Contact angle of spherical drops inside a smooth and homogeneous cylindrical capillary with hemispherical head

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Abstract

To investigate the wettability of spherical drops in a smooth and homogeneous cylindrical capillary with hemispherical head, based on Gibbs's method of dividing surface and Rusanov's concept of dividing line, the contact angle of spherical droplets has been successfully derived considering the effects of the line tension. Additionally, under the condition of ignoring the line tension, the equation describing the contact angle is simplified as the classical Young equation.

***Keywords*:** Liquid droplet; Contact angle; Young equation; Line tension; Hemisphere head

1. Introduction

In the last two decades, the investigations in wetting and spreading of liquid drops on a solid substrate have increased substantially, particularly since 2010 [1-4]. The contact angle between liquid drops and solids is a crucial parameter that characteristics the wetting performance in many industrial applications and our everyday life [5-9]. Wettability of ideal surfaces is presented by the well-known Young equation [10]

$$\cos\theta_Y = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} \tag{1}$$

where θ_Y is the Young angle, and σ_{SV}, σ_{SL} and σ_{LV} are the surface tensions at the solid/liquid, solid/liquid and liquid/vapor interfaces, separately.

In wetting phenomena, the line at which solid, liquid and vapor phases contact each other is called the triple phase line. The characteristic of the triple phase line plays a key role in actual wetting applications. The line tension defined as the free energy per unit length of the triple phase line is a crucial parameter in surface wetting. The concept of the line tension was first proposed thermodynamically by Gibbs. W. C. Jensen and D. Q. Li [11] measured the line tension of the capillary rise in a conical tube. A. I. Rusanov et al [12] studied the line tension dependence on the curvature radius of the triple phase line. A. Amirfazli and A. W. Neumann [13] reviewed both theoretically and experimentally the line tension studies. B. V. Toshev [14] presented the thermodynamic theory of thin liquid films considering the impacts of the line tension. B. M. Law et al [15] summarized the effects of the line tension on drops and particles at surfaces.

Many scholars have ever growing interest in understanding the wetting and spreading phenomena of liquids on solids due regard to its extensive applications. However, the wetting of spherical drops in a smooth and homogeneous cylindrical capillary with hemisphere head has not been investigated to this day. In this paper, based on Gibbs's method of dividing surface and Rusanov's concept of dividing line, the contact angle describing the wetting of spherical drops in a smooth and homogeneous cylindrical capillary with hemisphere head is derived considering the effects of the line tension. Accordingly, the generalized Young equation of the derived contact angle is simplified as the classical Young equation when neglecting the line tension.

2. Calculation of free energies

Consider a single-component spherical liquid droplet (phase L) contacting with vapor (phase V) in equilibrium, placed in a smooth and homogeneous cylindrical capillary (phase S) with hemisphere head, as illustrated in Figure 1.

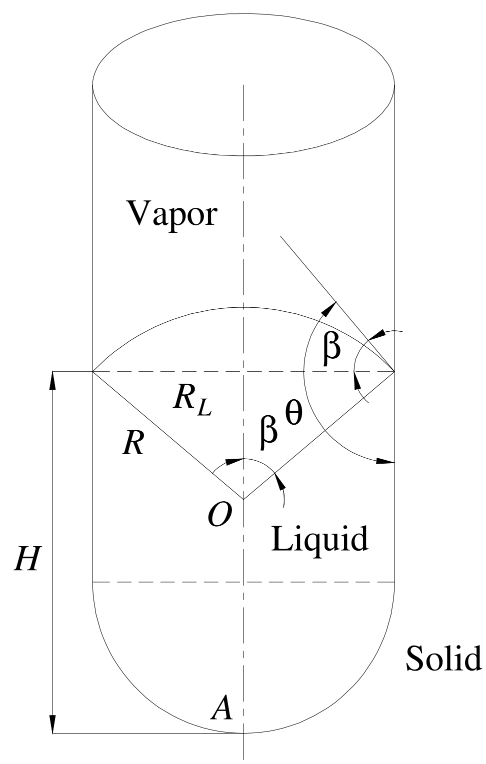

Figure 1. Spherical droplet in a smooth and homogeneous cylindrical capillary with hemisphere head

For sake of generality, assume that the height of the liquid drop exceeds the hemisphere head in Figure 1, that is, $H > R\sin\beta$. According to both Gibbs's theory of dividing surface and Rusanov's approach of dividing line, the free energy of the solid-liquid-vapor system in Figure 1 is given by [16]

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

where

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

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

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

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

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

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

where F is the free energy (the single, double, and triple subscripts denote the quantities concerning the corresponding phases, such as the subscript SLV being the triple phase line), p is the pressure, V is the volume, μ is the chemical potential, N is the mole number of molecule, σ is the surface energy of unit area, A is the surface area, k is the line tension, and L is the length of the triple phase line.

For simplicity, suppose that the gravity and the other forces or fields are neglected, so the equilibrium shape of the spherical drop in Figure 1 is the combination of both a hemisphere, a cylindricity and a segment. As a result, the drop volume V_L appearing in Eq. (3) is expressed as

$$V_L = \frac{2\pi}{3}R^3\sin^3\beta + \pi R^2\left(H - R\sin\beta\right)\sin^2\beta + \frac{\pi}{3}R^3\left(1-\cos\beta\right)^2\left(2+\cos\beta\right) \tag{9}$$

where R is the drop radius, β is the apparent contact angle, and H is the drop height.

The entire volume V_t of the system is

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

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

$$A_{LV} = 2\pi R^2\left(1-\cos\beta\right) \tag{11}$$

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

$$A_{SL} = 2\pi RH\sin\beta \tag{12}$$

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

$$A_t = A_{SL} + A_{SV} \tag{13}$$

The length of the triple phase line is

$$L_{SLV} = 2\pi R\sin\beta \tag{14}$$

Based on the relations stated above, various free energies can be represented, separately, as

$$F_L = -p_L \cdot \left[\frac{2\pi}{3} R^3 \sin^3\beta + \pi R^2 \left(H - R\sin\beta\right)\sin^2\beta + \frac{\pi}{3} R^3 \left(1-\cos\beta\right)^2 \left(2+\cos\beta\right) \right] + \mu_L N_L \tag{15}$$

$$F_V = -p_V \cdot \left\{ V_t - \left[\frac{2\pi}{3} R^3 \sin^3\beta + \pi R^2 \left(H - R\sin\beta\right)\sin^2\beta + \frac{\pi}{3} R^3 \left(1-\cos\beta\right)^2 \left(2+\cos\beta\right) \right] \right\} + \mu_V N_V \tag{16}$$

$$F_{SL} = \sigma_{SL} \cdot 2\pi RH \sin\beta + \mu_{SL} N_{SL} \tag{17}$$

$$F_{SV} = \sigma_{SV} \cdot \left[A_t - 2\pi RH \sin\beta \right] + \mu_{SV} N_{SV} \tag{18}$$

$$F_{LV} = \sigma_{LV} \cdot 2\pi R^2 \left(1-\cos\beta\right) + \mu_{LV} N_{LV} \tag{19}$$

$$F_{SLV} = k \cdot 2\pi R \sin\beta + \mu_{SLV} N_{SLV} \tag{20}$$

Consequently, putting Eqs. (15-20) into Eq. (2), one has

$$\begin{aligned} F = &-\left(p_L - p_V\right) \cdot \left[\frac{2\pi}{3} R^3 \sin^3\beta + \pi R^2 \left(H - R\sin\beta\right)\sin^2\beta \right. \\ &\left. + \frac{\pi}{3} R^3 \left(1-\cos\beta\right)^2 \left(2+\cos\beta\right) \right] - p_V \cdot V_t + \sigma_{LV} \cdot 2\pi R^2 \left(1-\cos\beta\right) \\ &+ \left(\sigma_{SL} - \sigma_{SV}\right) \cdot 2\pi RH \sin\beta + \sigma_{SV} \cdot A_t + k \cdot 2\pi R \sin\beta \\ &+ \mu_L N_L + \mu_V N_V + \mu_{LV} N_{LV} + \mu_{SL} N_{SL} + \mu_{SV} N_{SV} + \mu_{SLV} N_{SLV} \end{aligned} \tag{21}$$

3. Derivation of contact angle

The total potential energy Ω of the system presented in Section 2 is defined by the equation

$$\Omega = F - \left(\mu_L N_L + \mu_V N_V + \mu_{LV} N_{LV} + \mu_{SL} N_{SL} + \mu_{SV} N_{SV} + \mu_{SLV} N_{SLV} \right) \tag{22}$$

Using the free energy Eq. (21) and potential energy Eq. (22), the potential energy Ω can be rewritten as

$$\begin{aligned} \Omega = &-\left(p_L - p_V\right) \cdot \left[\frac{2\pi}{3} R^3 \sin^3\beta + \pi R^2 \left(H - R\sin\beta\right)\sin^2\beta \right. \\ &\left. + \frac{\pi}{3} R^3 \left(1-\cos\beta\right)^2 \left(2+\cos\beta\right) \right] - p_V \cdot V_t + \sigma_{LV} \cdot 2\pi R^2 \left(1-\cos\beta\right) \\ &+ \left(\sigma_{SL} - \sigma_{SV}\right) \cdot 2\pi RH \sin\beta + \sigma_{SV} \cdot A_t + k \cdot 2\pi R \sin\beta \end{aligned} \tag{23}$$

Minimizing the potential energy Ω with respect to the radius R, namely

$$\left[\frac{d\Omega}{dR} \right] = 0 \tag{24}$$

Due to the surface tensions σ_{SL} and σ_{SV} independent of the dividing surface [12], one obtains

$$\begin{cases} \left[\dfrac{d\sigma_{SL}}{dR}\right]=0 \\ \left[\dfrac{d\sigma_{SV}}{dR}\right]=0 \end{cases} \tag{25}$$

By utilizing equations (23-25), the following expression is obtained

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

From geometry, the following relations can be easily obtained

$$R_L=R\sin\beta=const \tag{27}$$

$$H-R\cos\beta=\overline{OA}=const \tag{28}$$

$$\beta=\theta-\frac{\pi}{2} \tag{29}$$

Taking the derivation of Eqs. (27-28) with respect to the radius R, one finds that

$$\frac{d\beta}{dR}=-\frac{\sin\beta}{R\cos\beta} \tag{30}$$

$$\frac{dH}{dR}=\frac{1}{\cos\beta} \tag{31}$$

$$\frac{dR_L}{dR}=0 \tag{32}$$

Similarly, we take the derivation of Eqs. (9, 11, 12, 14) with respect to the radius R and apply Eqs. (30-31), leading to

$$\left[\frac{dV_L}{dR}\right]=2\pi R^2\left(1-\cos\beta\right) \tag{33}$$

$$\left[\frac{dA_{LV}}{dR}\right]=4\pi R\left(1-\cos\beta\right)-2\pi R\cdot\frac{\sin^2\beta}{\cos\beta} \tag{34}$$

$$\left[\frac{dA_{SL}}{dR}\right]=\frac{2\pi R\sin\beta}{\cos\beta} \tag{35}$$

$$\left[\frac{dL_{SLV}}{dR}\right]=0 \tag{36}$$

The Laplace equation [16] of the spherical drop in vapor is formulated as

$$p_L-p_V=\frac{2\sigma_{LV}}{R}+\left[\frac{d\sigma_{LV}}{dR}\right] \tag{37}$$

Now putting Eqs. (33-37) into Eq. (26), we find

$$\sin\beta=\frac{\sigma_{SL}-\sigma_{SV}}{\sigma_{LV}}+\frac{\cos\beta}{\sigma_{LV}}\cdot\left[\frac{dk}{dR}\right] \tag{38}$$

According to Eq. (29), Eq. (38) can be rewritten as

$$\cos\theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} - \frac{\sin\theta}{\sigma_{LV}} \cdot \left[\frac{dk}{dR}\right] \tag{39}$$

If the familiar Young equation (1) is substituted into Eq. (39), we arrive at a new generalized Young equation that describes the contact angle of spherical drops inside a smooth and homogeneous cylindrical capillary with hemisphere head

$$\cos\theta = \cos\theta_Y - \frac{\sin\theta}{\sigma_{LV}} \cdot \left[\frac{dk}{dR}\right] \tag{40}$$

In addition, if the effects of the line tension are neglected, Eq. (39) is simplified to the classical Young equation (1).

4. Conclusion

In this paper, using Gibbs's method of dividing surface and Rusanov's concept of dividing line, the wettability of a spherical droplet in a smooth and homogeneous cylindrical capillary with hemisphere head is studied thermodynamically. Considering the effects of the line tension, the contact angle of spherical droplets in a smooth and homogeneous cylindrical capillary with hemisphere head was successfully derived. When ignoring the effects of the line tension, this generalized Young equation reduces to the classical Young equation.

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REFERENCES

[1] C. A. Ward, and K. Sefiane, "Adsorption at the solid-liquid interface as the source of contact angle dependence on the curvature of the three-phase line", *Advances in Colloid and Interface Science*, **161**, 171-180 (2010)

[2] M. Soleimani, R. J. Hill, and G. M. Ven, "Bubbles and drops on curved surfaces", *Langmuir*, **29**, 14168-14177 (2013)

[3] B. B. Straumal, A. A. Mazilkin, and B. Baretzky, "Grain boundary complexions and pseudopartial wetting", *Current Opinion in Solid State and Materials Science*, **20**, 247-256 (2016)

[4] E. Bormashenko, "Progress in understanding wetting transitions on rough surfaces", *Advances in Colloid and Interface Science*, **222**, 92-103 (2015)

[5] T. M. Bucher, and H. V. Tafreshi, "Modeling air-water interface in disordered fibrous media with heterogeneous wettabilities", *Colloids and Surfaces A*, **461**, 323-335 (2014)

[6] J. H. Yang, Q. Z. Yuan, and Y. P. Zhao, "Evolution of the interfacial shape in dissolutive wetting: coupling of wetting and dissolution", *International Journal of Heat and Mass Transfer*, **118**, 201-207 (2018)

[7] G. Ahmed, O. A. Tash, J. Cook, A. Trybala, and V. Starov, "Biological applications of kinetics of wetting and spreading", *Advances in Colloid and Interface Science*, **249**, 17-36 (2017)

[8] J. M. Rasul, G. S. Ghataora, and M. P. N. Burrow, "The effect of wetting and drying on the performance of stabilized subgrade soils", *Transportation Geotechnics*, **14**, 1-7 (2018)

[9] A. Ciesielski, L. Skowronski, M. Trzcinski, and T. Szoplik, "Controlling the optical parameters of self-assembled silver films with wetting layers and annealing", *Applied Surface Science*, **421**, 349-356 (2017)

[10] T. Young, "An essay on the cohesion of fluids", *Philos. Trans. Roy. Soc. London*, **95**, 65-87 (1805)

[11] W. C. Jensen, and D. Q. Li, "Determination of line tensions from the capillary rise in a conical tube", *Colloids and Surfaces A*, **156**, 519-524 (1999)

[12] A. I. Rusanov, A. K. Shchekin, and D. V. Tatyanenko, "The line tension and the generalized Young equation: the choice of dividing surface", *Colloids and Surfaces A*, **250**, 263-268 (2004)

[13] A. Amirfazli, and A. W. Neumann, "Status of the three-phase line tension", *Advances in Colloid and Interface Science*, **110**, 121-141 (2004)

[14] B. V. Toshev, "Thermodynamic theory of thin liquid films including line tension effects", *Current Opinion in Colloid & Interface Science*, **13**, 100-106 (2008)

[15] B. M. Law, S. P. McBride, J. Y. Wang, H. S. Wi, G. Paneru, S. Betelu, B. Ushijima, Y. Takata, B. Flanders, F. Bresme, H. Matsubara, T. Takiue, and M. Aratono, "Line tension and its influence on droplets and particles at surfaces", *Progress in Surface Science*, **92**, 1-39 (2017)

[16] J. S. Rowlinson and B. Widom, *Molecular theory of capillarity* (Clarendon Press, Oxford, 1982)