Mechanical Engineering Research; Vol. 6, No. 1; 2016
ISSN 1927-0607 E-ISSN 1927-0615
Published by Canadian Center of Science and Education

Contact Angle for Spherical Nanodroplet in Cylindrical Cavity with Quadratic Curve Generatrix

Ai-Jun Hu[1] & Bao-Zhan Lv[1]

[1] School of Mechanical and Power Engineering, Henan Polytechnic University, Henan 454003, China

Correspondence: Ai-Jun Hu, School of Mechanical and Power Engineering, Henan Polytechnic University, Henan 454003, China. E-mail: ajhu127@163.com

Received: April 13, 2016 Accepted: April 26, 2016 Online Published: May 17, 2016

doi:10.5539/mer.v6n1p96 URL: http://dx.doi.org/10.5539/mer.v6n1p96

Abstract

Wetting of a spherical nanodroplet in smooth and homogeneous cylinder surface rotated by quadratic curve was studied by methods of thermodynamics. The solid-liquid-vapor system was separated into six parts using Gibbs method of dividing surface. The system free energy was calculated. A generalized Young equation for the equilibrium contact angle is proposed taking the line tension effects into consideration. On the basis of some assumptions, this generalized Young equation is the same as the classical Young's equation.

Keywords: thermodynamics; nanodroplet; line tension; quadratic curve; contact angle; cylinder

1. Introduction

The wetting of solid surfaces is very familiar in various natural and technological devices (Quéré, de Gennes, Brochard-Wyart, & Reisinger, 2004; Prabhu, Fernades, & Kumar, 2009; Waghmare & Mitra, 2010; Promraksa & Chen, 2012; Raufaste & Cox, 2013; Snoeyink, Barman, & Christopher, 2015). The contact angle for a liquid nanodroplet on a substrate surface is usually used to describe the wetting characteristic. The Young' equation predicted the equilibrium contact angle (Young, 1805)

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

where θ_Y is the contact angle, σ_{SG}, σ_{SL}, σ_{LG} represent the thermodynamic surface tension of solid-vapor interface, solid-liquid interface and liquid-vapor interface, respectively. Equation (1) is applicable for a liquid nanodroplet on an ideal smooth and homogeneous solid substrate surface. But, it didn't taking the influences of the line tension into consideration.

Gibbs firstly presented the line tension as a surface thermodynamics concept (Gibbs, 1961). Gibbs believed the triple phase contact line bears significant role in triple phase systems. From that time, the line tension impacts on the contact angle were studied by many researchers. The significance of the line tension in three-phase systems was discussed in relation to contact angle measurements by Jaroslaw (Drelich, 1996). A.Amirfazli found the drop size dependence of contact angles for high-energy system yields a positive line tension (Amirfazli, Chatain, & Neumann, 1998). On the basis of the Irving-Kirkwood stress tensor of statistical mechanics, line tension at a curved edge of a solid is direct calculated by Anatoly (Rusanov & Brodskaya, 2014). Although, the thermodynamics line tension still remains disputable. It is thought the line tension is responsible for the many wetting phenomena. When taking the line tension effects into consideration, the Young equation should be modified. For a nanodroplet in an inclined solid cone surface of revolution, Dongqing Li presented the following equation of equilibrium contact angle (Li, 1996)

$$\cos\theta = \cos\theta_Y - \frac{k\cos\beta_L}{\sigma_{LG} R_L} \tag{2}$$

where R_L is the radius of the triple phase contact line, k is the corresponding line tension, β_L is the angle of inclination of the solid surface at the triple phase contact line. In Equation (2), Dongqing Li supposed the line tension is constant and the cone surface shapes from the rotation by line. When a nanodroplet within the cone surface of rotation by a nonlinear curve, the contact angle should be different from the Equation (2).

According to the practical situation, the line tension can be variable. Rusanov established a modified Young's equation (Rusanov, Shchekin, & Tatyanenko, 2004) utilizing Gibbs method of dividing surfaces

$$\cos\theta = \cos\theta_Y - \frac{k}{\sigma_{LG} R_L} - \frac{1}{\sigma_{LG}}\left[\frac{dk}{dR_L}\right] \tag{3}$$

where the line tension derivative $\left[\frac{dk}{dR_L}\right]$ express the variation of the k due to the variation of the radius R_L of the contact line.

Equation (3) is suitable for the flat surfaces. For a nanodroplet on curved surface, the Young equation should be different with Equation (3).

In previous references, wetting of nanodroplet in cavity surface rotated by a quadratic curve has seldom been studied. In this work, taking the line tension effects into consideration, wetting of a spherical nanodroplet in a smooth and homogeneous cylindrical cavity rotated by a quadratic curve is studied. A generalized Young equation of contact angle for nanodroplet in a smooth and homogeneous cylinder cavity surface rotated by quadratic curve is obtained utilizing the methods of dividing surfaces of Gibbs based on thermodynamics.

2. Calculation of the total Helmholtz free energy

In this study, we assume the cylindrical cavity is created by using the quadratic function $\frac{x^2}{a^2} - \frac{z^2}{b^2} = 1$ as a generatrix to rotate around z axis. The illustration of the wetting is shown in Figure 1, in which the droplet was cut by a plane parallel to the z axis. β is the angle between the substrate surfaces tangent and the principal plane of the three-phase contact line. α is the angle between the liquid nanodroplet surface tangent and the local principal plane of contact line. In this study, the nanodroplet gravity is neglected. The equilibrium shape of nanodroplet in cylindrical cavity above the principal plane of the three-phase contact line bears the shape of a spherical part.

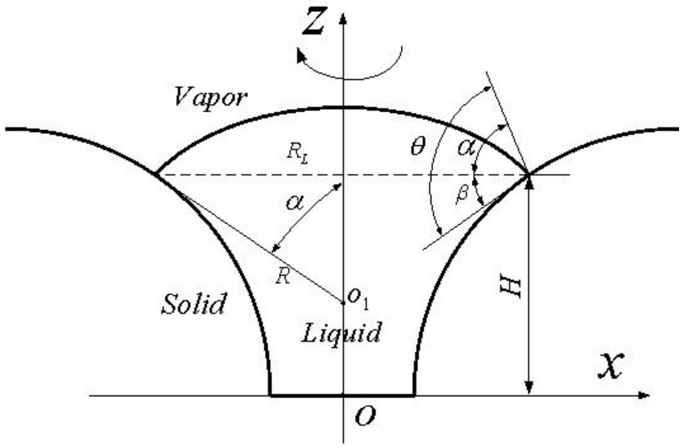

Figure 1. Wetting of a spherical nanodroplet within a smooth and homogeneous cylinder solid rotated by $\frac{x^2}{a^2} - \frac{z^2}{b^2} = 1$ around z axis

On the basis of the method of Gibbs's dividing surface, we separated the solid-liquid-vapor system into six portions, liquid phase, vapor phase, solid-liquid interface, solid-vapor interface, liquid-vapor interface, and the three phase contact line. The whole Helmholtz free energy F of the system is described by the following expression

$$F = F_L + F_G + F_{SL} + F_{SG} + F_{LG} + F_{SLG} \tag{4}$$

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

We have the free energies of six portions (Young, 1805; Rowlinson & Widom, 2013)

$$F_L = -p_L V_L + \mu_L N_L \tag{5}$$

$$F_G = -p_G V_G + \mu_G N_G \tag{6}$$
$$F_{SL} = \sigma_{SL} A_{SL} + \mu_{SL} N_{SL} \tag{7}$$
$$F_{SG} = \sigma_{SG} A_{SG} + \mu_{SG} N_{SG} \tag{8}$$
$$F_{LG} = \sigma_{LG} A_{LG} + \mu_{LG} N_{LG} \tag{9}$$
$$F_{SLG} = kL_{SLG} + \mu_{SLG} N_{SLG} \tag{10}$$

where p_L and V_L denote the pressure and volume of liquid phase, respectively. p_G and V_G denote the pressure and volume of vapor phase, respectively. μ_L , μ_G , μ_{LG} , μ_{SL} , μ_{SG} , μ_{SLG} denote the chemical potential of liquid phase, vapor phase, liquid-vapor interface, solid-liquid interface, solid-vapor interface and the three-phase contact line, respectively. N_L , N_G , N_{LG} , N_{SL} , N_{SG} , N_{SLG} denote the mole number of molecule, respectively. A_{LG} , A_{SL} , A_{SG} denote the surface areas of liquid-vapor interface, solid-liquid interface and solid-vapor interface, respectively. k is the line tension. L_{SLG} is the length of the triple phase contact line.

The volume V_L of liquid phase is

$$V_L = \int_0^H \pi x^2 dz + \frac{\pi}{3} R^3 (2 + \cos\alpha)(1 - \cos\alpha)^2 \tag{11}$$

where R and H denote the radius of spherical cap of the liquid and height from local principal plane of the contact line to the bottom of the cylinder.

The whole volume V_t of the system is given by

$$V_t = V_L + V_G \tag{12}$$

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

$$A_{LG} = 2\pi R^2 (1 - \cos\alpha) \tag{13}$$

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

$$A_{SL} = \int_0^H 2\pi x \sqrt{1 + (x_z)^2}\, dz \tag{14}$$

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

$$A_t = A_{SL} + A_{SG} \tag{15}$$

The length of the three-phase contact line can be written as

$$L_{SLG} = 2\pi R \sin\alpha \tag{16}$$

According to above equations, we have the following equations of the free energy

$$F_L = -p_L \left[\int_0^H \pi x^2 dz + \frac{\pi}{3} R^3 (2 + \cos\alpha)(1 - \cos\alpha)^2 \right] + \mu_L N_L \tag{17}$$

$$F_G = -p_G \left\{ V_t - \left[\int_0^H \pi x^2 dz + \frac{\pi}{3} R^3 (2 + \cos\alpha)(1 - \cos\alpha)^2 \right] \right\} + \mu_G N_G \tag{18}$$

$$F_{SL} = \sigma_{SL} \left[\int_0^H 2\pi x \sqrt{1 + (x_z)^2}\, dz \right] + \mu_{SL} N_{SL} \tag{19}$$

$$F_{SG} = \sigma_{SG} \left\{ A_t - \left[\int_0^H 2\pi x \sqrt{1 + (x_z)^2}\, dz \right] \right\} + \mu_{SG} N_{SG} \tag{20}$$

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

$$F_{SLG} = 2\pi k R \sin\alpha + \mu_{SLG} N_{SLG} \tag{22}$$

Substituting the Equations (17-22) into Equation (4), we obtained the whole Helmholtz free energy in the following from

$$\begin{aligned} F = &-(p_L - p_G) \left[\int_0^H \pi x^2 dz + \frac{\pi}{3} R^3 (2 + \cos\alpha)(1 - \cos\alpha)^2 \right] \\ &- p_G V_t + \sigma_{LG} \cdot 2\pi R^2 (1 - \cos\alpha) + (\sigma_{SL} - \sigma_{SG}) \cdot \int_0^H 2\pi x \sqrt{1 + (x_z)^2}\, dz \\ &+ \sigma_{SG} A_t + 2\pi k R \sin\alpha + \mu_L N_L + \mu_G N_G + \mu_{LG} N_{LG} + \mu_{SL} N_{SL} + \mu_{SG} N_{SG} + \mu_{SLG} N_{SLG} \end{aligned} \tag{23}$$

3. Derivation of Generalized Young Equation

The grand thermodynamic potential Ω of the solid-liquid-vapor system is

$$\Omega = F - \sum_i \mu_i N_i \tag{24}$$

where the mark i denotes the amount of subsystems of the system.

Putting Equation (23) into Equation (24), we have the following expression

$$\begin{aligned}\Omega = &-(p_L - p_G)\left[\int_0^H \pi x^2 dz + \frac{\pi}{3}R^3(2+\cos\alpha)(1-\cos\alpha)^2\right] \\ &- p_G V_t + \sigma_{LG}\cdot 2\pi R^2(1-\cos\alpha) + (\sigma_{SL}-\sigma_{SG})\cdot\int_0^H 2\pi x\sqrt{1+(x_z)^2}\,dz \\ &+\sigma_{SG}A_t + 2\pi kR\sin\alpha\end{aligned} \tag{25}$$

The grand thermodynamic potential Ω, the surface tensions σ_{SL} and σ_{SG} do not depend upon the notional variation of the radius R of the nanodroplet, the following constraints can be obtained (Rusanov, Shchekin, & Tatyanenko, 2004)

$$\left[\frac{d\Omega}{dR}\right] = 0 \tag{26}$$

$$\left[\frac{d\sigma_{SL}}{dR}\right] = 0,\ \left[\frac{d\sigma_{SG}}{dR}\right] = 0 \tag{27}$$

Substituting Equation (25) into Equation (26), we have

$$\begin{aligned}&-(p_L - p_G)\cdot\left[\frac{dV_L}{dR}\right] + \left[\frac{d\sigma_{LG}}{dR}\right]\cdot A_{LG} + \sigma_{LG}\cdot\left[\frac{dA_{LG}}{dR}\right] + (\sigma_{SL}-\sigma_{SG})\cdot\left[\frac{dA_{SL}}{dR}\right] \\ &+\left[\frac{dk}{dR}\right]\cdot L_{SLG} + k\cdot\left[\frac{dL_{SLG}}{dR}\right] = 0\end{aligned} \tag{28}$$

The dividing surface positions of liquid-vapor interface of a spherical liquid nanodroplet in cylindrical cavity should be parts of concentric and conformal spherical surfaces. So, we have the following expressions

$$H - R\cos\alpha = const$$

$$\frac{(R\sin\alpha)^2}{a^2} - \frac{H^2}{b^2} = 1 \tag{29}$$

$$R_L = R\sin\alpha \tag{30}$$

and

$$\frac{d\alpha}{dR} = \frac{\cos\alpha\sqrt{(abR\sin\alpha)^2 - a^4b^2} - b^2R(\sin\alpha)^2}{R\sin\alpha\sqrt{(abR\sin\alpha)^2 - a^4b^2} + b^2R^2\sin\alpha\cos\alpha} \tag{31}$$

$$\frac{dH}{dR} = \frac{b^2R}{\sqrt{(abR\sin\alpha)^2 - a^4b^2} + b^2R\cos\alpha} \tag{32}$$

$$\frac{dR_L}{dR} = \frac{\cos\beta}{\sin(\alpha+\beta)} \tag{33}$$

According to Eqs.(11, 13, 14, 16) and Eqs.(31-32), we obtained the following equations

$$\left[\frac{dV_L}{dR}\right] = 2\pi R^2(1-\cos\alpha) \tag{34}$$

$$\left[\frac{dA_{LG}}{dR}\right] = 4\pi R(1-\cos\alpha) + \frac{2\pi R\sin\alpha\cdot\cos(\alpha+\beta)}{\sin(\alpha+\beta)} \tag{35}$$

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

$$\left[\frac{dL_{SLG}}{dR}\right] = \frac{2\pi\cos\beta}{\sin(\alpha+\beta)} \tag{37}$$

On the basis of the well-known Laplace' equation (Rowlinson & Widom, 2013; Ono, Kondo, & Flügge, 1960) of a free spherical liquid droplet in vapor, the following equation is obtained

$$p_L - p_G = \frac{2\sigma_{LG}}{R} + \left[\frac{d\sigma_{LG}}{dR}\right] \tag{38}$$

It can be used for the nanodroplet in this study.

In order to simplify calculation, we study only the case that z is greater than zero. So, according to the illustration in Figure 1, the following relations were obtained

$$\tan\beta = \frac{b^2 R\sin\alpha}{\sqrt{(abR\sin\alpha)^2 - a^4 b^2}}$$
$$\theta = \alpha + \beta \tag{39}$$

Substituting Eqs.(34-38) into Equation (28) and using Equation (39), we have the following equation

$$\cos\theta = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}} - \frac{k\cos\beta}{\sigma_{LG} R\sin\alpha} - \frac{\sin\theta}{\sigma_{LG}} \cdot \left[\frac{dk}{dR}\right] \tag{40}$$

Using Eqs.(33), Equation (40) can be rewritten as

$$\cos\theta = \cos\theta_Y - \frac{k}{\sigma_{LG} R_L}\sqrt{\frac{a^2 R_L^2 - a^4}{(a^2+b^2)R_L^2 - a^4}} - \frac{1}{\sigma_{LG}}\sqrt{\frac{a^2 R_L^2 - a^4}{(a^2+b^2)R_L^2 - a^4}} \cdot \left[\frac{dk}{dR_L}\right] \tag{41}$$

Equation (41) is the generalized Young's equation for the contact angle of the spherical nanodroplet in cylindrical cavity rotated by quadratic function $\frac{x^2}{a^2} - \frac{z^2}{b^2} = 1$. It is valid for any dividing surfaces between liquid and vapor phases.

If b^2 is very very small, then $\sqrt{\frac{a^2 R_L^2 - a^4}{(a^2+b^2)R_L^2 - a^4}}$ tend to one, the generalized Young's equation Equation (41) is the same as equation (3) established by Rusanov.

If line tension effects are negligible, Equation (41) changes to the classical Young equation (1).

4. Conclusion

In this work, the wetting of a spherical nanodroplet in cylindrical cavity rotated by quadratic function $\frac{x^2}{a^2} - \frac{z^2}{b^2} = 1$ is investigated on the basis of Gibbs's method of dividing surface. Considering the effects of line tension, a generalized Young equation for the contact angle of a spherical nanodroplet in cylindrical cavity rotated by quadratic function is proposed. This generalized Young equation changes to the Rusanov's equation and the classical Young's equation under certain assumption.

Acknowledgments

This work was supported by the Project of Natural Science of the Education of Henan Province (Grant No. 2011A460006), and the Doctor Research Foundation of Henan Polytechnic University (Grant No. B2009-16).

References

Amirfazli, A., Chatain, D., & Neumann, A. W. (1998). Drop size dependence of contact angles for liquid tin on silica surface: line tension and its correlation with solid–liquid interfacial tension. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *142*(2), 183-188.

Drelich, J. (1996). The significance and magnitude of the line tension in three-phase (solid-liquid-fluid) systems. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *116*(1), 43-54.

Gibbs, J. W. (1961). *The scientific papers of J. Willard Gibbs* (Vol. 1). New York: Dover.

Li, D. (1996). Drop size dependence of contact angles and line tensions of solid-liquid systems. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *116*(1), 1-23.

Ono, S., Kondo, S., & Flügge, S. (1960). Encyclopedia of Physics. *Molecular Theory of Surface Tension in Liquids, Springer, Berlin*, 134.

Prabhu, K. N., Fernades, P., & Kumar, G. (2009). Effect of substrate surface roughness on wetting behaviour of vegetable oils. *Materials & Design*, *30*(2), 297-305.

Promraksa, A., & Chen, L. J. (2012). Modeling contact angle hysteresis of a liquid droplet sitting on a cosine wave-like pattern surface. *Journal of colloid and interface science*, *384*(1), 172-181.

Quéré, D., de Gennes, P. G., Brochard-Wyart, F., & Reisinger, A. (2004). *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*. New York: Springer-Verlag.

Raufaste, C., & Cox, S. (2013). Deformation of a free interface pierced by a tilted cylinder: variation of the contact angle. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *438*, 126-131.

Rowlinson, J. S., & Widom, B. (2013). *Molecular theory of capillarity*. Courier Corporation.

Rusanov, A. I., & Brodskaya, E. N. (2014). Line tension at curved edge of a molecular solid. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *448*, 175-180.

Rusanov, A. I., Shchekin, A. K., & Tatyanenko, D. V. (2004). The line tension and the generalized Young equation: the choice of dividing surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *250*(1), 263-268.

Snoeyink, C., Barman, S., & Christopher, G. F. (2015). Contact Angle Distribution of Particles at Fluid Interfaces. *Langmuir*, *31*(3), 891-897.

Waghmare, P. R., & Mitra, S. K. (2010). Contact angle hysteresis of microbead suspensions. *Langmuir*, *26*(22), 17082-17089.

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