one composed of patches of both air and solid . Such surfaces have varied effects on the contact angles of wetting liquids . Cassie ? Baxter and Wenzel are the two main models that attempt to describe the wetting of textured surfaces . However , these equations only apply when the drop size is sufficiently large compared with the surface roughness scale . When the droplet size is comparable to that of the underlying pillars , the effect of line tension should be considered . .

= = = Wenzel 's model = = =

 The Wenzel model (Robert N. Wenzel 1936) describes the homogeneous wetting regime , as seen in Figure 7 , and is defined by the following equation for the contact angle on a rough surface :
 <formula>
 where <formula> is the apparent contact angle which corresponds to the stable equilibrium state (i.e. minimum free energy state for the system) . The roughness ratio , r , is a measure of how surface roughness affects a homogeneous surface . The roughness ratio is defined as the ratio of true area of the solid surface to the apparent area .
 ? is the Young contact angle as defined for an ideal surface . Although Wenzel 's equation demonstrates the contact angle of a rough surface is different from the intrinsic contact angle , it does not describe contact angle hysteresis .

= = = Cassie ? Baxter model = = =

 When dealing with a heterogeneous surface , the Wenzel model is not sufficient . A more complex model is needed to measure how the apparent contact angle changes when various materials are involved . This heterogeneous surface , like that seen in Figure 8 , is explained using the Cassie ? Baxter equation (Cassie 's law) :
 <formula>