

Generalized Young Equation of Cylindrical Drops within a Homogeneous and Smooth Annular Two-layer Capillary

Long Zhou¹, Guang-Hua Sun², Xiao-Song Wang³

¹School of Mechanical and Power Engineering, Henan Polytechnic University, No. 2001, Century Avenue, Jiaozuo, Henan 454003, China

²School of Business Administration, Henan Polytechnic University, No. 2001, Century Avenue, Jiaozuo, Henan 454003, China

³School of Mechanical and Power Engineering, Henan Polytechnic University, No. 2001, Century Avenue, Jiaozuo, Henan 454003, China

ABSTRACT

In order to study the wetting characteristics of cylindrical droplets in a homogeneous and smooth annular two-layer capillary, based on the approaches of Gibbs's dividing surface and Rusanov's dividing line, a generalized Young equation describing contact angles has been successfully derived considering the effects of the line tension. Besides, under the hypothesis that the line tension is a constant, we also analyze this generalized Young equation to be reduced to the well known Young equation.

Keywords: Generalized Young equation, Cylindrical drop, Homogeneous and smooth, Contact angle, Capillary

1. INTRODUCTION

Surface wetting has been extensively used, for more than one century, to investigate the displacement of two immiscible fluids (universally, one fluid is vapor/gas, another one is liquid) settling on the solid surface [1], and plays a crucial role in numerous theoretical studies and industrial processes, such as flotation [2], dental implant [3], self-cleaning [4], pore material [5] and droplet evaporation [6]. Research into wetting properties is of great interest in designing products and applications that deal with the relationship between liquids and solids [7]–[11]. Wettability phenomenon is an area that involves the interaction of physics, chemistry, as well as other aspects, and is generally characterized by contact angles. Thomas Young [12] first presented the relation between three surface tensions, that is, solid/vapor interfacial tension (σ_{SV}), solid/liquid interfacial tension (σ_{SL}), and liquid/vapor interfacial tension (σ_{LV}), and the contact angle (so-called Young angle θ_Y) for a liquid on a homogeneous and perfectly flat solid substrate is determined by

$$\cos \theta_Y = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} \quad (1)$$

In fact, the above expression does not consider the line tension that has significant effects on the surface wetting. Since Gibbs introduced the concept of the line tension [13], the wetting investigations including the line tension have attracted a great deal of attention because of their engineering applications [14]–[18].

Dumitrascu and Borcia proposed an approach for precisely determining the contact angle between a liquid droplet and a cylindrical solid surface using the differential equation describing the dimensions of the drop [19]. Du et al. theoretically derived the dimensions and surface areas of liquids, and provided a good agreement between the theoretical and experimental results [20]. Liang et al. experimentally observed the effects of single butanol droplets for a wetted cylindrical surface and numerically simulated the spreading process of liquid drops in the directrix direction of a cylinder [21]. In short, substantial investigations have been performed concerning the wetting behaviors of cylindrical droplets.

However, up to now, there are still no reports regarding the wetting properties of liquid drops in an annular two-layer capillary. Therefore, in this manuscript, according to the methods of Gibbs's dividing surface and Rusnaov's dividing line, we derive a generalized Young equation for contact angles of cylindrical droplets in an annular two-layer capillary by means of thermodynamics. Moreover, we yet analyze the simplified formula of this generalized Young equation under the corresponding assumption.

2. CALCULATION OF SYSTEM FREE ENERGY

We begin by considering a single-component cylindrical drop (phase L), which are placed in a homogeneous and smooth annular two-layer capillary (phase S), and immersed in a vapor (phase V) in equilibrium, as shown in Figure 1.

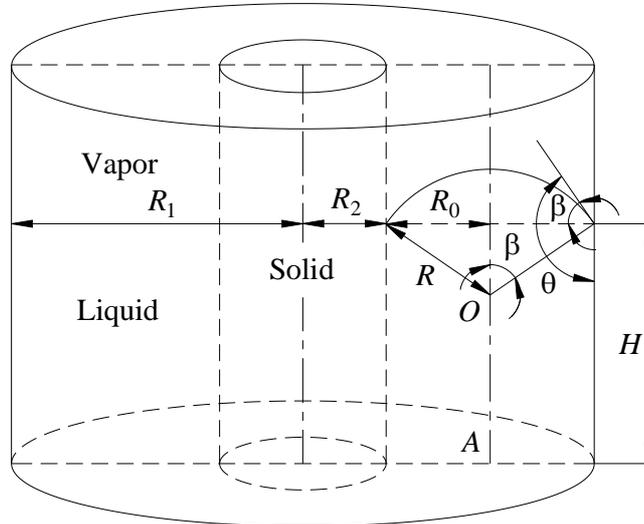


Figure 1 A cylindrical droplet in a homogeneous and smooth annular two-layer capillary

Based on the theory of Gibbs's dividing surface, the system in Figure 1 consists of six subsystems: liquid phase, vapor phase, solid-liquid interface, solid-vapor interface, liquid-vapor interface, as well as the triple phase line. And then, the Helmholtz free energy F of the total system can be described as

$$F = F_L + F_V + F_{SL} + F_{SV} + F_{LV} + F_{SLV} \tag{2}$$

where F_L , F_V , F_{SL} , F_{SV} , F_{LV} and F_{SLV} denote the Helmholtz free energies of the above six subparts, separately, the subscripts represent the quantities in relation to the homologous phases, interfaces and the three phase line (for example, the subscripts V and LV stand for the vapor phase and liquid-vapor interface, respectively), separately.

The Helmholtz free energies of various subparts are given in forms [22]

$$F_L = -p_L V_L + \mu_L N_L \tag{3}$$

$$F_V = -p_V V_V + \mu_V N_V \tag{4}$$

$$F_{SL} = \sigma_{SL} A_{SL} + \mu_{SL} N_{SL} \tag{5}$$

$$F_{SV} = \sigma_{SV} A_{SV} + \mu_{SV} N_{SV} \tag{6}$$

$$F_{LV} = \sigma_{LV} A_{LV} + \mu_{LV} N_{LV} \tag{7}$$

$$F_{SLV} = k L_{SLV} + \mu_{SLV} N_{SLV} \tag{8}$$

where p is the pressure, V is the volume, μ is the chemical potential, N is the molecular mole number, σ is the surface tension, A is the interfacial area, k is the line tension, and L is the length of the triple phase line.

For the goal of simplicity, without considering the gravitational forcing, consequently the equilibrium morphology of the cylindrical droplet in Figure 1 is an annular barrel with a cylindrical cap.

The volume V_L of the liquid phase is determined as

$$V_L = \pi(R_1^2 - R_2^2)H + \pi R^2(R_1 + R_2)(\beta - \sin \beta \cos \beta) \tag{9}$$

where R_1 and R_2 are the inner and outer radii of the annular capillary, separately, H is the vertical distance from the bottom of the annular capillary to the lower end of the cylindrical cap, R is the radius of the drop, and β is the apparent contact angle.

The volume V_t of the entire system is determined by

$$V_t = V_L + V_V \tag{10}$$

The surface area A_{LV} of the liquid-vapor interface is determined by

$$A_{LV} = 2\pi R\beta(R_1 + R_2) \quad (11)$$

The surface area A_{SL} of the solid-liquid interface is determined by

$$A_{SL} = 2\pi(R_1 + R_2)H + \pi(R_1^2 - R_2^2) \quad (12)$$

The total surface area A_t of the solid-liquid and solid-vapor interfaces is determined by

$$A_t = A_{SL} + A_{SV} \quad (13)$$

The length of the triple phase line is determined by

$$L_{SLV} = 2\pi(R_1 + R_2) \quad (14)$$

According to the above relationships, the free energies of various subparts can be further rewritten as

$$F_L = -p_L \cdot \left[\pi(R_1^2 - R_2^2)H + \pi R^2(R_1 + R_2) \right. \\ \left. (\beta - \sin \beta \cos \beta) \right] + \mu_L N_L \quad (15)$$

$$F_V = -p_V \cdot \left\{ V_t - \left[\pi(R_1^2 - R_2^2)H + \pi R^2(R_1 + R_2) \right. \right. \\ \left. \left. (\beta - \sin \beta \cos \beta) \right] \right\} + \mu_V N_V \quad (16)$$

$$F_{SL} = \sigma_{SL} \cdot \left[2\pi(R_1 + R_2)H + \pi(R_1^2 - R_2^2) \right] + \mu_{SL} N_{SL} \quad (17)$$

$$F_{SV} = \sigma_{SV} \cdot \left\{ A_t - \left[2\pi(R_1 + R_2)H + \pi(R_1^2 - R_2^2) \right] \right\} \\ + \mu_{SV} N_{SV} \quad (18)$$

$$F_{LV} = \sigma_{LV} \cdot 2\pi R\beta(R_1 + R_2) + \mu_{LV} N_{LV} \quad (19)$$

$$F_{SLV} = k \cdot 2\pi(R_1 + R_2) + \mu_{SLV} N_{SLV} \quad (20)$$

Now substituting the Eqs. (15-20) before into Eq. (2), we can write

$$F = -(p_L - p_V) \cdot \left[\pi(R_1^2 - R_2^2)H + \pi R^2(R_1 + R_2) \right. \\ \left. (\beta - \sin \beta \cos \beta) \right] - p_V \cdot V_t + (\sigma_{SL} - \sigma_{SV}) \cdot \\ \left[2\pi(R_1 + R_2)H + \pi(R_1^2 - R_2^2) \right] + \sigma_{LV} \cdot \\ 2\pi R\beta(R_1 + R_2) + \sigma_{SV} \cdot A_t + k \cdot 2\pi(R_1 + R_2) \\ + \mu_L N_L + \mu_V N_V + \mu_{LV} N_{LV} + \mu_{SL} N_{SL} + \mu_{SV} N_{SV} \\ + \mu_{SLV} N_{SLV} \quad (21)$$

3. DERIVATION OF GENERALIZED YOUNG EQUATION

The grand potential Ω of the system containing a solid, a single-component liquid drop and its equilibrium vapor is thermodynamically defined to be

$$\Omega = F - \sum_i \mu_i N_i \quad (22)$$

where the subscript i is the number of subparts of the total system.

Putting Eq. (21) into Eq. (22) to obtain again the grand potential Ω as

$$\Omega = -(p_L - p_V) \cdot \left[\pi(R_1^2 - R_2^2)H + \pi R^2(R_1 + R_2) \right. \\ \left. (\beta - \sin \beta \cos \beta) \right] - p_V \cdot V_t + (\sigma_{SL} - \sigma_{SV}) \cdot \\ \left[2\pi(R_1 + R_2)H + \pi(R_1^2 - R_2^2) \right] + \sigma_{LV} \cdot \\ 2\pi R\beta(R_1 + R_2) + \sigma_{SV} \cdot A_t + k \cdot 2\pi(R_1 + R_2) \quad (23)$$

Minimizing the grand potential Ω in regard to the radius R , there is

$$\left[\frac{d\Omega}{dR} \right] = 0 \quad (24)$$

On account of the interfacial tensions σ_{SL} and σ_{SV} without depending on the dividing surface [15], and then, we can write

$$\left[\frac{d\sigma_{SL}}{dR} \right] = 0, \left[\frac{d\sigma_{SV}}{dR} \right] = 0 \quad (25)$$

Substituting Eq. (23) into Eq. (24), and using Eq. (25), we have

$$\begin{aligned} & -(p_L - p_V) \cdot \left[\frac{dV_L}{dR} \right] + \left[\frac{d\sigma_{LV}}{dR} \right] \cdot A_{LV} + \sigma_{LV} \cdot \left[\frac{dA_{LV}}{dR} \right] \\ & + (\sigma_{SL} - \sigma_{SV}) \cdot \left[\frac{dA_{SL}}{dR} \right] + \left[\frac{dk}{dR} \right] \cdot L_{SLV} + k \cdot \left[\frac{dL_{SLV}}{dR} \right] = 0 \end{aligned} \quad (26)$$

In addition, the following expressions may be acquired from Figure 1

$$R \sin \beta = \frac{R_1 - R_2}{2} = R_0 = \text{const} \quad (27)$$

$$H - R \cos \beta = \overline{OA} = \text{const} \quad (28)$$

$$\theta = \beta + \frac{\pi}{2} \quad (29)$$

Taking the derivatives of Eqs. (27-28) with respect to the radius R arrives at

$$\frac{d\beta}{dR} = -\frac{\sin \beta}{R \cos \beta} \quad (30)$$

$$\frac{dH}{dR} = \frac{1}{\cos \beta} \quad (31)$$

By using both Eqs. (9, 11, 12, 14, 27) and Eqs. (30-31), we obtain

$$\left[\frac{dV_L}{dR} \right] = 2\pi R \beta (R_1 + R_2) \quad (32)$$

$$\left[\frac{dA_{LV}}{dR} \right] = 2\pi (R_1 + R_2) \left(\beta - \frac{\sin \beta}{\cos \beta} \right) \quad (33)$$

$$\left[\frac{dA_{SL}}{dR} \right] = 2\pi (R_1 + R_2) \frac{1}{\cos \beta} \quad (34)$$

$$\left[\frac{dL_{SLV}}{dR} \right] = 0 \quad (35)$$

For the cylindrical liquid drop with its equilibrium vapor, the pressure difference between the liquid and vapor phases is governed by the Laplace equation [22]

$$p_L - p_V = \frac{\sigma_{LV}}{R} + \left[\frac{d\sigma_{LV}}{dR} \right] \quad (36)$$

Now substituting Eqs. (32-36) into Eq. (26) yields

$$\sin \beta = \frac{\sigma_{SL} - \sigma_{SV}}{\sigma_{LV}} + \frac{\cos \beta}{\sigma_{LV}} \cdot \left[\frac{dk}{dR} \right] \quad (37)$$

Using Eq. (29), Eq. (37) becomes

$$\cos \theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} - \frac{\sin \theta}{\sigma_{LV}} \cdot \left[\frac{dk}{dR} \right] \quad (38)$$

Putting the familiar Young equation (1) into Eq. (38) satisfies

$$\cos \theta = \cos \theta_Y - \frac{\sin \theta}{\sigma_{LV}} \cdot \left[\frac{dk}{dR} \right] \quad (39)$$

Therefore, for cylindrical drops within a homogeneous and smooth annular two-layer capillary, Eq. (39) is the generalized Young equation which applies to random surfaces dividing both the liquid and vapor phases. Provided that the derivative of the line tension is equal to zero, i.e., the line tension is a constant, Eq. (39) reduces to the classical Young equation (1).

4. CONCLUSIONS

In the present work, according to both Gibbs's way concerning the dividing surface and Rusanov's approach with respect to the dividing line, the wetting properties of cylindrical drops within a homogeneous and smooth annular two-layer capillary are investigated thermodynamically. Accounting for the impacts of the line tension, a generalized Young equation depicting contact angles between cylindrical drops and the inner wall surface of an annular two-layer capillary has been derived by method of thermodynamics. Only if we assume that the line tension is a constant, this generalized Young equation will decrease to the Young equation used commonly.

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