# CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Surface Tension: The Young-Laplace Equation

Surface tension (or excess surface free energy) arises from unequal interaction forces in vertical direction between molecules in the surface region and their neighbors. Surface tension depends on the magnitude of molecular pairwise interaction energy. Energy is required to promote molecules from bulk liquid to the surface or interfacial region. Molecules at the surface region have excess energy, entropy, and Gibbs free energy, compared to molecules in the bulk. Work is required to move molecules from bulk to surface region (Scamehorn, 2000).
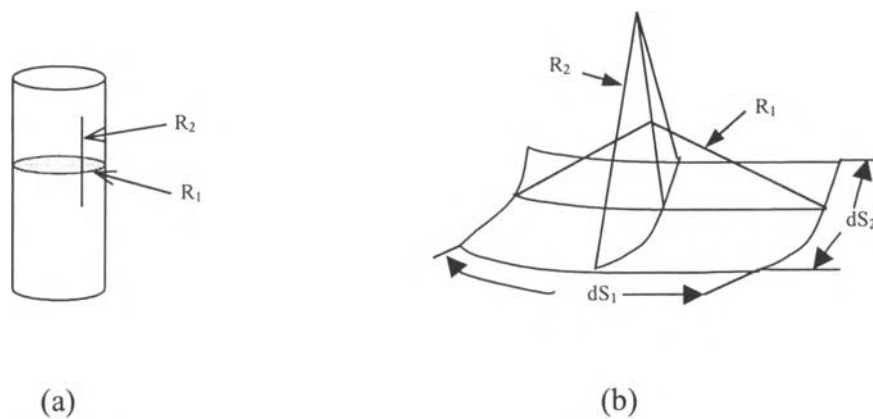
Surface
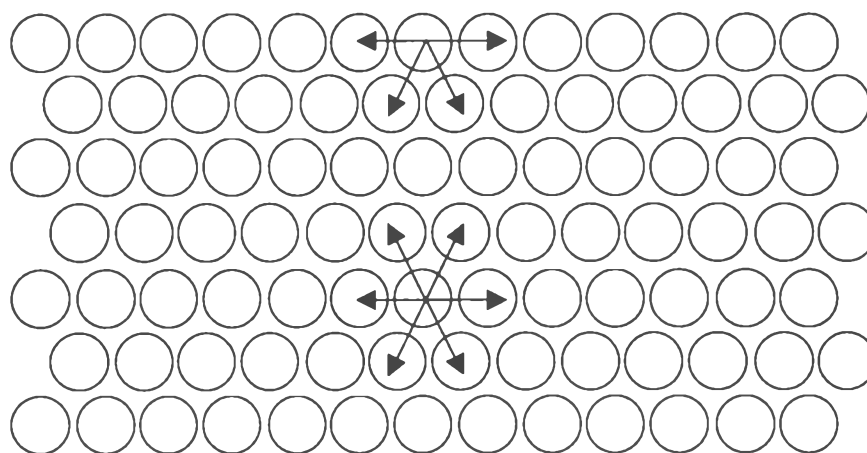
Figure 2.1 Surface forces on molecules in bulk and at interface.

A magnitude of surface tension then depends on the cohesive energy density of molecules. Hydrocarbon liquids have lower surface tension than polar liquids like water because interaction energy in liquid hydrocarbons is weaker (Van der Waal attraction and hydrogen bonding). Of liquids well below their critical temperatures, fluorocarbons have the lowest cohesive energy densities and surface tension.

Interfacial tension can give rise to a pressure difference across an interface that separates a pair of immiscible fluids, implying that the surface is in tension. And that pressure difference can be calculated from the shape and size of the interface, which are characterized by the curvature of a surface. Consider the surface of a cylinder (Figure 2a), lines R_1 and R_2 on the surface of the cylinder are a particular pair of lines which are orthogonal. Line R_1 is the arc of a circle whose radius is that of the cylinder. Line R_2 is a straight line in the surface, parallel to the axis of the cylinder. It is not a curve, but may be regarded as the arc of a circle with an infinite radius. Hence, for a cylindrical surface, the radii of curvature of the surface in the chosen pair of orthogonal directions are different. One radius is that of the cylinder, and the other is infinite.

(a)   (b)

Figure 2.2 (a) The curved surface of a cylinder. (b) Differential area in the surface separating two immiscible fluids.

Assumption is made for the sake of simplicity. For any surface, there is a pair of orthogonal curves at any point on the surface and each curve is approximated as the arc of a circle. The curvature of a surface, at a point, is described in terms of the radii R_1 and R_2 of the curves corresponding to that point.

Using force balance on the area separating two immiscible fluids for the condition of equilibrium of normal stresses across a static interface yields the so-called Young-Laplace equation (Middleman, 1998):

$$p_i - p_o = \sigma \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \qquad (2.1)$$

where p_i =   the pressure on the concave side ("inside") of the interface

           p_0 =   the gas side (outside) pressure

Physically, the equation tells that interfacial tension causes an increased pressure on the "inside" of a surface, the magnitude depending on the radii of curvature of the surface. It also shows that there is a corresponding discontinuity in normal stress, which acts perpendicular to the surface, across the boundary.
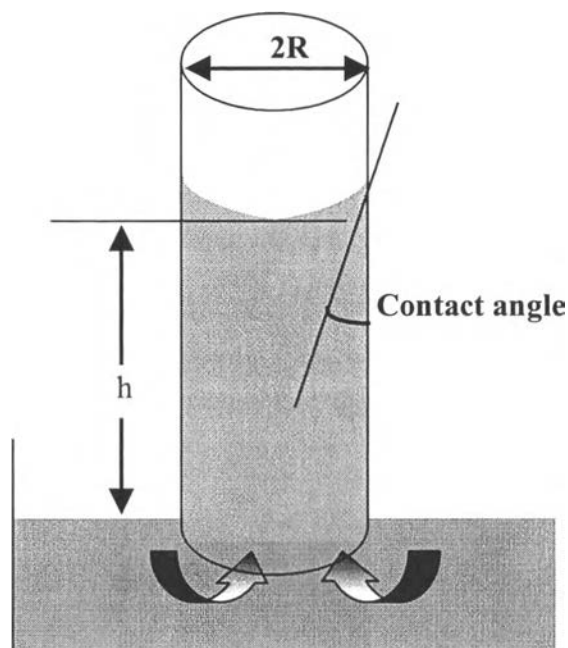
2.2 Capillary Rise in a Cylinder

The capillary rise method is attributed to be one of the most accurate methods for measuring interfacial tension. The schematic diagram of the capillary rise in a cylindrical tube is shown in Figure 3. A capillary tube is dipped into a liquid that wets the tube. The liquid rises in a capillary by means of capillary force and force of surface tension between the liquid and the tube.

Factors on which the height of the rising liquid depend are the radius of the tube, the surface tension of the liquid, the density of the liquid, and the contact angle between the tube wall, the air, and the liquid. With an assumption of zero-contacted angle, the equation that has been used widely to treat such the phenomenon is

$$\sigma = \frac{\rho g h R}{2} \qquad (2.2)$$

where σ =   the surface tension of the liquid

          g   =   the gravitation constant

          R   =   the radius of the capillary tube

          ρ =   the density of the test liquid

          h   =   the height of the liquid rise in the capillary tube

Figure 2.3 The schematic diagram of the capillary rise in a cylinder method.

2.3 Literature Survey

Chatelier *et al.* (1997) used the capillary rise measurement in two parallel-flat plates to determine the intrinsic acid-base dissociation constant and site density of ionizable surface groups. Their results show that the equilibrium capillary height is related to the change in gravitational potential energy, the intrinsic wettability of the un-ionized surface, and the free energy of formation of the ionizable surface in aqueous solution. They presented a theoretical approach to model the equilibrium capillary height of electrolyte solutions between ionizable surfaces on flat plates as a function of pH.

A new method to determine interfacial tension using a micropipet technique was proposed by Lee *et al.* (2001). They measured the radius of curvature of the interface for a series of pressure change to determine the equilibrium interfacial tension between the two phases on the basis of the Laplace equation. While assuming the contact angle was zero, their results were consistent with the interfacial tension values reported in the literature measured by other techniques for microscopic interfaces.

Grzybowski *et al.* (2001) obtained analytical solutions of the Laplace equation for two infinitely long faces in terms of the meniscus height and the distance between plate to plate. Then, they used the relation to calculate the energy of the system by means of the sum of the capillary and gravitational energy terms. Moreover, they used Finite Element Method to model the contours of the menisci. They suggested that the Finite Element Method is a reliable tool in predicting the shapes of the menisci and in estimating the lateral capillary interactions.

Chibowski and Perea-Carpio (2002) described methodologies to avoid problem of overestimated contact angle values calculated from Washburn's equation that resulted from the porous layer imbibition technique. They investigated contact angles of water for various solids as determined from directed contact angle measurements (CA) and from thin layer wicking (TW) and show that the surface free energy is increased as the solid is ground.

Capillary rise of liquid in different vanes under variable residual acceleration was studied to model the capillary rise in closed and opened geometries under variable residual acceleration to get reliable predictions for the fluid behavior in capillary vanes (Strange, 2002). They changed the shape of the climbing meniscus by disturbing acceleration. They found that the change of the meniscus shape affected the capillary force and thus the flow velocity of the liquid. The free surfaces at the sides of the vane also deviated from their original shape. This effect can influence the liquid rise as well.