Application of Infinitesimal Fluid Element Approach to Analyze Contact Angle with Surfactant Effect

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***Abstract*—After the establishment of the concept of surface tension, Young's equation depicting the contact angle for a liquid drop resting on a planar surface has been extensively applied for different designs and extended to various physical situations, the Boruvka-Neumann equation especially. Instead of the traditional free energy minimization method, in this paper, we use the infinitesimal fluid element approach to derive the contact-angle equations for a liquid resting on a curved surface and take the effect of surfactant into consideration. This method makes it possible to deform the solid substrate into other shapes and elucidates the characteristics of contact angle more directly. The results could be reduced to a planar solid surface or a vertical tube. Hence, the derived equations could be considered as an extended form of the Boruvka-Neumann equation. A liquid with angular velocity in an axisymmetric solid container also has been analyzed and it is found that the contact angle is insensitive to the angular velocity.**

Keywords—Surface tension, contact angle, Young's equation, Boruvka-Neumann equation, surfactant

I. INTRODUCTION

The concept of surface tension was almost constructed simultaneously by Laplace [1] and Young [2]. In Laplace's work, he argued that there shall be an appropriate contact angle between the liquid and solid substrate to make the liquid drop stay stably on the solid substrate. Later, Young [2] proceeded to discuss the Laplace's formulation and clarify the results without any formula. Since then, the equation depicting contact angle has been called Young's equation. Several decades later, the line tension along the triple contact line was argued by Gibbs [3] and others [4-6] in which the Young's equation was derived in a more general form giving a more precise relation between the contact angle and surface tensions. This is the so-called Boruvka-Neumann equation. Young's equation has been extensively applied for many research fields such as those involving coating [7] and electrowetting [8-10] problems. From Young's equation, we learn that the major factor affecting the contact angle is the surface tension, and the magnitude of surface tension may be changed under various circumstances, for example, the presence of surfactant. Surfactants are used widely in numerous applications due to their ability to lower the surface tension. Accordingly, the contact angle also may be affected by the addition of surfactant in the liquid and its effect has received much attention in the literature [11,12]. Most studies considered the liquid is put on a planar solid surface. Recently, a liquid drop resting on an inclined plane [13, 14] or on a curved surface [15,16] also has been considered.

In the present study, we consider the force balance of an infinitesimal fluid element on the contact line to recover Young's law. This infinitesimal fluid element approach makes the behaviors of surface tension and line tension visible which is very different from the conventional free energy minimization method [6,15-19]. Hence, it becomes possible to deform the solid substrate into other shapes and investigate the corresponding characteristics. There are two equations being derived to describe the relationship between the surface tensions and the contact angles in which the adhesive force and the surfactant concentration at the contact line are taken into consideration. One depicts the force balance in the horizontal direction and the other is in the tangential direction. Both equations can be reduced to the special cases that involve a planar surface or a vertical tube. When the tangential force balance is considered, the adhesive term can be removed [15,16] and the result is more succinct. The other advantage of the infinitesimal fluid element approach is to explain the reason why the gravity and rotational effect are absent in Young's equation. It has been proved that the contact angle is irrelevant to the rotational effect for a planar surface [18] and a vertical surface [20]. Here we further consider a liquid with angular velocity in an axisymmetric solid container and prove the contact angle is also insensitive to the angular velocity as the phenomenon in a planar or vertical case. The present results could be generalized for the studies of axisymmetric and nonaxisymmetric curved surfaces. The details of the derivation are described in the following.

II. THE INFINITESIMAL FLUID ELEMENT APPROACH TO YOUNG'S EQUATION FOR NON-PLANAR SURFACES

The contact angle of a liquid drop resting on a planar solid surface is related to the original Young's equation. Consider the line tension τ along the circumference, the contact angle θ satisfies the Boruvka-Neumann equation [4-6],

$$\sigma_{lv}\cos\theta + \sigma_{sl} - \sigma_{sv} + \frac{\tau}{r_0} = 0, \quad (1)$$

where σ_{lv}, σ_{sl} and σ_{sv} are respectively the surface tensions between the liquid/vapor, solid/liquid, and solid/vapor interfaces, and r_0 is the radius of the boundary of the liquid. In this paper, we denote the liquid by a subscript l, the vapor atmosphere by v, and the solid surface by s.

The formulation of Young's equation and Boruvka-Neumann equation contain significant geometric meaning which can be thought as a result of force balance. Firstly, we derive the magnitude of the centripetal force caused by the line tension. Consider a circle with radius r_0 and a constant line tension τ as shown in Figure 1. A sector with central angle 2α is affected by the line tension τ. Hence, there is a centripetal force $F_{\tau,\alpha}$ acting on the arc of the sector. Obviously, the arc length l_α is $2r_0\alpha$ and the centripetal force $F_{\tau,\alpha}$ is $2\tau\sin\alpha$. The behavior of the centripetal force at an infinitesimal element can be found when $\alpha \to 0^+$. Therefore, the centripetal force per unit length at the circle produced by the line tension is

$$\lim_{\alpha\to 0^+}\frac{F_{\tau,\alpha}}{l_\alpha} = \lim_{\alpha\to 0^+}\frac{2\tau\sin\alpha}{2r_0\alpha} = \frac{\tau}{r_0}. \quad (2)$$

In the horizontal direction, there are four forces indicated by σ_{sv}, σ_{sl}, σ_{lv}, and τ. Equation (2) acquaints us the magnitude of the centripetal force caused by the line tension. Thus, for an infinitesimal fluid element on the triple contact line, the summation of these forces per unit length in the horizontal direction results in (1).

In general, the solid substrate may be non-planar and the liquid shape may be non-axisymmetric. We consider a liquid stably in a solid container with an arbitrary shape as shown in Figure 2. We partition the contact into two angles, θ_1 and θ_2, which are above and below the horizontal plane, respectively. The contact angles θ_1 and θ_2 may not be constant along the triple contact line. It is assumed that the triple contact line is located on a horizontal plane and a sufficiently smooth plane curve. For an assigned point P on the contact line, the infinitesimal region close to P is approximated to a portion of the osculating circle with radius r_0, where r_0 is the radius of curvature of the triple contact line at point P. The point O is set to be the center of the osculating circle along the contact line at P. Let α be a small angle, and Q_1 and Q_2 are the two points on the contact line which satisfy $\angle Q_1OP = \angle Q_2OP = \alpha$. According to (2), we can derive the centripetal force per unit length at P produced by the line tension is τ / r_0 when α approaches zero. Because the solid/liquid interface may be non-horizontal, the adhesive force between the liquid and solid shall be concerned. By using f to account for the adhesive force per unit length at the contact line, the formula depicting the contact angle relation for an arbitrary shape is

$$\sigma_{lv}\cos\theta_1 + \sigma_{sl}\cos\theta_2 - \sigma_{sv}\cos\theta_2 + \frac{\tau}{r_0} - f\sin\theta_2 = 0. \quad (3)$$

Note that τ, f, θ_1, and θ_2 are the functions of the position on the triple contact line. For the special case as the liquid rests on a planar surface, $\theta_2 = 0$, equation (3) reduces to (1), which is the original Young's equation or Boruvka-Neumann equation.

Generally, it is hard to measure the adhesive force f. Therefore, we concern the force balance in the direction which is tangent to the container instead of the horizontal direction due to the reason that the adhesive force is normal to the solid/liquid interface. The force balance equation becomes

$$\sigma_{lv}\cos(\theta_1+\theta_2) + \sigma_{sl} - \sigma_{sv} + \frac{\tau}{r_0}\cos\theta_2 = 0, \quad (4)$$

which has been demonstrated by minimizing the free energy [15,16]. When θ_2 equals $\pi/2$, the solid surface becomes a vertical tube and (4) reduces to

$$\sigma_{sv} + \sigma_{lv}\sin\theta_1 - \sigma_{sl} = 0, \quad (5)$$

which is exactly the force balance in the vertical direction [21].

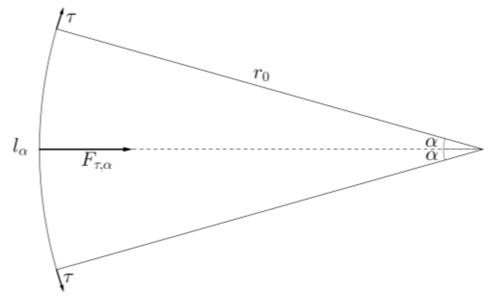

Fig. 1. *A sector with central angle 2α and radius r_0. The arc is acted by the line tension τ along the tangent direction and the arc length is l_α. $F_{\tau,\alpha}$ is the total centripetal force caused by the line tension τ.*

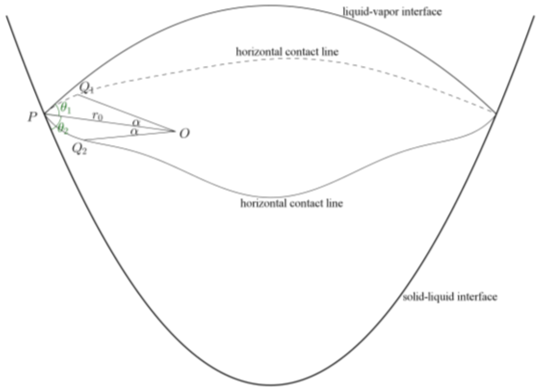

Fig. 2. *Liquid stably put in a solid container with an arbitrary shape. The triple contact line is assumed to be located on a horizontal plane. On the contact line, A point P on the contact line is chosen to illustrate the contact angles θ_1 and θ_2. Here r_0 is the radius of curvature of the triple contact line at the point P, and O is the center of the osculating circle along the contact line at P. For an assigned small angle α, Q_1 and Q_2 are the two points on the contact line satisfying $\angle Q_1OP = \angle Q_2OP = \alpha$.*

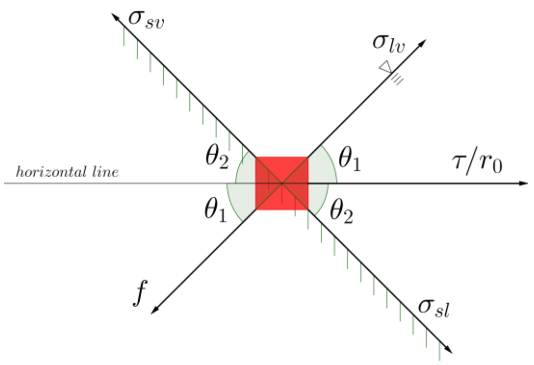

Fig. 3. *The five forces caused by surface tension and line tension exert on an infinitesimal element around a triple contact line. In the horizontal direction, the summation of the five forces should be zero.*

Figure 3 shows the equilibrium of the surface tension, the adhesive force, and the line tension in the horizontal direction which results in the formula (3). This is exactly the main idea of graphical interpretation that the surface tensions maintain the equilibrium of a material element around a triple contact line [22].

Comparing (4) with (1), we can find both equations give the same interpretation that the total force tangent to the solid substrate should be zero. The only difference is that the force produced by the line tension in Figure 3 may not be parallel to the solid/liquid interface. Accordingly, the term caused by the line tension in (1) should be multiplied by $\cos\theta_2$. The magnitude of gravitational force acting on liquid is ρg per unit volume, where ρ is the density of the liquid but the other forces is measured per unit length. It is a comprehensive way to realize why the contact angle satisfies (3) or (4) and not affected by gravity directly.

III. The Contact Angle with the Effect of Surfactant

Because the surface tensions are sensitive to the presence of surfactant, here we further consider the concentration of the surfactant in the liquid. It is well known that surfactants may decrease the interfacial tension. Let Γ be the concentration of the surfactant in the liquid. The formation of micelles as the concentration of surfactant is greater than the critical micelle concentration, precipitation due to gravity, and other reasons may cause a non-uniform distribution of surfactant concentration in the liquid. Hence, Γ is a function of position and time. In general, the surfactant concentration changes slowly. Hence, we suppose the concentration of surfactant alters the surface tension linearly through the relations

$$\sigma_{lv} = \sigma_{lv,0} - E_{lv}(\Gamma - \Gamma_0), \tag{6}$$

$$\sigma_{sl} = \sigma_{sl,0} - E_{sl}(\Gamma - \Gamma_0), \tag{7}$$

where $\sigma_{lv,0}$ is a constant surface tension on the liquid/vapor interface at a constant surfactant concentration Γ_0 and $E_{lv} = -\partial\sigma_{lv}/\partial\Gamma > 0$. The surface tension $\sigma_{sl,0}$ and corresponding variable E_{sl} are defined in a similar way. As a result, equation (3) could be written in the following form

$$\begin{aligned}&\left(\sigma_{lv,0} - E_{lv}(\Gamma - \Gamma_0)\right)\cos\theta_1 + \left(\sigma_{sl,0} - E_{sl}(\Gamma - \Gamma_0)\right)\cos\theta_2 \\ &\qquad - \sigma_{sv}\cos\theta_2 + \frac{\tau}{r_0} - f\sin\theta_2 = 0,\end{aligned} \tag{8}$$

and by considering the force balance in the tangent direction, equation (4) could be expressed as

$$\begin{aligned}&\left(\sigma_{lv,0} - E_{lv}(\Gamma - \Gamma_0)\right)\cos(\theta_1 + \theta_2) \\ &\qquad + \left(\sigma_{sl,0} - E_{sl}(\Gamma - \Gamma_0)\right) - \sigma_{sv} + \frac{\tau}{r_0}\cos\theta_2 = 0.\end{aligned} \tag{9}$$

IV. The Contact Angle for Liquid in a Channel

Liquid in a channel with invariable cross-sectional area as shown in Figure 4 is a limiting case of the situation in Figure 2, in which all the triple contact lines are straight and the radius of curvature of the contact line is infinite everywhere. Thus, the line tension makes no contribution for the equation of force balance for an infinitesimal fluid element on the contact line. Therefore, equation (8) becomes

$$\begin{aligned}&\left(\sigma_{lv,0} - E_{lv}(\Gamma - \Gamma_0)\right)\cos\theta_1 + \left(\sigma_{sl,0} - E_{sl}(\Gamma - \Gamma_0)\right)\cos\theta_2 \\ &\qquad - \sigma_{sv}\cos\theta_2 - f\sin\theta_2 = 0,\end{aligned} \tag{10}$$

and (9) reduces to

$$\begin{aligned}&\left(\sigma_{lv,0} - E_{lv}(\Gamma - \Gamma_0)\right)\cos(\theta_1 + \theta_2) \\ &\qquad + \left(\sigma_{sl,0} - E_{sl}(\Gamma - \Gamma_0)\right) - \sigma_{sv} = 0.\end{aligned} \tag{11}$$

For stead fully developed open channel flow with a constant cross-section, the shape of the liquid/vapor interface is invariable and the flow velocity is independent of time and perpendicular to the cross-section. It implies that the result still does not be affected because the force balance is the same as the configuration shown in Figure 4. Consequently, equation (11) exhibits an important boundary condition in the simulation of surface tension dominated flows.

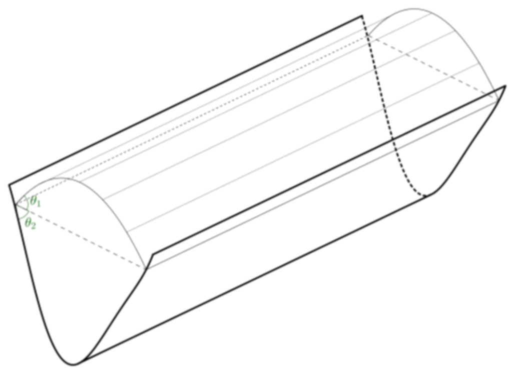

Fig. 4. *Liquid in a channel with a constant cross-section. The two contact lines are assumed to be located on the horizontal plane. The contact angles θ_1 and θ_2 are above and below the horizontal plane, respectively.*

V. The case for axisymmetric surfaces with angular velocity

In this section, we consider the case of an axisymmetric liquid container with an ideal axisymmetric solid surface surrounded by a gaseous phase. In addition, the solid container rotates and the liquid in it has an angular velocity ω with respect to the axis of symmetry. Note that the angular velocity ω is a function of position. Here we restrict the problem to a stationary case, namely, the shape of liquid inside the container is fixed and the angular velocity ω is time-independent.

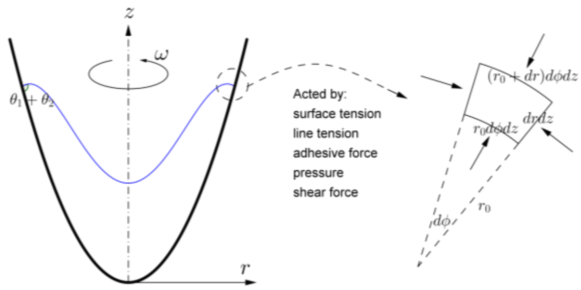

Fig. 5. *Liquid rotates with an angular velocity ω. For an infinitesimal element on the contact line, it is acted by the forces of surface tension, line tension, adhesive force, pressure, and friction in the horizontal direction.*

The magnitude of the centripetal force acting on the liquid is $\rho d\omega^2$ per unit volume, where d is the distance from the location of liquid to the axis of symmetry. For an infinitesimal fluid element on the contact line as shown in Figure 5, there are surface tension, line tension, adhesive force, pressure, and friction acting on it by considering the force balance in the horizontal direction. As a result, we can obtain

$$\begin{aligned}&(\sigma_{sv}\cos\theta_2 + f\sin\theta_2 - \sigma_{lv}\cos\theta_1 - \sigma_{sl}\cos\theta_2 - \tau / r_0)(r_0 + dr)d\phi dz \\ &+ pr_0 d\phi dz - (p + \frac{\partial p}{\partial r}dr)(r_0 + dr)d\phi dz + 2pdrdz\sin\frac{d\phi}{2} \\ &+ F_{shear} r_0 dr d\phi dz = -\rho(r_0 dr d\phi dz)r_0\omega^2\end{aligned} \tag{12}$$

where F_{shear} means the friction per unit volume. By dividing (12) with $r_0 d\phi dz$, equation (3) or (8) is derived again as dr approaches zero. We have known that (8) accounts for the force balance per unit length for an infinitesimal element. Thus, the rotating effect does not impact the contact angle directly. This result implies the relation between the contact angles is the same as indicated in (8) or (9) even though the container is rotating.

It is found that the contact angle is irrelevant to the rotating effect with a fixed surfactant concentration. The reason is similar to that for the phenomenon that the contact angle is almost independent of gravity which has been proved by the method of free energy minimization for the cases of planar surface [18] and vertical surface [20]. In reality, the rotating effect may change the surfactant concentration on the contact line, so the contact angle may be affected indirectly.

VI. Discussion

It is obvious that the summation of θ_1 and θ_2 in (9) and (11) have the same meaning as the contact angle θ_1 in (1). Both of them express the contact angle between the liquid-vapor interface and the solid substrate. The summation of θ_1 and θ_2 could be approximated by to the contact angle θ in (1) once the line tension τ is ignored. In general, it is true because the magnitude of line tension is much weaker than that of the surface tension. For example, the contact angle of mercury in a vertical tube made of soda-lime glass and exposed to air is about 140° [23], so the summation θ_1 and θ_2 for a mercury flow in an open channel made of soda-lime glass is also about 140°.

VII. Conclusions

The present work investigates the force balance of a liquid resting on a non-planar solid surface and derives the equations which can be considered as an extension of Boruvka-Neumann equation to depict a general relation between the contact angles, surface tensions, and surfactant concentration. These equations represent the force balance in the horizontal direction and the tangential direction by the employment of an infinitesimal fluid element approach. The horizontal one contains the adhesive force and the corresponding Boruvka-Neumann equation is exactly the force balance in the horizontal direction for the case of planar surface. For the force balance in the tangential direction, the adhesive force is absent and the result is more concise than that in the horizontal direction. The equations in the works of Rusanov [15] and Bormashenko [16] considered the force balance in the tangential direction only by the method of free energy minimization. The present results are more general including the force balance in both horizontal and tangential directions, and manifest the relationship between the contact angles and surface tensions on the free surface of a liquid resting on a non-planar surface with the surfactant effect, in which the concentration of surfactant is supposed to alter with the surface tension linearly.

The infinitesimal fluid element approach has the advantage of graphical interpretation of the Boruvka-Neumann equation by using the difference between the units of gravity and surface tension to conclude that the contact angle is independent of gravity. The result that the contact angle is independent of the angular velocity is due to the same reason. The line tension is generally much weaker than the surface tension, so the term representing the effect of line tension approaches zero when the radius of curvature of the triple contact line is large enough. In summary, the data of contact angles for various materials are applicable for most situations from a macroscopic point of view.

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