CHAPTER 2

Theory: Wetting Phenomena
Chapter 2

Theory: Wetting Phenomena

2.1 Introduction

Wetting phenomena are ubiquitous in nature and technology. Wetting phenomena are an area where chemistry, physics, and engineering intersect. Macroscopically the word “Surface” means a two dimensional plane that separates two phases. But, microscopically a third dimension, however small, exists. The thickness of this interfacial layer ranges all the way from interatomic distances to a few nanometers. In reality, while dealing with all the physical and chemical properties of the surfaces, we will always be dealing with the properties of the interface between the two phases. In general, properties of an interface are affected by changes in either of the two phases involved. The five interfaces possible in terms of the three states of matter are gas-liquid, gas-solid, liquid-liquid, liquid-solid and solid-solid.

A general prerequisite for the stable existence of interface between the two phases is that the free energy of formation of interface is positive. If it is negative or zero the effect of accidental fluctuations could be to expand the surface region continuously that would lead to eventual complete dispersion of one material into the other, e.g. gas-gas interface or interface between two miscible liquids or solids [1]. The surface properties are of greater importance to the industry also. Contact angle representing a balance between surface tension at a three phase boundary, is central to the flotation industry. Wetting, adhesion and detergency depend importantly on the control of interfacial energies. The surface-active agents can be used for the stabilization of the emulsion and foams and so on.

Many practical processes especially related to the paints and lubricants require the spreading of a liquid on a solid surface. On the other hand, for some processes like prevention of rusting, non-wetting behavior of solid surface is an important aspect. In porous solid bodies, liquid tends to get sucked into the pores of the solid if the solid is wettable by the liquid. Tertiary oil recuperation
also involves the penetration of water into the channels of porous rock, which were originally filled mainly by oil. Therefore, the study of solid-liquid interface is an active field of research since many years. Typical examples for wetting-dependent processes in daily life, biology, and industry include adhesion, printing, cleaning, painting, lubrication, and many more. Therefore, the characterization of wettability of solid surfaces has attracted much attention. Owing to its complexity, wetting has been studied over many years and much is yet to be explained. Some of the concepts related to these interactions are discussed in this chapter.

2.2 Surface tension

A liquid flows readily; yet it can adopt extremely stable shapes. A drop of oil in water or a soap bubble forms a perfect sphere that is smooth on an atomic scale and is hardly deformable. The fluctuations of the surface thickness are of the order of a mere angstrom. A liquid surface can be thought of as a stretched membrane characterized by a force called surface tension that opposes its distortion. Surface tension is also regarded as the free energy per unit area i.e. the work required to bring molecules from the interior of the phase into the surface region to form more surface. The corresponding unit is joules/(meter)$^2$ (J/m$^2$) which is dimensionally same as Newton/meter (N/m).

As the temperature rises, the surface tension of the liquid diminishes almost linearly. This means that the temperature co-efficient $d\gamma/dT$ (where $\gamma$ is surface tension, $T$ is temperature) has an almost negative value up to temperatures which are close to the critical temperature. At the critical temperature, the difference between boundary phases disappears and the surface tension becomes zero [2].

A liquid is a condensed state in which molecules attract one another. When the attraction is stronger than the thermal agitation, molecules switch from a gas phase to a phase that is dense, although still disordered - what we call a liquid. A molecule in the midst of a liquid benefits from interactions with all its neighbors and finds itself in a stable state. By contrast, a molecule that
wanders to the surface loses half its cohesive interactions, as shown in Figure 2.1 and becomes unstable. That is, the fundamental reason that liquids adjust
their shape in order to expose the smallest possible surface area. When dry, our
hair is full and thick, whereas the moment it gets wet, it sticks together in a
drab droopy mass.

![Diagram of a liquid surface with molecule interactions](image)

**Figure 2.1: An unstable molecule at the surface; other stable molecule in the midst of the liquid.**

When segregated to the surface, a liquid molecule is in an unfavorable
energy state. If the cohesion energy per molecule is $U$ inside the liquid, a
molecule sitting at the surface finds itself short of roughly $U/2$. The surface
tension is a direct measure of this energy shortfall per unit surface area. If ‘a’ is
the molecule’s size and $a^2$ is its exposed area, then the surface tension is of the
order $\gamma \cong U/(2a^2)$ [3]. For most oils, for which the interactions are of the van der
Waal’s type, we have \( U \approx kT \), which is the thermal energy where \( k \) is the Boltzmann constant. At a temperature of 25°C, \( kT \) is equal to 1/40 eV, which gives \( \gamma = 20 \text{ mJ/m}^2 \).

### 2.3 Capillary force

Liquid rises in a capillary tube because in doing so, it replaces a solid-vapour interface with solid-liquid interface, gaining energy equal to \( 2\pi rh (\gamma_{SV} - \gamma_{SL}) \), where 'r' is radius of the tube and 'h' is the height to which the liquid rises. The liquid does work against gravity equal to \( P_c \Delta V \), where '\( P_c \)' is called the capillary pressure and the volume of the liquid raised is \( \Delta V = \pi r^2 h \).

Equating the work done to the energy gained, the capillary pressure is found to be:

\[
P_c = \frac{-2 (\gamma_{SV} - \gamma_{SL})}{r} = - \frac{2 \gamma_{lv} \cos \theta}{r} \quad (2.1)
\]

The negative sign indicates that the liquid is in tension. For a cylindrical capillary, Laplace proved that the pressure difference across a curved liquid-vapour interface is equal to [4]:

\[
\Delta P = \frac{2 \gamma_{lv}}{R} \quad (2.2)
\]

where 'R' is the radius of curvature of the interface.

Figure 2.2 shows the various geometrical shapes formed by the liquid at the solid-liquid-vapour interface on capillary rise depending on the contact angle, \( \theta \) of the liquid with the solid surface of the capillary tube. When \( \theta \) has a value less than 90°, the liquid rises in the capillary up to a certain height 'h' as shown in the Figure 2.2 (a). Figure 2.2 (b) corresponds to the \( \theta \) value of 90°. At this value, capillary pressure '\( P_c \)' is zero and hence the capillary rise does not take place i.e. \( h=0 \). If \( \theta \) has a value greater than 90°, liquid opposes the rise in the capillary tube and it actually dips down by a height 'h' as shown in the Figure 2.2 (c).
Wetting refers to the study of how a liquid deposited on a solid or a liquid substrate spreads out. Understanding wetting enables us to explain why water spreads readily on a clean glass but not on a plastic sheet. ‘Controlling’ it, means being able to modify a suitable surface to turn a non-wettable solid into one that is wettable or vice-versa. For instance, it is possible to turn glass just as non-wettable as Teflon by depositing a thin coating of fluorinated molecules on it. The phenomenon is pertinent to numerous industrial areas, a few of which are listed below [5]:

\[ \theta < 90^\circ \]  
\[ \theta = 90^\circ \]  
\[ \theta > 90^\circ \]

Figure 2.2: The nature of the capillary rise of liquid depending upon the contact angle (\(\theta\)) of the liquid with the solid surface of the capillary.

2.4 Wetting

Wetting refers to the study of how a liquid deposited on a solid or a liquid substrate spreads out. Understanding wetting enables us to explain why water spreads readily on a clean glass but not on a plastic sheet. ‘Controlling’ it, means being able to modify a suitable surface to turn a non-wettable solid into one that is wettable or vice-versa. For instance, it is possible to turn glass just as non-wettable as Teflon by depositing a thin coating of fluorinated molecules on it. The phenomenon is pertinent to numerous industrial areas, a few of which are listed below [5]:
Chemical industry (paints, ink, insecticides).
Automobile manufacturing (surface preparation prior to painting, treatment of tyres to promote adhesion even on wet or juicy roadways).
Construction (waterproofing of concrete, protection of monuments, treatment of greenhouse plastic).
It plays a role in biological sciences. A few notable examples are:
• Inflation of lungs at birth initiated by surfactant molecules that lower the surface energy of the lungs. In some premature babies, these molecules are missing and the lungs are not ready to function on their own. This respiratory stress syndrome, known as hyaline membrane disease, is alleviated by the immediate delivery of suitable surfactants.
• Wetting of the eye. The cornea is by nature very hydrophobic, yet a normal eye is wet. Proteins called mucins, present in tears, turn the surface of the eye hydrophilic, stabilizing the lachrymal film. If one accidentally smears a fatty cream on the eye, it dries up, causing considerable discomfort. Some individuals suffer from ‘dry eyes’ and must apply artificial tears to compensate for their natural deficiency in mucins.

2.4.1 Types of wetting
There are two types of wetting:
• Total wetting, when the liquid has a strong affinity for the solid (or liquid) and
• Partial wetting, in the opposite case.
When a water drop is placed on a clean glass plate, it spreads completely. On the other hand, the same drop deposited on a sheet of plastic remains stuck in place. The conclusion is that there exist two regimes of wetting as shown in Figure 2.3. The parameter that distinguishes them is called the spreading parameter, $S$ that measures the difference between the surface energy (per unit area) of the substrate when dry and wet:

$$S = [E_{\text{substrate}}]_{\text{dry}} - [E_{\text{substrate}}]_{\text{wet}}$$

Or

$$S = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv})$$ (2.3)

where the co-efficients $\gamma_{sv}$, $\gamma_{sl}$ and $\gamma_{lv}$ are the surface tensions at the solid/air, solid/liquid and liquid/air interfaces, respectively.

**Total wetting: $S > 0$**

If the spreading parameter $S$ is positive, the liquid spreads completely in order to lower its surface energy ($\theta=0$). The final outcome is a film of nanoscopic thickness resulting from competition between molecular and capillary forces.

Figure 2.3: The two wetting regimes for sessile drops.
Partial wetting: $S < 0$

If the spreading parameter, $S$ is negative, the drop does not spread but at equilibrium forms a spherical cap resting on the substrate with a contact angle ($\theta$). A liquid is said to be ‘mostly wetting’ when $\theta \leq \pi/2$ and ‘mostly non-wetting’ when $\theta > \pi/2$. However, it should be noted that, $\theta = \pi/2$ plays no particularly significant role from a thermodynamical viewpoint. But, in contrast, $\theta=0$ corresponds to a condition of wetting transition. A ‘mostly wetting’ liquid spontaneously invades a capillary, a porous medium or a sponge.

Atoms on the surface have higher energy than those within the bulk, so there is energy associated with the existence of any interface. When the specific energy ($J/m^2$) of the solid-vapour interface, $\gamma_{sv}$, is greater than that of the solid-liquid interface, $\gamma_{sl}$, liquid tends to flow over an exposed solid surface. When a small liquid droplet is put in contact with a flat solid surface, distinct equilibrium regions may be found as shown in Figure 2.4: partial wetting (Figure 2.4(a) and 2.4(b)) with finite contact angle $\theta$; complete wetting, $\theta = 0$ (Figure 2.4(c)) or complete non-wetting, $\theta = 180^\circ$ (Figure 2.4(d)) [6]. In the case of partial wetting, the wetted portion of the surface is determined by certain ‘contact line’. A layer of liquid on a plane solid surface (Figure 2.4(c)) has two interfaces: solid-liquid $'\gamma_{sl}'$ and liquid-vapor $'\gamma_{lv}'$. Therefore, the change in energy ($\Delta E$) produced by spreading of the liquid film is:

$$\Delta E = \gamma_{sl} + \gamma_{lv} - \gamma_{sv}$$  \hspace{1cm} (2.4)

If $\Delta E<0$ the energy of the system is reduced so that the liquid will spread spontaneously (i.e. $\theta = 0$); otherwise the solid-liquid-vapour will be characterized by a finite contact angle.
2.4.2 Young’s equation

When three phases are in contact, the boundary of the three phases is called contact line. A drop of water on a piece of glass is a common example of contact between three phases—water, glass and air. The rim of the water droplet at the point of its contact with glass is the “contact line”. Such a system shows three interfaces—solid-liquid, liquid-vapour and solid-vapour. It is observed that the tangent to the liquid-vapour interface drawn at the contact line makes an angle with the solid surface which is characteristic of the three phase system. The angle is therefore considered as a thermodynamic property. It is called the “contact angle”. Note that it is measured from the solid surface, through the liquid phase, to the tangent as shown in Figure 2.5.

![Contact angles diagram](image)
There are three forces acting on the contact line due to the interfacial tension as shown in Figure 2.5. Under equilibrium, sum of these forces acting on the line of contact is zero. When normalized to a unit length, these forces are the interface tensions between the three phases - solid, liquid and air. By projecting the equilibrium forces onto the solid plane, one obtains Young’s equation [7]:

\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \]  

(2.5)

Substituting (2.5) in (2.3) yields

\[ S = \gamma_{lv} (\cos \theta - 1) \]  

(2.6)

From the above equation, it is evident that \( \theta \) can be defined only if the spreading parameter is negative. A contact angle increases when the liquid is non-wetting.

2.4.3 Wetting criteria: Zisman’s rule

To some extent, one can predict whether a solid surface is wettable or not depending upon the ‘nature’ of the surface. Surfaces, in general are classified into two categories [5]:

Figure 2.5: A solid-liquid-vapour system; contact rim and contact angle.
‘High energy’ (HE) surfaces are those for which the chemical binding energy is of the order of 1 eV, on which nearly any liquid spreads. High-energy surfaces are made of materials that are ionic, covalent or metallic. If ‘a’ is the drop size, the exposed surface area is of the order of $a^2$. Then, the interface tension is given by,

$$\gamma_{sv} \approx \frac{E_{\text{binding}}}{a^2} \approx 500 - 5000 \text{ mN/m}$$ \hspace{1cm} (2.7)

‘Low energy’ (LE) surfaces for which the chemical binding energy is of the order of $kT$ are generally hardly wettable. They include molecular crystals and plastics. In this case, we have

$$\gamma_{sv} \approx \frac{kT}{a^2} \approx 10 - 50 \text{ mN/m}$$ \hspace{1cm} (2.8)

But, it should be noted that, the surface energy $\gamma_{sv}$ in contact with air is not altogether sufficient to predict wettability. What is in fact needed is the sign of the spreading parameter $S$ given by equation 2.3.

As described above, all liquids spread on glass, metals and ionic crystals. By contrast, the wetting may be total or partial on plastics and molecular crystals, depending on which specific liquid is used. The empirical criterion worked out by Zisman allows us to classify solids. Each solid substrate has a critical surface tension, $\gamma_c$ such that if $\gamma > \gamma_c$, there is partial wetting and if $\gamma < \gamma_c$, there is total wetting, where $\gamma$ is the surface tension of the liquid.

2.5 Contact angle

2.5.1 Measurement of static contact angle

The methods of measuring contact angles may be classified into those which do, and those which do not require the knowledge of surface tension, $\gamma_{lv}$ of the liquid [8]. The first group naturally is related to those methods of
measuring $\gamma_{LV}$ in which a solid is involved. For a cylindrical capillary, the contact angle can be obtained using the equation:

$$\cos \theta = \frac{g \rho h r}{2 \gamma_{LV}}$$

(2.9)

where $g$ is the acceleration due to gravity, $\rho$ is the difference between the densities of the liquid and the vapor, $h$ is the height of the capillary rise, $\gamma_{LV}$ is the surface tension and $r$ is the radius of the capillary. For the capillary rise between two parallel walls, the analogous equation is:

$$\cos \theta = \frac{g \rho h \delta}{2 \gamma_{LV}}$$

(2.10)

where $\delta$ is the distance between the parallel walls.

The direct measurement of $\theta$ probably is more popular than any other method. A drop (often designated as a sessile drop) is placed on a flat solid surface or a bubble is trapped under a solid, or a meniscus at a vertical wall is realized. The three phase line is observed with unaided eye or with a microscope, and the contact angle measured with a protractor or a goniometer. The meniscus, or a part of it, can also be photographed and $\theta$ measured on an enlargement. A technique which can not be recommended consists of melting a grain of solid substance on a higher melting support, cooling the system, and measuring the $\theta$ on the solidified drop; the deformation which occurs during the freezing may markedly alter the true value of the contact angle.

Some experimenters prefer to measure $\theta$ by means of reflection of light. In Figure 2.6, 1 is the vapor, 2 is the liquid and 3 is the solid. It is clear that the beam emitted by the microscope tube, T (provided with a vertical illuminator) is reflected back into the microscope only when the tube direction is perpendicular to the liquid surface. If the microscope is focused on this surface at the three-phase line, the angle which the tube makes with the vertical, when the liquid appears bright, is equal to the contact angle.
Whatever the technique, direct determination of $\theta$ within, say, $\pm 2^\circ$ is easy, but it is difficult to reduce the relative error to, say, $\pm 0.5\%$. This is so because, the direction of liquid profile rapidly changes with the distance on the three phase line. Often, the contact angle, $\theta$ is observed at just one point of the three phase line; for instance, at the right hand end of the drop profile. This is insufficient. Usually, the visible $\theta$ varies along the base of the drop. Thus, it should be measured for at least three points and, if the spread of the values is not excessive, the arithmetic mean should be taken.

The level surface method is a little less simple and little more precise than the direct measurement. The essential part of the instrument used is schematically shown in the Figure 2.7. Plate 1 is partly immersed in a pool of liquid 2 and then cautiously rotated about the axis 3 until the liquid surface remains plain all the way to the plate. The absence of a curved meniscus can be ascertained visually or the reflection of a light beam may be used analogously to the method of Figure 2.6. The contact angle is read on protractor scale 4. As large volumes of liquid are required, the method is used mainly for water and other common substances.

**Figure 2.6: Measurement of $\theta$ by light reflection.**
Computation of $\theta$ from the drop dimensions has been performed many times. It is quite simple as long as the drop is so small that its deviation from the part-spherical shape may be neglected. Then (see Figure 2.8) the height, $h$ of the drop is $R(1-\cos \theta)$, $R$ being the radius of the spherical segment, and the diameter, $\Delta$ of the base is $2R \sin \theta$. Consequently, the ratio $h/\Delta$ is independent of $R$ and is equal to $(1-\cos \theta)/2\sin \theta$, so that [9]:

$$\frac{2\sin^2 (\theta/2)}{2\sin (\theta/2) \cos (\theta/2)} = \frac{2h}{\Delta}$$

i.e., $\tan(\theta/2) = \frac{2h}{\Delta}$

Or $\theta = 2 \tan^{-1} \left( \frac{2h}{\Delta} \right)$ \hspace{1cm} (2.11)
The droplets have to be of microscopic dimensions to justify the application of equation 2.11. The drops, whose $h$ and $\Delta$ can be measured without an optical magnification, are so distorted by gravity that much more elaborate calculations are needed to obtain $\theta$ from drop dimensions. The optimum drop size is given by the capillary length $\kappa^{-1}$ [10]:

$$\kappa^{-1} = \left( \frac{\gamma_{lv}}{\rho g} \right)^{1/2}$$  \hspace{1cm} (2.12)

For water, surface tension, $\gamma_{lv} = 72 \text{ mN/m}$, density, $\rho = 10^3 \text{ kg/m}^3$ and $g = 9.8 \text{ ms}^{-2}$. Hence, the value of $\kappa^{-1}$ is 2.7 mm. A droplet smaller than $\kappa^{-1}$ generally remains stuck when placed on solid surface because of contact angle hysteresis. On the other hand, gravity would flatten a drop of radius $r > \kappa^{-1}$ [11]. The formula (2.11) has been widely used in this work for the determination of the contact angle in the laboratory using a microscope.

2.5.2 Contact angle hysteresis

The contact angle of a given meniscus or a drop often can be measured with a reasonable precision (for example, $\pm 2^\circ$). Unfortunately, determination of $\theta$ in a supposedly identical system frequently gives grossly different results in

Figure 2.8: Calculation of contact angle ($\theta$) from drop dimensions.
another laboratory or at another time. Several reasons for the poor reproducibility of contact angle values are known, and the hysteresis of wetting generally is the most important of them.

Deposit a drop, as shown in figure 2.9 (a), on a horizontal plain surface; a contact angle (or a new range of contact angles) will be established along the three phase line. Add a small volume of the same liquid to the drop. The drop will get taller but its base will not change, as indicated in figure 2.9 (b); thus, the contact angle will be greater than before the addition. Subtract a small volume from the drop identical with that of figure 2.9 (a). Again, the base will not contract (or expand) but the drop will become flatter so that its contact angle will be smaller than before. This state is shown in figure 2.9 (c). Devices to achieve a controlled variation in the drop size have been described.

![Figure 2.9: Hysteresis of wetting.](image)

Figure 2.9: Hysteresis of wetting.

Figure 2.10 represents, graphically, the contact angle hysteresis when the size of the liquid drop is systematically varied.

![Figure 2.10: The contact angle hysteresis](image)

Figure 2.10: The contact angle hysteresis [8]

The angles obtained by adding liquid to a sessile drop are called advancing contact angles and usually are denoted by the symbol, $\theta_A$. When too much liquid is added, the droplet spreads, usually with a jerk, so that the three
phase line really advances over the solid-vapor interface. The angle at which this sudden spreading occurs is known as maximum advancing contact angle. Receding contact angles, $\theta_R$, are observed when small volumes of liquid are removed from the drop. When the drop becomes too flat, it suddenly contracts, and the angle at which this happens is the minimum receding contact angle [8].

Both advancing and receding angles can be seen on one drop when the solid support is tilted as shown in Figure 2.11. The angle at the lowest point is of the advancing type; it is greater than the receding angle seen at the highest point of the drop.

![Figure 2.11: A drop on a tilted plane, $\alpha$ is the angle of tilt, $\theta_A$ the advancing and $\theta_R$ the receding contact angle [8].](image)

### 2.5.3 Contact angle on a rough solid surface

When the surface energy is lowered, the hydrophobicity is enhanced. The Young’s equation [7] for the contact angle ($\theta$) of a liquid droplet can be applied only to a flat surface and not to a rough one. The effect of surface roughness on wetting behavior is explained by the model developed by Wenzel, where it is assumed that the space between the protrusions on the
surface is filled by the liquid. Wenzel had modified the Young’s equation as in the following [12]:

\[
\cos \theta' = \frac{r \left( \gamma_{sv} - \gamma_{sl} \right)}{\gamma_{lv}} = r \cos \theta
\]

(2.13)

where, \( \gamma_{sv} \), \( \gamma_{sl} \) and \( \gamma_{lv} \) are solid-vapour, solid-liquid and liquid-vapour interfacial energies, respectively. Where \( \theta' \) and \( \theta \) are contact angles of droplet on a rough surface and contact angle of the same droplet on the same surface without roughness that is calculated using Young’s equation, and \( r \) is the ratio of rough interfacial area over flat interfacial area under the droplet. Since \( r \) is always larger than unity, the surface roughness enhances both the hydrophilicity of hydrophilic surfaces and the hydrophobicity of hydrophobic ones. In contrast, Cassie and Baxter [13] proposed an equation:

\[
\cos \theta' = -1 + f (\cos \theta + 1)
\]

(2.14)

where, \( \theta' \) and \( \theta \) are the contact angles with and without (i.e. on a flat surface) considering air trapping and \( f \) is the real surface area over the apparent surface area. The Cassie-Baxter model assumes that a droplet is suspended on the rough structures and allows air trapping between the rough structures on a surface underneath the droplet.
The concepts of Young, Wenzel and Cassie-Baxter are outlined in Figure 2.12. During the regime where the Wenzel mode is dominant, the contact angle on hydrophobic rough surface increases as the roughness factor increases. Cassie proposed the contact angle $\theta'$ at a surface composed of solid and air. When a unit area of the surface has a wetted solid surface area fraction
Chapter 2  

Theory: Wetting Phenomena

2.6 Dynamic contact angle: Sliding angle

Sliding angle is defined as the critical angle where a water droplet with a certain weight begins to slide down the inclined surface (plate) [14]. While the contact angle of water has been commonly used as a criterion for the evaluation of the hydrophobicity of the surface, this alone is insufficient for the evaluation of the sliding properties of water droplets on surfaces. A surface with a high contact angle does not always show a low sliding angle. Therefore, when we discuss hydrophobicity, the sliding property of water droplets should be evaluated separately from the contact angle.

Bikerman investigated sliding angles on stainless steel plates with different finishes, having the contact angles around 90°, and proposed that the surface roughness provides resistance for the sliding of water droplets [15]. Johnson and Dettre theoretically simulated the effect of the surface roughness on the difference between the advancing and receding contact angles which is termed contact angle hysteresis and is commonly used as a criterion for the sliding properties [16]. They suggested that the hysteresis on the hydrophobic surfaces increases with increase in surface roughness in the low roughness region but decreases drastically when the roughness becomes large and the composite configuration, in which the liquid does not penetrate into the troughs, is energetically preferred. Xu et al [17] prepared the superhydrophobic surface with sliding angle of only 1° by a simple sol-gel method involving removable nanometer-sized polymeric spheres. Zhang and Kwok [18] and Anantharaju et al [19] studied the effect of three-phase (air, water, and solid substrate) contact line on the dynamics of the sliding process of a water droplet on a superhydrophobic surface by simulation. Furmidge derived an equation describing the relationship between the hysteresis and the sliding angle [20]:

\[
\frac{(mg \sin \alpha)}{w} = \gamma_l (\cos \theta_R - \cos \theta_A)
\]  

(2.15)
where, $\alpha$ is the sliding angle, $m$ is the mass of the water droplet, $w$ is the width of the droplet, $\gamma_{lv}$ is free energy of the liquid at the liquid-vapor interface, and $\theta_R$ and $\theta_A$ are the receding and advancing contact angles, respectively. As this equation indicates, surfaces with the same hysteresis values do not always show the same water sliding angles because the $m/w$ value varies with different contact angles. Therefore, to evaluate the sliding properties of surfaces with different contact angles, the direct comparison of the sliding angle itself is preferable.

The sliding angle (SA) is the incline angle at which the tailing edge of a drop of known mass will just begin to move and is a manifestation of the force required to dislodge a liquid from a surface. The maximum frictional force ($f_{\text{max}}$) required to dislodge a liquid from a surface can be calculated via the formula shown below;

$$f_{\text{max}} = mg \sin \alpha$$  \hspace{1cm} (2.16)

where, $m$ and $g$ are the mass of water droplet and the acceleration due to gravity, respectively. Where $\alpha$ represents the minimal sliding angle of the water droplet on the hydrophobic surface.

### 2.7 Solid surface tension

Although the solid surface tensions (energy) can be estimated using different independent approaches, the contact angle is believed to be the simplest and hence widely used.

In the literature, various approaches are mentioned which makes it possible to evaluate the solid surface tension using measured contact angles by liquids with known or pre-characterized surface energy parameters. Depending on the theoretical basis of the approaches, contact angles with one or more than one liquid are required on the solid surface for which surface energy is required. As stated earlier, Thomas Young [7] proposed contact angle of a liquid as mechanical equilibrium of the drop resting on a plane solid surface at the three-phase boundary. The three forces at the interface are the surface
tensions at liquid-vapor, $\gamma_{lv}$, solid-liquid, $\gamma_{sl}$ and solid-vapor, $\gamma_{sv}$, interfaces which in equilibrium gives the following relation:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (2.17)$$

The above equation contains the known parameters of $\gamma_{lv}$ and $\cos \theta$, and it is understood that this equation provides the unknown solid surface tension (energy), $\gamma_{sv}$; the only drawback being the unknown solid-liquid interfacial energy, $\gamma_{sl}$. If this parameter could be represented or expressed in terms of solid and liquid surface energies then the problem would be solved.

One of the methods is to express $\gamma_{sl}$ in terms of the solid and liquid surface energy using some mathematical formulation and then evaluating the unknown $\gamma_{sv}$. The first attempts were made in 1898 where the solid-liquid interfacial energy was expressed in terms of a geometric mean of solid and liquid surface energies. This method is followed to date in the form of the equation of state approach for which the latest formulation has been published as recently as 2000.

The Neumann’s equation for the solid-liquid interfacial energy is [21]:

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2 \frac{\gamma_{lv} \gamma_{sv}}{\sqrt{\gamma_{lv} \gamma_{sv}}} \exp (-\beta (\gamma_{lv} - \gamma_{sv})^2) \quad (2.18)$$

where $\beta$ is a constant which was found to be 0.0001247 m$^4$ mJ$^{-2}$. Combining the equation 2.17 with equation 2.18 yields,

$$\cos \theta = -1 + 2 \frac{\gamma_{sv}}{\gamma_{lv}} / \frac{\gamma_{sl}}{\gamma_{lv}} \exp (-\beta (\gamma_{lv} - \gamma_{sv})^2) \quad (2.19)$$

In this equation, only the surface tension of the solid, $\gamma_{sv}$, is unknown and it is a function of the contact angle ($\theta$). Hence, the solid-vapor interfacial tension can be calculated.
2.8 Surface treatments

The surfaces can be either hydrophobic or hydrophilic. The surface roughness can control the degree of wettability (for a given surface chemistry) by enhancing the material’s natural tendency. As the roughness increases, a hydrophilic substance becomes even more hydrophilic, while one that starts hydrophobic can become literally ‘superhydrophobic’ [22].

2.8.1 Converting hydrophilic surfaces into hydrophobic surfaces

We have seen that glass and silicon are high-energy solids that are wetted by all liquids (with the exception of mercury) because their critical surface tension, $\gamma_c$ is quite high (of the order of 150 mN/m). It is possible to lower $\gamma_c$ by coating such solids with a hydrophobic molecular layer of the type -(CH$_2$)- or -(CF$_2$)-. This process can create surfaces with extremely low energies, mimicking Teflon. The parameter, $\gamma_c$ drops down to values of the order of 20mN/m for hydrogenated coatings and 10 mN/m for fluorinated ones. Practically no liquid spreads on a fluorinated surface. There are several substances capable of altering the wetting properties of the surface and they are called the hydrophobic reagents. A few of them are methyltrimethoxysilane (MTMS), dimethylchlorosilane (DMCS), methyltriethoxysilane (MTES), dimethyldichlorosilane (DMDCS), trimethylchlorosilane (TMCS), trimethylethoxysilane (TMES) and Hexadecyltrimethoxysilane (HDTMS).

2.8.2 Converting hydrophobic surfaces into hydrophilic surfaces

Green houses are often covered with transparent plastic sheets. Morning dew condensing into fine droplets on the plastic scatters the light and robs flowers and plants of the much-needed sunlight. It is desirable to find a way to force water into a continuous film, in other words, to ‘wet’ the material. There are ‘Plasma’ treatments that can create hydrophilic groups on the surface of plastic, thereby lowering $\gamma_c$.

The human cornea is extremely hydrophobic. Our tears ‘treat’ the surface of the cornea by depositing hydrophilic proteins that stabilize the
lachrymal films. Plastics and molecular crystals generally have a low \( \gamma_c \) and therefore, are very poorly wettable by water. One technique to increase their wettability is to coat them with gold. However, it would be a mistake to believe that gold-coated plastic behaves like bulk gold. The liquid does interact with gold, but that does not mean that interactions with plastic substrate are entirely masked. While a very thin liquid film ‘thinks’ it sits on pure gold, a thick one still ‘senses’ the underlying substrate. This paradoxical situation leads to ‘pseudopartial’ wetting, where the liquid covers the solid with an extremely thin film without truly spreading (the contact angle \( \theta \) remains finite).

2.9 Adsorption

Many of the useful properties of solids arise from the reactions between the solid surface and various gases. These reactions are mainly limited to the interfacial regions. The adsorption of gases or vapours can be made to yield information about the surface area and pore structure of the solid. Adsorption is a process of condensation of gases on free surface, whereas absorption is the process in which the molecules of the gas penetrate into the mass of the absorbing solid [23]. The solid surface on which the gas adsorbs is called an adsorbent. Most of the practical adsorbents are very porous solids with high internal surface area.

Molecules and atoms can attach themselves onto a surface in two ways:
(i) Physical adsorption (physisorption) and
(ii) Chemical adsorption (chemisorption).

2.9.1 Physisorption

There is a weak van der Waals attraction of the adsorbate to the surface. The attraction to the surface is weak but long ranged and the energy released during physisorption is around 2-5 kcal/mole, which is of the same order of magnitude as enthalpy of condensation. During the process of physisorption, the chemical identity of the adsorbate remains intact. Physisorption is usually observed at low temperatures or on relatively inert surfaces.
2.9.2 Chemisorption

The adsorbate sticks to the solid by the formation of a chemical bond with the surface. This interaction is much stronger than physisorption and alters the chemical nature of the surface. Chemisorption gives rise to a high heat of adsorption, usually of the order of 15-20 kcal/mole, and is often characterized to be taking place at the activated surfaces and elevated temperatures. It may be dissociative, non-dissociative or reactive in nature.
Chapter 2

Theory: Wetting Phenomena

References


