Generalized Cassie-Baxter equation for wetting of a spherical droplet within a smooth and heterogeneous conical cavity

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Abstract

Introducing the concepts of both Gibbs's dividing surface and Rusanov's dividing line, the wettability behaviors of spherical drops inside a smooth and heterogeneous conical cavity are studied. A new generalized Cassie-Baxter equation for contact angles including the influences of the line tension is derived thermodynamically. Additionally, various approximate formulae of this generalized Cassie-Baxter equation are also discussed correspondingly under some assumptions.

Keywords: Contact angle; Generalized Cassie-Baxter equation; Line tension; Cone; Dividing surface

1. Introduction

Strong understanding the wetting phenomena of liquid droplets on solid surfaces is very important for designing and controlling wettability characteristics in industrial applications and daily lives. Extensive interests have been attracted to investigate the wetting cases of solids by liquids for about three centuries, particularly in recent twenty years. The most fundamental theory about the wetting behaviors is the Young's equation [1] for contact angle θ_Y of liquid droplets on smooth and chemically homogeneous solid surfaces given by,

$$\cos\theta_Y = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}} \tag{1}$$

where σ_{SG}, σ_{SL} and σ_{LG} are the surface tensions of the solid-vapor, solid-liquid, and liquid-vapor interfaces, separately.

Evidently, the Young equation (1) only applies to smooth and homogeneous cases, but real solid surfaces are usually rough and heterogeneous. Fortunately, the Wenzel equation was developed in the 1930s for the wettability of rough surfaces. Subsequently, in the 1940s, for the wetting of smooth and heterogeneous surfaces, the classical Cassie-Baxter equation [2] for contact angle θ was proposed by

$$\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{2}$$

where θ_1 and θ_2 are the contact angles that liquid droplets make with solid surfaces 1 and 2, f_1 and f_2 are the area fractions of 1 and 2 surfaces below droplets.

Despite the theoretical basis for wetting properties of drops is established by the above mentioned Young equation, Wenzel equation, and Cassie-Baxter equation, all of them ignore the influences of the line tension. A large number of investigations [3-10] show that the line tension considerably depends on the curvature radius of the triple phase line. A review of earlier studies about the line tension can be obtained in reference [11].

In fact, since Gibbs introduces the concept of the line tension primitively, the classical Young's equation is generalized so as to include the effects of the line tension [6, 9]. For example, the generalized Young's equation proposed by Pethica [3] satisfies

$$\cos\theta = \cos\theta_Y - \frac{k}{\sigma_{LG} R_L} \tag{3}$$

where R_L is the radius of the three phase line, and k is the corresponding line tension.

In 2004, through the method of Gibbs's dividing surface, Rusanov [4] also developed a generalized Young's equation

$$\cos\theta = \cos\theta_Y - \frac{k}{\sigma_{LG} R_L} - \frac{1}{\sigma_{LG}}\left[\frac{dk}{dR_L}\right] \tag{4}$$

where the quantity in square bracket stands for the derivation of the line tension k by the radius R_L of the triple phase line.

In terms of the wetting of drops on heterogeneous solid surfaces, many investigators have carried out considerable works. Swain [12] developed a new generalized Young equation for liquid droplets on a rough and heterogeneous solid by a novel minimization method. Fang [13] applied the Neumann-Good parallel strip model to analyze the contact angle hysteresis of drops on a heterogeneous surface. Towles [14] analyzed the influences of the contact angle on the packing, or thickness mismatch contribution to the line tension. Raj [15] thermodynamically studied the effects of the contact line distortion to the wetting of drops on heterogeneous and superhydrophobic surfaces. In a recent paper, Kwon [16] investigated the static and dynamic characteristics of nano-scale drops on chemically heterogeneous surfaces using the method of molecular dynamics simulations. In addition, Zhang [17] discussed the influences of surface heterogeneities on the evaporation of drops from solid surfaces also utilizing molecular dynamics simulations.

However, up to now, the wetting of spherical droplets inside a smooth and heterogeneous conical cavity has not been performed. In this paper, based on the theories of both Gibbs's dividing surface and Rusanov's dividing line, the wetting of spherical droplets within a smooth and heterogeneous cone is studied. At the same time, a new generalized Cassie-Baxter equation of drops inside a smooth and heterogeneous conical cavity is derived accordingly. This equation is applicable to random dividing surface between the liquid and vapor phases. Additionally, we yet analyze various simplified expressions of this generalized Cassie-Baxter equation through some hypotheses.

2. Calculating the free energy of the system

Let us now consider a single component spherical droplet (phase L) located inside a smooth and chemically heterogeneous cone (phase S) with its equilibrium vapor (phase G), as illustrated in Figure 1.

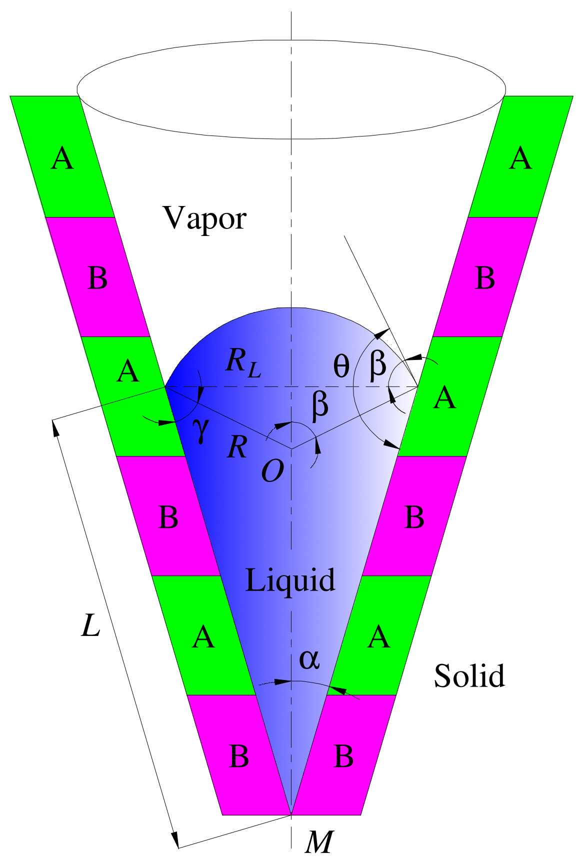

Figure 1. Schematic representation of a spherical droplet in a smooth and chemically heterogeneous conical cavity

For the purpose of simplicity, it can be seen from Figure 1 that the cone is composed of two types of different materials A and B. Consequently, there are two kinds of solid/liquid interfaces, two sorts of solid/vapor interfaces, as well as two classes of triple phase lines. The Young equation describing contact angles $\theta_i\ (i=1,2)$ of two heterogeneous solids can be together given by,

$$\cos\theta_i = \frac{\sigma_{SGi} - \sigma_{SLi}}{\sigma_{LG}} \tag{5}$$

where σ is the surface tension, the triple subscripts denote the quantities with respect to the corresponding interfaces (such as the subscript SGi marks the solid-vapor interface, where i being the label of solid and having two values of 1 and 2.).

Via the theories of both Gibbs's dividing surface and Rusanov's dividing line, the overall solid/liquid/vapor system in Figure 1 includes six parts, i.e., liquid phase, vapor phase, solid-liquid interface, solid-vapor interface, liquid-vapor interface, together with the three phase line. Thus, the Helmholtz free energy F of the entire system is

$$F = F_L + F_G + F_{SL} + F_{SG} + F_{LG} + F_{SLG} \tag{6}$$

where F_L, F_G, F_{SL}, F_{SG}, F_{LG} and F_{SLG} are the Helmholtz free energies of the six parts mentioned above.

The Helmholtz free energies of these six parts can be given respectively by [18],

$$F_L = -p_L V_L + \mu_L N_L \tag{7}$$

$$F_G = -p_G V_G + \mu_G N_G \tag{8}$$

$$F_{LG} = \sigma_{LG} A_{LG} + \mu_{LG} N_{LG} \tag{9}$$

$$F_{SL} = \left(f_1\sigma_{SL1} + f_2\sigma_{SL2}\right) A_{SL} + \mu_{SL} N_{SL} \tag{10}$$

$$F_{SG} = \left(f_1\sigma_{SG1} + f_2\sigma_{SG2}\right) A_{SG} + \mu_{SG} N_{SG} \tag{11}$$

$$F_{SLG} = \left(g_1 k_1 + g_2 k_2\right) L_{SLG} + \mu_{SLG} N_{SLG} \tag{12}$$

where p is the pressure, V is the volume, μ is the chemical potential, N is the mole number of molecule, A is the surface area, σ is the surface tension, k is the line tension, and L is the length of the three phase line, f_1 and f_2 are the fractional surface areas occupied by two solid-liquid interfaces or two solid-vapor interfaces such that $f_1 + f_2 = 1$, and g_1 and g_2 are the fractional lengths of two three phase lines such that $g_1 + g_2 = 1$.

In order to highly calculate the geometrical quantities in the above equations, we assume that the gravity and other forces or fields are ignored simultaneously. Hence, the equilibrium shape of droplets in a conical cavity is the sum of a cone and a segment.

The volume V_L of the liquid phase is

$$V_L = \frac{\pi}{3} R^3 \sin^3\beta \frac{\cos\alpha}{\sin\alpha} + \frac{\pi}{3} R^3 \left(1-\cos\beta\right)^2 \left(2+\cos\beta\right) \tag{13}$$

where R is the radius of the droplet, α is the half cone angle, and β is the apparent contact angle.

The total volume V_t of the system is

$$V_t = V_L + V_G \tag{14}$$

The surface area A_{LG} of the liquid-vapor interface is

$$A_{LG} = 2\pi R^2 \left(1-\cos\beta\right) \tag{15}$$

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

$$A_{SL} = \pi R^2 \frac{\sin^2\beta}{\sin\alpha} \tag{16}$$

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

$$A_t = A_{SL} + A_{SG} \tag{17}$$

The length of the triple phase line is

$$L_{SLG} = 2\pi R\sin\beta \tag{18}$$

Applying the above relations, the free energies of six subsystems can be rewritten by,

$$F_L = -p_L \cdot \left[\frac{\pi}{3}R^3\sin^3\beta\frac{\cos\alpha}{\sin\alpha} + \frac{\pi}{3}R^3\left(1-\cos\beta\right)^2\left(2+\cos\beta\right)\right] + \mu_L N_L \tag{19}$$

$$F_G = -p_G \cdot \left\{V_t - \left[\frac{\pi}{3}R^3\sin^3\beta\cdot\frac{\cos\alpha}{\sin\alpha} + \frac{\pi}{3}R^3\left(1-\cos\beta\right)^2\left(2+\cos\beta\right)\right]\right\} + \mu_G N_G \tag{20}$$

$$F_{LG} = \sigma_{LG}\cdot 2\pi R^2\left(1-\cos\beta\right) + \mu_{LG}N_{LG} \tag{21}$$

$$F_{SL} = \left(f_1\sigma_{SL1} + f_2\sigma_{SL2}\right)\cdot\pi R^2\frac{\sin^2\beta}{\sin\alpha} + \mu_{SL}N_{SL} \tag{22}$$

$$F_{SG} = \left(f_1\sigma_{SG1} + f_2\sigma_{SG2}\right)\cdot\left[A_t - \pi R^2\frac{\sin^2\beta}{\sin\alpha}\right] + \mu_{SG}N_{SG} \tag{23}$$

$$F_{SLG} = \left(g_1k_1 + g_2k_2\right)\cdot 2\pi R\sin\beta + \mu_{SLG}N_{SLG} \tag{24}$$

By putting the above Eqs. (19-24) into Eq. (6), the free energy F of the overall system has the form,

$$\begin{aligned} F = &-\left(p_L - p_G\right)\cdot\left[\frac{\pi}{3}R^3\sin^3\beta\cdot\frac{\cos\alpha}{\sin\alpha} + \frac{\pi}{3}R^3\left(1-\cos\beta\right)^2\left(2+\cos\beta\right)\right] \\ &- p_G\cdot V_t + \sigma_{LG}\cdot 2\pi R^2\left(1-\cos\beta\right) + \mu_L N_L + \mu_G N_G + \mu_{LG}N_{LG} \\ &+ \left[\left(f_1\sigma_{SL1} + f_2\sigma_{SL2}\right) - \left(f_1\sigma_{SG1} + f_2\sigma_{SG2}\right)\right]\cdot\pi R^2\frac{\sin^2\beta}{\sin\alpha} \\ &+ \left(f_1\sigma_{SG1} + f_2\sigma_{SG2}\right)\cdot A_t + \left(g_1k_1 + g_2k_2\right)\cdot 2\pi R\sin\beta + \\ &+ \mu_{SL}N_{SL} + \mu_{SG}N_{SG} + \mu_{SLG}N_{SLG} \end{aligned} \tag{25}$$

3. Derivation of a new generalized Cassie-Baxter equation

The grand potential Ω of a system composed of liquid droplets in contact with solid and vapor phases may be expressed as

$$\Omega = F - \sum_i \mu_i N_i \tag{26}$$

where the subscript i stands for the sum of both phases and interfaces of the system.
Substituting Eq. (25) into Eq. (26), the grand potential Ω can be rewritten as,

$$\begin{aligned}\Omega = &-\left(p_L - p_G\right)\cdot\left[\frac{\pi}{3}R^3\sin^3\beta\cdot\frac{\cos\alpha}{\sin\alpha}+\frac{\pi}{3}R^3\left(1-\cos\beta\right)^2\left(2+\cos\beta\right)\right]\\ &- p_G\cdot V_t + \sigma_{LG}\cdot 2\pi R^2\left(1-\cos\beta\right)\\ &+\left[\left(f_1\sigma_{SL1}+f_2\sigma_{SL2}\right)-\left(f_1\sigma_{SG1}+f_2\sigma_{SG2}\right)\right]\cdot\pi R^2\frac{\sin^2\beta}{\sin\alpha}\\ &+\left(f_1\sigma_{SG1}+f_2\sigma_{SG2}\right)\cdot A_t+\left(g_1k_1+g_2k_2\right)\cdot 2\pi R\sin\beta\end{aligned} \tag{27}$$

Minimizing the grand potential Ω with respect to the radius R, we have

$$\left[\frac{d\Omega}{dR}\right]=0 \tag{28}$$

Because four surface tensions σ_{SL1}, σ_{SL2}, σ_{SG1}, and σ_{SG2} don't depend on the choice of the dividing surface [6], one obtains

$$\left[\frac{d\sigma_{SL1}}{dR}\right]=\left[\frac{d\sigma_{SL2}}{dR}\right]=0 \tag{29}$$

$$\left[\frac{d\sigma_{SG1}}{dR}\right]=\left[\frac{d\sigma_{SG2}}{dR}\right]=0 \tag{30}$$

By utilizing equations (27-30), we have

$$\begin{aligned}&-\left(p_L-p_G\right)\cdot\left[\frac{dx_1}{dR}\right]+\left[\frac{d\sigma_{LG}}{dR}\right]\cdot x_2+\sigma_{LG}\cdot\left[\frac{dx_2}{dR}\right]\\ &+\left[\left(f_1\sigma_{SL1}+f_2\sigma_{SL2}\right)-\left(f_1\sigma_{SG1}+f_2\sigma_{SG2}\right)\right]\cdot\left[\frac{dx_3}{dR}\right]\\ &+\left[\frac{d\left(g_1k_1+g_2k_2\right)}{dR}\right]\cdot x_4+\left(g_1k_1+g_2k_2\right)\cdot\left[\frac{dx_4}{dR}\right]=0\end{aligned} \tag{31}$$

where,

$$x_1=\frac{\pi}{3}R^3\sin^3\beta\frac{\cos\alpha}{\sin\alpha}+\frac{\pi}{3}R^3\left(1-\cos\beta\right)^2\left(2+\cos\beta\right) \tag{32}$$

$$x_2=2\pi R^2\left(1-\cos\beta\right) \tag{33}$$

$$x_3=\pi R^2\frac{\sin^2\beta}{\sin\alpha} \tag{34}$$

$$x_4=2\pi R\sin\beta \tag{35}$$

From Figure 1 we can obtain the following expressions

$$R_L = R\sin\beta = L\sin\alpha \tag{36}$$

$$L\cos\alpha - R\cos\beta = \overline{OM} = const \tag{37}$$

$$\begin{cases} \gamma = \beta - \alpha \\ \theta = \gamma + \dfrac{\pi}{2} \end{cases} \tag{38}$$

In Eqs. (36-37), the derivation with respect to the radius R leads to

$$\frac{d\beta}{dR} = -\frac{\sin(\beta-\alpha)}{R\cos(\beta-\alpha)} \tag{39}$$

$$\frac{dL}{dR} = \frac{1}{\cos(\beta-\alpha)} \tag{40}$$

$$\frac{dR_L}{dR} = \frac{\sin\alpha}{\cos(\beta-\alpha)} \tag{41}$$

Using Eqs. (32-35) and Eqs. (39-40), we have

$$\left[\frac{dx_1}{dR}\right] = -\pi R^2\sin^3\beta\cdot\frac{\sin(\beta-\alpha)}{\cos(\beta-\alpha)} + \pi R^2\cdot\frac{\sin^2\beta\cos\alpha}{\cos(\beta-\alpha)} + \pi R^2(1-\cos\beta)^2(2+\cos\beta) \tag{42}$$

$$\left[\frac{dx_2}{dR}\right] = 4\pi R(1-\cos\beta) - 2\pi R\sin\beta\cdot\frac{\sin(\beta-\alpha)}{\cos(\beta-\alpha)} \tag{43}$$

$$\left[\frac{dx_3}{dR}\right] = \frac{2\pi R\sin\beta}{\cos(\beta-\alpha)} \tag{44}$$

$$\left[\frac{dx_4}{dR}\right] = \frac{2\pi\sin\alpha}{\cos(\beta-\alpha)} \tag{45}$$

The Laplace's equation [18] of a free spherical liquid drop yields

$$p_L - p_G = \frac{2\sigma_{LG}}{R} + \left[\frac{d\sigma_{LG}}{dR}\right] \tag{46}$$

By introducing Eqs. (42-46) into Eq. (31), we get

$$\begin{aligned}\sin(\beta-\alpha) = &-f_1\frac{\sigma_{SG1}-\sigma_{SL1}}{\sigma_{LG}} - f_2\frac{\sigma_{SG2}-\sigma_{SL2}}{\sigma_{LG}} + \frac{(g_1k_1+g_2k_2)\sin\alpha}{R\sin\beta\cdot\sigma_{LG}} \\ &+\frac{\cos(\beta-\alpha)}{\sigma_{LG}}\cdot\left\{g_1\left[\frac{dk_1}{dR}\right]+g_2\left[\frac{dk_2}{dR}\right]\right\}\end{aligned} \tag{47}$$

Putting Eq. (38) into Eq. (47) arrives at

$$\begin{aligned}\cos\theta = &f_1\frac{\sigma_{SG1}-\sigma_{SL1}}{\sigma_{LG}} + f_2\frac{\sigma_{SG2}-\sigma_{SL2}}{\sigma_{LG}} - \frac{(g_1k_1+g_2k_2)\sin\alpha}{\sigma_{LG}R\sin\beta} \\ &-\frac{\sin\theta}{\sigma_{LG}}\left\{g_1\left[\frac{dk_1}{dR}\right]+g_2\left[\frac{dk_2}{dR}\right]\right\}\end{aligned} \tag{48}$$

Substituting Eq. (5) into Eq. (48), we have

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 - \frac{\left(g_1k_1 + g_2k_2\right)\sin\alpha}{\sigma_{LG}R\sin\beta} - \frac{\sin\theta}{\sigma_{LG}}\left\{g_1\left[\frac{dk_1}{dR}\right] + g_2\left[\frac{dk_2}{dR}\right]\right\} \tag{49}$$

Utilizing Eqs. (36, 38, 41), Eq. (49) may be rewritten as

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 - \frac{\left(g_1k_1 + g_2k_2\right)\sin\alpha}{\sigma_{LG}R_L} - \frac{\sin\alpha}{\sigma_{LG}}\left\{g_1\left[\frac{dk_1}{dR_L}\right] + g_2\left[\frac{dk_2}{dR_L}\right]\right\} \tag{50}$$

Hence, for the spherical droplet in a smooth and heterogeneous conical cavity, Eq. (50) is the new generalized Cassie-Baxter equation applicable to arbitrary dividing surface between the liquid and vapor phases.

If we suppose that $\alpha = \frac{\pi}{2}$, then $\sin\alpha = 1$, the conical surfaces convert into flat surfaces, Eq. (50) is the generalized Cassie-Baxter equation suitable for the wetting of droplets on flat surfaces. Then, if we assume that the cone only contains a kind of solid, namely

$$\sigma_{SL1} = \sigma_{SL2}, \sigma_{SG1} = \sigma_{SG2}, k_1 = k_2 \tag{51}$$

Then Eq. (50) decreases to the generalized Young equation (4) established by Rusanov. Subsequently, when we assume that the line tension is constant, Eq. (50) changes to the equation (3) developed by Pethica. Finally, if the influences of the line tension are not considered, Eq. (50) reduces to the familiar Young's equation (1).

Moreover, if we neglect the effects of the line tension directly in Eq. (50), then Eq. (50) is simplified as the classical Cassie-Baxter equation (2).

4. Conclusion

On the basis of the theories of Gibbs's dividing surface and Rusanov's dividing line, we investigated the wetting characteristics of spherical droplets in a smooth and heterogeneous conical cavity by means of thermodynamics. Taking the influences of the line tension into account, a generalized Cassie-Baxter equation for the contact angle between spherical droplets and the inner surface of a cone, has been derived in terms of the concept of Gibbs's dividing surface. Based on some hypotheses, this generalized Cassie-Baxter equation decreases to the Cassie-Baxter equation suitable for planar surfaces, the Rusanov's equation, the Pethica's equation, the Young's equation along with the classical Cassie-Baxter equation.

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