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Wetting of cylindrical droplet on heterogeneous and cylindrical solid substrate

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Abstract

By methods of thermodynamics, wetting of cylindrical droplet on heterogeneous and smooth but chemically non-deformable cylindrical outer surfaces is investigated in this paper. For the three-phase system, we suppose the solid substrate is composed of two types of materials. Using Gibbs's method of dividing surface, the system can be separated into six segments. On the assumption that the temperature and chemical potential are constant, a generalized Cassie-Baxter equation is derived taking the line tension effects into consideration. This generalized Cassie-Baxter equation is discussed based on some assumptions.

***Keywords*:** Cylindrical droplet; Contact angle; Cassie-Baxter equation; Surface tension; Line tension

1. Introduction

Wetting phenomena of a droplet on solid substrate is topic of interest in various fields. Many researchers studied the wetting phenomena over the years [1-9]. Interfacial phenomena in solid-liquid-vapor systems are often depicted by the contact angles. For a drop resting on a plane smooth solid surface, Young described the equilibrium contact angle θ_Y by the well-know equation [10],

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

where σ_{SG}, σ_{SL}, σ_{LG} are the thermodynamics surface tension of solid-vapor interface, liquid-vapor interface and solid-liquid interface respectively. Equation(1) is suitable for an ideal smooth surface and it takes no account of the three-phase molecular interactions at contact line.

Gibbs described the surface thermodynamics concept of line tension in his classical theory of capillarity[11]. He thought the three-phase contact line has the important role in wetting. Since then, the excess energy of the contact line along the surface per unit perimeter length has been ascribed to the line tension [12, 13]. The experimental and theoretical studies to the line tension effects of the three-phase contact line have been studied by many academicians [12, 14-17]. Despite many researchers have various views to line tension. However, when line tension effects being not negligible, the equation of the contact angle should be different from Young Equation (1) when taking the line tension effects into consideration.

In condition, line tension cannot be constant. Considering the line tension effects and using Gibbs method of dividing surfaces, for the case of liquid droplet on a planar smooth homogeneous solid surface, a generalized Young's equation was developed by Rusanov et al [18].

$$\cos\theta = \cos\theta_Y - \frac{k}{\sigma_{LG}R_L} - \frac{1}{\sigma_{LG}}\left[\frac{dk}{dR_L}\right] \qquad (2)$$

Where θ is the contact angle, R_L is the radius of three-phase contact line, k is the corresponding line tension. The line tension derivative $\left[dk/dR_L\right]$ with respect to the dividing surface location in the substrate plane at a fixed physical state of the system is determined by an arbitrary choice of the dividing line and the liquid-vapor dividing surface.

Real solid surfaces are usually chemically heterogeneous. For the cases of chemically heterogeneous but smooth solid substrate, Cassie obtained the following equation for the wetting of solid surfaces consisting of two different materials [19].

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 \qquad (3)$$

where θ is the equilibrium contact angle, θ_1 and θ_2 are the contact angles of the two species of solid surface respectively, f_1 and f_2 are the fractional surface areas of the two type of materials.

For the case of spherical droplet on the planar surfaces, Equation (3) described by Cassie-Baxter is applicable. But, when considering the line tension effects and the solid substrate having curved surfaces, Equation (3) is not applicable. In this work, considering the line tension effects to the contact angle, we dedicated ourselves to studying the wetting phenomena of cylindrical droplet on heterogeneous and cylindrical solid outer surfaces. A new Cassie-Baxter equation for wetting of cylindrical droplet on heterogeneous and cylindrical outer surfaces was derived.

2. Calculation of the total Helmholtz free energy of the three-phase system

The wetting of a cylindrical droplet on the chemically heterogeneous and cylindrical outer surfaces is shown in the following Figure (refer to Figure1). In the Figure, θ is the contact angle, β is the angle between the substrate surfaces and the local principal plane of the three-phase contact line, α is the angle between the liquid-vapor surface tangent and the local principal plane of the three-phase contact line, and $\alpha = \theta + \beta$. R is the radius of the cylindrical droplet, R_0 is the radius of the cylindrical solid substrate, R_L is the radius of the three-phase contact line. In this work, the cylindrical droplet is assumed to be sufficiently small for the effect of gravity on the shape to be negligible relative to interfacial forces.

For the sake of simplicity, we suppose that the solid substrate consists of only two type of substances. So, there are two type of solid-liquid interfaces, solid-vapor interfaces and solid-liquid-vapor contact lines. We described their thermodynamic surface tension, line tension by σ_{SL1}, σ_{SL2}, σ_{SG1}, σ_{SG2} and k_1, k_2 respectively.

Then, we have two contact angles θ_1 and θ_2 respectively. These two contact angles θ_1 and θ_2 are expressed by the following well-known Young's equation

$$\cos\theta_1 = \frac{\sigma_{SG1} - \sigma_{SL1}}{\sigma_{LG}},\ \cos\theta_2 = \frac{\sigma_{SG2} - \sigma_{SL2}}{\sigma_{LG}} \quad (4)$$

On the basis of Gibbs method of dividing surface [11] and dividing line, this solid-liquid-vapor system can be separated into six portions, i.e. liquid phase, vapor phase, the liquid-vapor interface, the solid-liquid interface, the solid-vapor interface and the three-phase contact line. We obtained the total Helmholtz free energy F of the three-phase system

$$F = F_L + F_G + F_{SL} + F_{SG} + F_{LG} + F_{SLG} \quad (5)$$

where F_L, F_G, F_{SL}, F_{SG}, F_{LG} and F_{SLG} indicate the free energies of six portions, respectively.

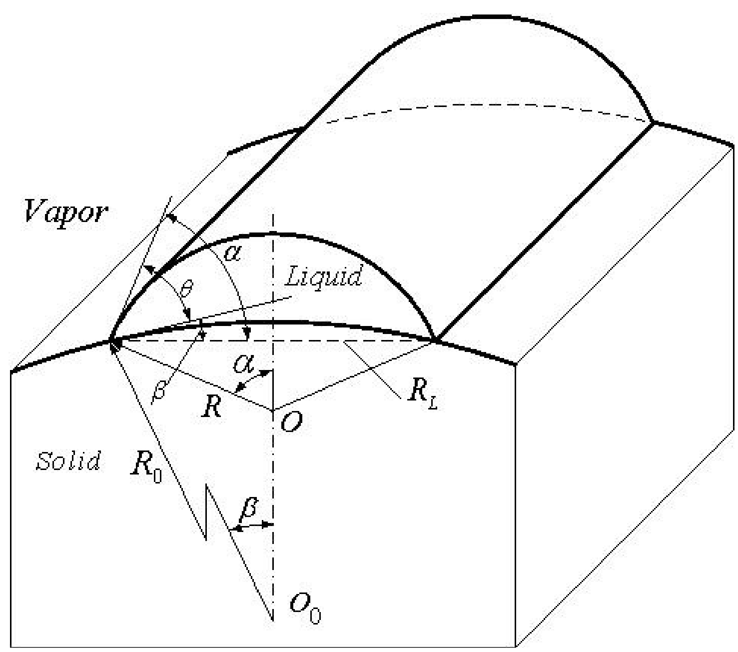

Fig. 1 An illustration of hydrophilic wetting of a cylindrical droplet on heterogeneous and smooth cylindrical solid outer surfaces

In this study, each areas of the two type of solid-liquid interfaces and the two type of solid-vapor interfaces are assumed to be extraordinary small in comparison with the size of the liquid cylindrical droplet. We also suppose that the individual length of the two type of three-phase contact lines are very short with respect to the size of the liquid cylindrical droplet. So, the following equation were obtained [18,20,22-25]

$$F_L = -p_L V_L + \mu_L N_L \quad (6)$$

$$F_G = -p_G V_G + \mu_G N_G \quad (7)$$

$$F_{LG} = \sigma_{LG} A_{LG} + \mu_{LG} N_{LG} \quad (8)$$

$$F_{SL} = (f_1 \sigma_{SL1} + f_2 \sigma_{SL2}) A_{SL} + \mu_{SL} N_{SL} \quad (9)$$

$$F_{SG} = (f_1 \sigma_{SG1} + f_2 \sigma_{SG2}) A_{SG} + \mu_{SG} N_{SG} \quad (10)$$

$$F_{SLG} = (g_1 k_1 + g_2 k_2) L_{SLG} \quad (11)$$

Where p, V, A indicate the pressures, volume and surface area, respectively. μ, N denote the chemical potential and the corresponding mole number of molecule of liquid phase and vapor phase, respectively. σ, k indicate the thermodynamic surface tension and line tension, respectively. Subscripts S, L, G denote solid, liquid and vapor phase, respectively. f_1 and f_2 are the fractional surface areas of the two kind of materials, so $f_1 + f_2 = 1$. L_{SLG} is the true value of the total length of the three-phase contact line, g_1 and g_2 are the fractional length of the two kind of three-phase contact lines, hence $g_1 + g_2 = 1$.

In order to simplify the calculation, we suppose that the equilibrium shape of a cylindrical droplet on a smooth and chemically heterogeneous cylindrical solid substrate is a segment of a cylinder.

The volume of liquid phase V_L can be written as

$$V_L = L[(R^2\alpha - R^3 \sin\alpha\cos\alpha) - (R_0^2\beta - R_0^2 \sin\beta\cos\beta)] \quad (12)$$

where R, L is the radius and length of the cylindrical liquid droplet, respectively.

The total volume V_t of the system is

$$V_t = V_L + V_G \quad (13)$$

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

$$A_{LG} = 2\alpha RL \quad (14)$$

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

$$A_{SL} = 2R_0\beta L \quad (15)$$

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

$$A_t = A_{SL} + A_{SG} \quad (16)$$

where A_{SG} is surface area of the solid-vapor interface.

The length of the three-phase contact line can be described by the following equation

$$L_{SLG} = 2L \quad (17)$$

Based on the above expressions, we obtained the free energy of the system by the following equations

$$F_L = -p_L L[(R^2\alpha - R^2 \sin\alpha\cos\alpha) - (R_0^2\beta - R_0^2 \sin\beta\cos\beta)] + \mu_L N_L \quad (18)$$

$$F_G = -p_G \left\{V_t - L[(R^2\alpha - R^2 \sin\alpha\cos\alpha) - (R_0^2\beta - R_0^2 \sin\beta\cos\beta)]\right\} + \mu_G N_G \quad (19)$$

$$F_{LG} = \sigma_{LG} \cdot 2\alpha RL + \mu_{LG} N_{LG} \quad (20)$$

$$F_{SL} = (f_1\sigma_{SL1} + f_2\sigma_{SL2}) \cdot 2R_0\beta L + \mu_{SL} N_{SL} \quad (21)$$

$$F_{SG} = (f_1\sigma_{SG1} + f_2\sigma_{SG2})(A_t - 2R_0\beta L) + \mu_{SG} N_{SG} \quad (22)$$

$$F_{SLG} = 2L(g_1 k_1 + g_2 k_2) \quad (23)$$

Substituting the above results into Equation (5), we have the total Helmholtz free energy F in the form

$$\begin{aligned} F = &-(p_L - p_G)L[(R^2\alpha - R^2 \sin\alpha\cos\alpha) - (R_0^2\beta - R_0^2 \sin\beta\cos\beta)] \\ &- p_G V_t + \sigma_{LG} \cdot 2\alpha RL + [(f_1\sigma_{SL1} + f_2\sigma_{SL2}) - (f_1\sigma_{SG1} + f_2\sigma_{SG2})] \cdot 2R_0\beta L \\ &+ (f_1\sigma_{SG1} + f_2\sigma_{SG2})A_t + 2L(g_1 k_1 + g_2 k_2) \\ &+ \mu_L N_L + \mu_G N_G + \mu_{LG} N_{LG} + \mu_{SL} N_{SL} + \mu_{SG} N_{SG} \end{aligned} \quad (24)$$

3. Derivation of a generalized Cassie-Baxter equation

The grand thermodynamic potential Ω of the three-phase system is

$$\Omega = F - \sum_i \mu_i N_i \tag{25}$$

where i is the number of subsystems of the system, μ_i are the corresponding chemical potentials of the subsystems, N_i are the corresponding mole numbers of molecules of the subsystems.

Substituting equation (24) into Equation(25), we described the total grand potential Ω of the system by the following equation

$$\begin{aligned}\Omega = &-(p_L - p_G)L[(R^2\alpha - R^2\sin\alpha\cos\alpha) - (R_0^2\beta - R_0^2\sin\beta\cos\beta)] \\ &- p_G V_t + \sigma_{LG}\cdot 2\alpha RL + [(f_1\sigma_{SL1} + f_2\sigma_{SL2}) - (f_1\sigma_{SG1} + f_2\sigma_{SG2})]\cdot 2R_0\beta L \\ &+ (f_1\sigma_{SG1} + f_2\sigma_{SG2})A_t + 2L(g_1k_1 + g_2k_2)\end{aligned} \tag{26}$$

The temperature and chemical potential are assumed to be constant in the system equilibrium. The actual physical characteristics of the system and external conditions are fixed. Therefore, the thermodynamic potential Ω is independent on the pure imaginary variation of radius R [18]. The following restriction is obtained

$$\left[\frac{d\Omega}{dR}\right] = 0 \tag{27}$$

Putting equation(26) into equation(27), the following result is obtained

$$\begin{aligned}&-(p_L - p_G)\cdot\left[\frac{dV_L}{dR}\right] + \left[\frac{d\sigma_{LG}}{dR}\right]\cdot A_{LG} + \sigma_{LG}\cdot\left[\frac{dA_{LG}}{dR}\right] \\ &+\left[\frac{d[(f_1\sigma_{SL1} + f_2\sigma_{SL2}) - (f_1\sigma_{SG1} + f_2\sigma_{SG2})]}{dR}\right]A_{SL} \\ &+[(f_1\sigma_{SL1} + f_2\sigma_{SL2}) - (f_1\sigma_{SG1} + f_2\sigma_{SG2})]\cdot\left[\frac{dA_{SL}}{dR}\right] \\ &+\left[\frac{d(g_1k_1 + g_2k_2)}{dR}\right]\cdot L_{SLG} + (g_1k_1 + g_2k_2)\cdot\left[\frac{dL_{SLG}}{dR}\right] = 0\end{aligned} \tag{28}$$

For the sake of simplify equation(28), the following expressions are assumed valid

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

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

The dividing surfaces of liquid-vapor interface of a liquid droplet on a homogeneous and solid substrate should be parts of concentric and conformal cylindrical surface. These dividing surfaces are segmental. So, the following equations are obtained

$$R\sin\alpha = R_0\sin\beta,\ R_0\cos\beta - R\cos\alpha = \overline{O_0O} = const \tag{31}$$

$$\frac{d\alpha}{dR} = \frac{\cos(\alpha-\beta)}{R\sin(\alpha-\beta)},\ \frac{d\beta}{dR} = \frac{1}{R_0\sin(\alpha-\beta)} \tag{32}$$

and

$$R_L = R\sin\alpha = R_0\sin\beta\ ,\ \frac{dR_L}{dR} = \frac{\cos\beta}{\sin(\alpha-\beta)} \tag{33}$$

Utilizing equation (31-32), the following results are obtained

$$\left[\frac{dV_L}{dR}\right] = 2R\alpha L \tag{34}$$

$$\left[\frac{dA_{LG}}{dR}\right] = 2\alpha L + 2L\frac{\cos(\alpha-\beta)}{\sin(\alpha-\beta)} \tag{35}$$

$$\left[\frac{dA_{SL}}{dR}\right] = \frac{2L}{\sin(\alpha-\beta)} \tag{36}$$

$$\left[\frac{dL_{SLG}}{dR}\right] = 0 \tag{37}$$

Based on the generalized Laplace's equation [21] of a free cylindrical droplet in vapor, we have the equation

$$p_L - p_G = \frac{\sigma_{LG}}{R} + \left[\frac{d\sigma_{LG}}{dR}\right] \tag{38}$$

It can be used for the cylindrical droplet in this work.

According to $\alpha = \theta + \beta$ and equation (29-30). Putting equations (34-38) into equation(28), we have

$$\cos\theta = f_1\frac{\sigma_{SG1}-\sigma_{SL1}}{\sigma_{LG}} + f_2\frac{\sigma_{SG2}-\sigma_{SL2}}{\sigma_{LG}} - \left(g_1\left[\frac{dk_1}{dR}\right] + g_2\left[\frac{dk_2}{dR}\right]\right)\frac{\sin\theta}{\sigma_{LG}} \tag{39}$$

This is a new generalized Cassie-Baxter equation for cylindrical droplet on chemically heterogeneous and cylindrical smooth but non-deformable solid substrate.

Using equation (4) and equation(33), equation(39) become of the following expression

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 - \left(g_1\left[\frac{dk_1}{dR_L}\right] + g_2\left[\frac{dk_2}{dR_L}\right]\right)\frac{\cos\beta}{\sigma_{LG}} \tag{40}$$

Equation (40) is a new generalized Cassie-Baxter equation for cylindrical droplet on heterogeneous and smooth cylindrical outer surfaces.

If we suppose $\beta = 0$, then $\cos\beta = 1$, the cylindrical surfaces reduce to the planar surfaces, further, if the line tension is assumed negligible, then equation(40) is the same as the classical Cassie-Baxter equation(3).

4. Conclusion

Based on Gibbs method of dividing surfaces and dividing lines, the wetting of cylindrical droplet on heterogeneous and smooth but chemically non-deformable cylindrical solid outer surfaces were studied by methods of thermodynamics. We derived a generalized Cassie-Baxter equation for contact angle between cylindrical droplet and heterogeneous smooth cylindrical solid outer surfaces, taking the line tension effects into consideration. If the line tension is assumed negligible, this generalized Cassie-Baxter equation is the same as the classical Cassie-Baxter Equation (3).

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REFERENCES

[1] Pierre-Gilles de Genes, Francoise Brochard-Wyart and Davie Quere, *Capillarity and wetting phenomena: drops, bubbles, pearls waves*, (New York: Springer-Verlag, 2004)

[2] N. Alleborn, H. Raszillier, "Spreading and sorption of a droplet on a porous substrate", *Chemical Engineering Science*, **59**, 2071-2088 (2004)

[3] Pierre Letellier, Alain Mayaffre, Mireille Turmine, "Drop size effect on contact angle explained by nonetensive thermodynamics", *Journal of Colloid and Interface Science*, **314**, 604-614, (2007)

[4] A. K. Das, P. K. Das, "Equilibrium shape and contact angle of sessile drops of different volumes-Computation by SPH and its further improvement by DI", *Chemical Engineering Science,* **65,** 4027-4037 (2010)

[5] Davide Mattia, Victor Starov, Sergey Semenov, "Thickness, stability and contact angle of liquid films on and inside nanofibres, nanotubes and nanochannels", *Journal of colloid and Interface Science*, **384**, 149-156 (2012)

[6] V.S. Nikolayev, V. Janecek, "Impact of the apparent contact angle on the bubble departure at boiling", *International Journal of Heat and Mass Transfer*, **55**, 7352-7354 (2012)

[7] Ying Wang and Ya-Pu Zhao, "Electrowetting on curved surfaces", *Soft Matter*, **8**, 2599-2606, (2012)

[8] Saeid Vafaei, Theodorian Borca-Tasciuc, Dongsheng Wen, "Investigation of nanofluid bubble characteristics under non-equilibrium conditions", *Chemical Engineering and Processing,* **86**, 116-124 (2014)

[9] B. Zhao L.S. Shvindlerman, G. Gottstein, "The line tension of grain boundary triple junctions in a Cu-Ni alloy", *Materials Letters*, 137, 304-306, (2014)

[10]Young T, "An essay on the cohesion of fluids", *Philosophical Transactions of the Royal Society of London*, **95**, 65-87, (1805)

[11] Gibbs JW, *The Scientific Papers of J. W. Gibbs*, vol. **1**. (New York: Dover; 1961)

[12] Drelich J., "The significance and magnitude of the line tension in three-phase systems", *Colloids and Surf. A*, **116,** 43-54 (1996)

[13] A. I. Rusanov, "Surface thermodynamics revisited", *Surface Science Reports*, **58,** 111-239 (2005)

[14] Rusanov A I, "Classification of line tension", *Colloids and Surf. A*, **156**, 315-322, (1999)

[15] Buehrle J, Herminghaus S, Mugele F, "Impact of line tension on the equilibrium shape of liquid droplets on patterned substrates", *Langmuir*, **18** (25), 9771-9777 (2002)

[16] Tadmor R, "Line energy and the relation between advancing, receding, and young contact angles", *Langmuir*, **20**(18), 7659-7664, (2004)

[17] Rafael T, "Line energy, line tension and drop size", *Surface Science Letters*; **602**, 108-111, (2008)

[18] Rusanov AI, Shchekin AK, Tatyanenko DV, "The line tension and the generalized Young equation: the choice of dividing surface", *Colloids and Surf. A*, **250**, 263-268, (2004)

[19] Cassie, ABD Baxter, S, "Wettability of porous surfaces", *Tran. Faraday. Soc.*, **40**, 546-551, (1944)

[20] Gibbs, JW, *The Collected Works of J. Willard. Gibbs, vol. 1, Thermodynamics*, (New Haven: Yale Univ. Press; 1928)

[21] M.~J.~P. Nijmeijer, Bruin C., A.~B. van Woerkom, and A.~F. Bakker. *J. Chem. Phys,* **96**, 565, (1992)

[22] Ono S, Kondo S, *Encyclopedia of Physics*, S. Flugge ed., vol. 10. (Berlin: Springer-Verlag; 1960)

[23] Rowlinson J S, Widom B, *Molecular Theory of Capillary* (Oxford: Clarendon Press; 1982)

[24] Wang Z X, *Thermodynamics*, 2 ed., in Chinese. (Beijing: Beijing University Press; 2005)

[25] Ai-Jun Hu, Bao-Zhan Lv, Xiao-Song Wang, Long Zhou. "The contact angle for a droplet on homogeneous and spherical concave surfaces", *Modern Physics Letters B*, **30**(7), (2016)