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A generalized Young's equation for contact angles of droplets on homogeneous and rough substrates

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Using Gibbs' method of dividing surfaces, the contact angle of a drop on a flat homogeneous rough non-deformable solid substrate is investigated. For this system, a new generalized Young's equation for the contact angle, including the influences of line tension and which valid for any dividing surface between liquid phase and vapor phase is derived. Under some assumptions, this generalized Young's equation reduces to the Wenzel's equation or Rosanov's equation valid for the surface of tension.

Keywords: contact angle; Young's equation; line tension; thermodynamics; dividing surface; dividing line

1. Introduction

Wetting phenomena are common in nature, for instance adhesions or adhesives, lubricants, biological membranes, capillary penetrations into porous media, and floatations. [1–8]

For the cases of smooth solid substrates, the contact angle θ_Y between a liquid and the solid (non-deformable) substrate is determined by the Young's equation [1]

$$\cos \theta_Y = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}}, \quad (1)$$

where σ_{SG} , σ_{SL} , and σ_{LG} are the thermodynamic surface tensions of the solid–gas interface, solid–liquid interface, and liquid–gas interface, respectively.

In fact, for a drop on a solid substrate, there is often the formation of an underlying (precursor) film modifying the solid surface and leading to a difference between and the surface tension of a 'bare' solid surface. The precursor film thickness makes the contact angle somewhat obscured. So, when we mention the contact angle, it means neglecting the precursor film thickness.

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Obviously, the Young's equation is not applicable to rough surfaces, and it does not contain the effect of the line tension of the three-phase contact line. It is natural to consider the effect of the line tension of the three-phase contact line and generalize the Young's equation to the cases of rough substrates.

Some generalized Young's equations [9–16] considered the cases of rough substrates, but without taking into account the effect of the tension of the three-phase contact line. For example, for the cases of rough non-deformable solid substrates, neglecting the effect of the line tension, Wenzel [9] established the following equation:

$$\cos \theta = r_S \cos \theta_Y, \quad (2)$$

where θ is the contact angle and r_S is the surface roughness ratio

$$r_S = \frac{A_{\text{real}}}{A_{\text{apparent}}} \times 100\%, \quad (3)$$

with A_{real} being the true value of the surface area and A_{apparent} being the apparent value. It is obvious that r_S is always bigger than one.

Rusanov et al. considered the line tension effects to obtain some generalized Young's equations, among which some are applicable to rough non-deformable solid substrates.[17–20] For example, in 2004, for smooth non-deformable solid substrates, using Gibbs concept of dividing surfaces, Rusanov et al. [20] obtained a generalized Young's equation

$$\cos \theta = \cos \theta_Y - \frac{\kappa}{\sigma_{\text{LG}} R_L} - \frac{1}{\sigma_{\text{LG}}} \left[\frac{d\kappa}{dR_L} \right], \quad (4)$$

where R_L is the radius of the three-phase contact line, κ is the corresponding line tension, and the differential in square bracket $\left[\frac{d\kappa}{dR_L} \right]$ denotes the change of the value of the line tension κ resulted from a mathematical variation in the value of the radius of the three-phase contact line R_L by the amount dR_L .

For rough non-deformable solid substrates, Rusanov [18] obtained a comprehensive result

$$\cos \theta = r_S \cos \theta_Y - \left[\frac{r_L \kappa}{R_L} + \frac{\partial(r_L \kappa)}{\partial R_L} \right] \frac{|\cos \varphi|}{\sigma_{\text{LG}}} \quad (5)$$

where φ is the angle between the substrate surface and the local principal plane of the three-phase contact line, and r_L is line roughness ratio

$$r_L = \frac{L_{\text{real}}}{L_{\text{apparent}}} \times 100\%, \quad (6)$$

where L_{real} is the true value of the length of the three-phase contact line and L_{apparent} is the apparent value.

However, Equation (5) is valid only for the special dividing surface, called the surface of tension [21], between the liquid phase and the vapor phase. In this study, we

will consider the case of a liquid on a flat homogeneous rough non-deformable solid substrate ($\varphi=0$) and derive a new generalized Young's equation for the contact angle θ , which will contain the effect of line tension and will be valid for any general dividing surface between the liquid phase and the vapor phase. In Section 2, the Helmholtz free energy F of this system will be given. The new generalized Young's equation for this system will be derived in Section 3.

2. The Helmholtz free energy for droplets on a rough substrate

For a droplet on a flat homogeneous rough non-deformable solid substrate, the solid surface may be either hydrophobic or hydrophilic (as an example, for hydrophilic wetting, refer to Figure 1). The contact angle θ is decided by the balance of the forces acting on the element of three-phase contact line. Among these forces, the contributions of surface forces σ_{SG} , σ_{SL} , and σ_{LG} are proportional to the length of the element of three-phase contact line. However, the contributions of gravitation are proportional to the volume of the element, which is zero; therefore the contact angle is independent of gravitation. Therefore, for the investigation of the contact angle, we can take the gravitation as zero in the following discussion. Thus, the equilibrium shape of a droplet on a solid substrate is a segment.

For a solid with a flat homogeneous rough non-deformable surface, the sole part that affects the wetting of the liquid on it is the surface of the solid; therefore, for simplicity, we can only consider the surface of the solid and the interior of the solid is not considered in our investigation of the contact angle. According to Gibbs's concept of dividing surface [21] and Boruvka–Neumann's concept of dividing line [17], the above simplified solid–liquid–gas physical system can be described by a model system consisting of six parts, i.e. liquid phase, gas phase, the liquid–gas interface, the solid–liquid interface, the solid–gas interface, and the three-phase contact line, and the definitions of all the extensive quantities of the model phases can be given. According to these definitions, any total extensive quantity of the model system is equal to that of the physical system. Any total extensive quantity of the model system, for instance the total real volume V , total real mole number N_i of molecules of class i , and total real

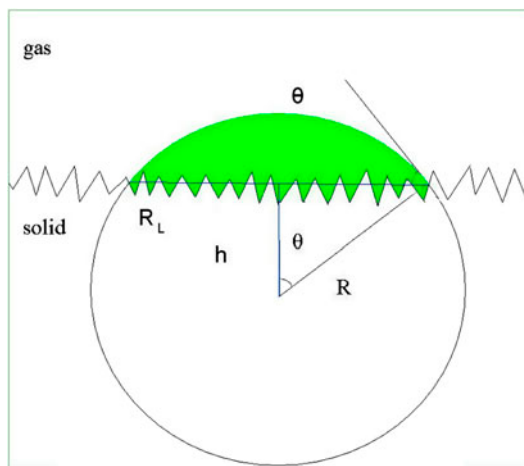


Figure 1. An illustration of hydrophilic wetting of a droplet on a flat homogeneous rough non-deformable solid substrate.

Helmholtz free energy F , is equal to the sum of those of the six parts. Therefore, the total Helmholtz free energy F of the model system is

$$F = F_L + F_G + F_{LG} + F_{SL} + F_{SG} + F_{SLG}, \quad (7)$$

where F_L , F_G , F_{LG} , F_{SL} , F_{SG} , and F_{SLG} are the Helmholtz free energies of the six parts, respectively,[22]

$$F_L = -p_L V_L + \sum_i \mu_i N_{iL} \quad (8)$$

$$F_G = -p_G V_G + \sum_i \mu_i N_{iG} \quad (9)$$

$$F_{LG} = \sigma_{LG} A_{LG} + \sum_i \mu_i N_{iLG} \quad (10)$$

$$F_{SL} = \sigma_{SL} A_{SL} + \sum_i \mu_i N_{iSL} \quad (11)$$

$$F_{SG} = \sigma_{SG} A_{SG} + \sum_i \mu_i N_{iSG} \quad (12)$$

$$F_{SLG} = \kappa L_{SLG} + \sum_i \mu_i N_{iSLG} \quad (13)$$

where p_L and p_G are the pressures of the liquid phase and vapor phase, respectively, V_L and V_G are the volumes of the liquid phase and vapor phase, respectively, μ_i is the chemical potentials of the molecule of class i , N_{iL} , N_{iG} , N_{iLG} , N_{iSL} , N_{iSG} , N_{iSLG} are the mole numbers of the molecules of class i in liquid phase, vapor phase, liquid–vapor interface, solid–liquid interface, solid–vapor interface, and the three-phase contact line, respectively, A_{LG} , A_{SL} and A_{SG} are the surface areas of liquid–vapor interface, solid–liquid interface, solid–vapor interface, respectively, σ_{LG} , σ_{SL} , and σ_{SG} are the surface tensions of liquid–vapor interface, solid–liquid interface, and solid–vapor interface, respectively, L_{SLG} is the length of the three-phase contact line, and κ is the line tension.

Now, let us calculate some related geometrical quantities in the above equations, respectively.

The volume of the liquid phase V_L is

$$V_L = \frac{\pi R^3}{3} (2 + \cos \theta) (1 - \cos \theta)^2, \quad (14)$$

where R is the radius of the spherical liquid droplet. The total volume V_t of the system is

$$V_t = V_L + V_G \quad (15)$$

The surface area A_{LG} of the liquid–gas interface is

$$A_{LG} = 2\pi R^2(1 - \cos \theta). \quad (16)$$

The apparent surface area A_{SLa} of the solid–liquid interface is

$$A_{SLa} = \pi R^2 \sin^2 \theta. \quad (17)$$

The real surface area A_{SL} of the solid–liquid interface is

$$A_{SL} = r_S A_{SLa} = r_S \pi R^2 \sin^2 \theta. \quad (18)$$

The total apparent surface area A_{ta} of the solid–liquid interface and the solid–gas interface is

$$A_{ta} = A_{SLa} + A_{SGa}, \quad (19)$$

where A_{SGa} is the apparent surface area of the solid–gas interface.

The real surface area of the solid–gas interface is

$$A_{SG} = r_S(A_{ta} - \pi R^2 \sin^2 \theta), \quad (20)$$

where r_S is the surface roughness factor.

The apparent length and the real length of the three-phase contact line are

$$L_a = 2\pi R_L = 2\pi R \sin \theta \quad (21)$$

and

$$L = r_L L_a = 2\pi R r_L \sin \theta, \quad (22)$$

respectively.

Based on the above relations, we have

$$F_L = -p_L \frac{\pi R^3}{3} (2 + \cos \theta)(1 - \cos \theta)^2 + \sum_i \mu_i N_{iL} \quad (23)$$

$$F_G = -p_G \left[V_i - \frac{\pi R^3}{3} (2 + \cos \theta)(1 - \cos \theta)^2 \right] + \sum_i \mu_i N_{iG} \quad (24)$$

$$F_{LG} = \sigma_{LG} 2\pi R^2 (1 - \cos \theta) + \sum_i \mu_i N_{iLG} \quad (25)$$

$$F_{SL} = \sigma_{SL} r_S \pi R^2 \sin^2 \theta + \sum_i \mu_i N_{iSL} \quad (26)$$

$$F_{SG} = \sigma_{SG} r_S (A_{ta} - \pi R^2 \sin^2 \theta) + \sum_i \mu_i N_{iSG} \quad (27)$$

$$F_{SLG} = \kappa r_L 2\pi R \sin \theta + \sum_i \mu_i N_{iSLG} \quad (28)$$

Putting the above results into Equation (7), we obtain the total Helmholtz free energy

$$\begin{aligned}
 F = & -(p_L - p_G) \frac{\pi R^3}{3} (2 + \cos \theta)(1 - \cos \theta)^2 - p_G V_t + \sigma_{LG} 2\pi R^2 (1 - \cos \theta) \\
 & + (\sigma_{SL} - \sigma_{SG}) r_S \pi R^2 \sin^2 \theta + \sigma_{SG} r_S A_{ta} + \kappa r_L 2\pi R \sin \theta + \sum_i \mu_i N_{iL} \\
 & + \sum_i \mu_i N_{iG} + \sum_i \mu_i N_{iSL} + \sum_i \mu_i N_{iLG} + \sum_i \mu_i N_{iSG} + \sum_i \mu_i N_{iSLG} \quad (29)
 \end{aligned}$$

3. A new generalized Young's equation in terms of the general dividing surface

The definition of the grand potential Ω of a system is

$$\Omega = F - \sum_i \mu_i N_i, \quad (30)$$

where N_i is the mole number of molecules of class i in the system.

From Equations (29) and (30), the total grand potential Ω of the system is obtained

$$\begin{aligned}
 \Omega = & -(p_L - p_G) \frac{\pi R^3}{3} (2 + \cos \theta)(1 - \cos \theta)^2 - p_G V_t + \sigma_{LG} 2\pi R^2 (1 - \cos \theta) \\
 & + (\sigma_{SL} - \sigma_{SG}) r_S \pi R^2 \sin^2 \theta + \sigma_{SG} r_S A_{ta} + \kappa r_L 2\pi R \sin \theta \quad (31)
 \end{aligned}$$

For an arbitrary choice of liquid–vapor dividing surface, the real physical quantities of the system and the external conditions are not changed. Therefore, the total grand potential Ω , σ_{SG} , and σ_{SL} are independent of the arbitrary choice of the position of the liquid–vapor dividing surface, and so we have the following restriction:

$$\left[\frac{d\Omega}{dR} \right] = 0, \quad (32)$$

$$\left[\frac{d\sigma_{SL}}{dR} \right] = 0, \quad \left[\frac{d\sigma_{SG}}{dR} \right] = 0, \quad (33)$$

where the differential in square bracket denotes the change in the value of the total grand potential free energy Ω resulted from a variation in the position of this dividing surface by the amount dR .

Putting Equation (31) into (32), we have

$$\begin{aligned}
 & -(p_L - p_G) \left[\frac{df_1}{dR} \right] + \left[\frac{d\sigma_{LG}}{dR} \right] f_2 + \sigma_{LG} \left[\frac{df_2}{dR} \right] \\
 & + (\sigma_{SL} - \sigma_{SG}) r_S \left[\frac{df_3}{dR} \right] + \left[\frac{d(r_L \kappa)}{dR} \right] f_4 + r_L \kappa \left[\frac{df_4}{dR} \right] = 0 \quad (34)
 \end{aligned}$$

where

$$f_1 = \frac{\pi R^3}{3} (2 + \cos \theta)(1 - \cos \theta)^2, \quad (35)$$

$$f_2 = 2\pi R^2 (1 - \cos \theta), \quad (36)$$

$$f_3 = \pi R^2 \sin^2 \theta, \quad (37)$$

$$f_4 = 2\pi R \sin \theta. \quad (38)$$

All dividing surfaces of liquid–gas interface of a liquid droplet on a flat homogeneous rough non-deformable solid substrate should be parts of concentric and conformal spherical surface. These dividing surfaces are segmental. Therefore, we have the following relationships:

$$\begin{aligned} R \cos \theta = h = \text{const}, \quad \frac{d\theta}{dR} &= \frac{\cos \theta}{R \sin \theta} \frac{dR_L}{dR} = \frac{1}{\sin \theta} \\ R \cos \theta = h = \text{const}, \quad \frac{d\theta}{dR} &= \frac{\cos \theta}{R \sin \theta} \end{aligned} \quad (39)$$

and

$$\frac{dR_L}{dR} = \frac{1}{\sin \theta} \quad (40)$$

Using Equations (36)–(39), we have the following results:

$$\left[\frac{df_1}{d\theta} \right] = 2\pi R^2 (1 - \cos \theta), \quad (41)$$

$$\left[\frac{df_2}{d\theta} \right] = 2\pi R (2 - \cos \theta), \quad (42)$$

$$\left[\frac{df_3}{d\theta} \right] = 2\pi R, \quad (43)$$

$$\left[\frac{df_4}{d\theta} \right] = \frac{2\pi}{\sin \theta}. \quad (44)$$

It is obvious that the generalized Laplace's equation of a free spherical droplet in vapor is [22]

$$p_L - p_G = \frac{2\sigma_{LG}}{R} + \left[\frac{d\sigma_{LG}}{dR} \right] \quad (45)$$

can be used for the segment.

Putting Equations (41)–(45) into Equation (34), we obtain

$$\cos \theta = r_S \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}} - \frac{r_L \kappa}{\sigma_{LG} R \sin \theta} - \frac{\sin \theta}{\sigma_{LG}} \left[\frac{d(r_L \kappa)}{dR} \right]. \quad (46)$$

Equation (46) is a new generalized Young's equations for droplets on a flat homogeneous rough non-deformable solid substrate for any dividing surface between liquid phase and vapor phase.

By using Young's equation, Equations (1) and (46) can be written as

$$\cos \theta = r_S \cos \theta_Y - \frac{r_L \kappa}{\sigma_{LG} R \sin \theta} - \frac{\sin \theta}{\sigma_{LG}} \left[\frac{d(r_L \kappa)}{dR} \right]. \quad (47)$$

Noticing Equations (21) and (40), we can write Equation (47) as

$$\cos \theta = r_S \cos \theta_Y - \frac{r_L \kappa}{\sigma_{LG} R_L} - \frac{1}{\sigma_{LG}} \left[\frac{d(r_L \kappa)}{dR_L} \right]. \quad (48)$$

Besides, for the surface of tension, we have

$$\left[\frac{d(r_L \kappa)}{dR_L} \right] = \left(\frac{\partial(r_L \kappa)}{\partial R_L} \right)_{T, \{\mu_i\}} \quad (49)$$

(where T is the absolute temperature), which can be derived by the method similar to Rusanov et al.'s proof for the Equation (49) with $r_L = 1$ under the condition of smooth substrate.[20] Then, Equations (48) and (49) give

$$\cos \theta = r_S \cos \theta_Y - \frac{r_L \kappa}{\sigma_{LG} R_L} - \frac{1}{\sigma_{LG}} \left(\frac{\partial(r_L \kappa)}{\partial R_L} \right)_{T, \{\mu_i\}}. \quad (50)$$

This equation is the same as Equation (5) with $\varphi = 0$.

If we suppose $r_S = 1$ and $r_L = 1$, then Equation (48) reduces to the generalized Young's equation, Equation (4), obtained by Rusanov et al. [20]

The dividing line is characterized by $R_L = R_{LT}$, satisfying

$$\left[\frac{d(\kappa r_L)}{dR_L} \right]_{R_L = R_{LT}} = 0 \quad (51)$$

can be called as the line of tension, which, by taking $r_L = 1$, will reduce to the definition of the line of tension of smooth surface.[20]

Therefore, for the line of tension, Equation (48) reduces to

$$\cos \theta = r_S \cos \theta_Y - \frac{r_L \kappa_t}{\sigma_{LG} R_{LT}}, \quad (52)$$

where

$$\kappa_l = \kappa|_{R_L=R_{LT}}.$$

If we ignore the line tension, then both Equations (50) and (52) reduce to the Wenzel Equation (2).

4. Conclusion

It is an interesting task to use the method of dividing surfaces and dividing lines to investigate the wetting phenomena of spherical droplets on rough substrates, including the influences of line tension. We have studied the wetting of droplets on rough non-deformable substrates by methods of thermodynamics with Gibbs's concept of dividing surface and Boruvka–Neumann's concept of dividing line. A generalized Young's equation for contact angles between droplets and rough non-deformable substrates, including the influences of line tension, has been derived in terms of general dividing surface. Under some assumptions, this generalized Young's equation reduces to the Wenzel's equation or Rosanov's equation in terms of surface of tension.

5. Discussion

In 2008, Dai and Zhao [23] established an electrowetting model for rough surfaces under low voltage. Further generalizations of Dai and Zhao's work by using the method of dividing surfaces used in this work may be possible. Recently, Wang and Zhao [8] studied the electrowetting on curved surfaces. This interesting and important work suggests that it is possible to further generalize our results to the case of wetting phenomena on curved surfaces.

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