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Generalized Wenzel equation for contact angle of droplets on spherical rough solid substrates

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Abstract
Applying Gibbs' concept of dividing surface and dividing line, the wetting of spherical droplets on spherical rough solid substrates was studied by methods of thermodynamics. Considering the influences of line tension, a generalized Wenzel's equation for contact angle between droplets and spherical rough solid substrates is derived. Under some assumptions, this generalized Wenzel's equation reduces to Rusanov's equation.

***Keywords*:** Wetting; contact angle; Wenzel equation; surface tension; line tension; thermodynamics.

1. Introduction
Wetting phenomena are common in solid-liquid-gas systems, for instance, wetting of liquids on solid surfaces, adhesives, lubricants, capillary penetration in to porous media and floation [1]. Wetting abilities are important in many industrial applications, for example, the wetting abilities of electrolytes on electrodes plays a key role in improving the specific energy density of supercapacitors [2] and lithium-ion batteries [3].

For the cases of smooth and chemically homogeneous substrates, the contact angles θ_Y are determined by the Young's equation [4]

$$\cos\theta_Y = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}}, \tag{1.1}$$

where σ_{SG}, σ_{LG} and σ_{SL} are the surface tension of solid-vapor interface, the liquid-vapor interface, and solid-liquid interface, respectively.

The Young's equation Eq. (1.1) is not applicable to rough surfaces. For the cases of rough non-deformable solid substrates, neglecting the effect of the line tension, Wenzel [5] established the following equation

$$\cos\theta = r_S \cos\theta_Y, \tag{1.2}$$

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

$$r_S = \frac{A_{real}}{A_{apparent}} \times 100\% \tag{1.3}$$

with A_{real} being the true value of the surface area and $A_{apparent}$ being the apparent value.

Considering the line tension effects and using Gibbs method of dividing surfaces, Rusanov et al. [6] obtained a generalized Young's equation

$$\cos\theta = \cos\theta_Y - \frac{\kappa}{\sigma_{LG} R_L} - \frac{1}{\sigma_{LG}}\left[\frac{d\kappa}{dR_L}\right], \tag{1.4}$$

where R_L is the radius of three-phase contact line, k is the corresponding line tension, and the differential in square bracket $[dk / dR_L]$ is determined by an arbitrary choice of the dividing line and the liquid-vapor interface.

For rough non-deformable solid substrates, Rusanov[7] obtained a comprehensive result

$$\cos\theta = r_S \cos\theta_Y - \left[\frac{r_L \kappa}{R_L} + \frac{\partial(r_L\kappa)}{\partial R_L}\right]\frac{|\cos\varphi|}{\sigma_{LG}} \tag{1.5}$$

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

$$r_L = \frac{L_{real}}{L_{apparent}} \times 100\% \tag{1.6}$$

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

Eq. (1.5) is valid only for the special dividing surface, called the surface of tension [8], between the liquid phase and the vapor phase. Considering the effect of the line tension, for the case of liquid on a flat homogeneous rough non-deformable solid substrates, we [9] obtained a generalized Young's equation for the contact angle θ,

$$cos\theta = r_S \cos\theta_Y - \frac{r_L \kappa}{\sigma_{LG} R_L} - \frac{1}{\sigma_{LG}}\left[\frac{d(r_L\kappa)}{dR_L}\right]. \tag{1.7}$$

Eq. (1.4) and Eq. (1.7) are valid only for the flat surface. Recently, we [10] studied the wetting of a droplet on a smooth spherical solid substrate and obtained the following generalized Young's equation

$$cos\theta = \cos\theta_Y - \frac{\kappa cos\beta}{\sigma_{LG} R_L} - \frac{\cos\beta}{\sigma_{LG}}\left[\frac{d\kappa}{dR_L}\right], \tag{1.8}$$

where β is the angle between the substrates surface and the local principal plane of the three-phase contact line

In this study, considering the effect of surface roughness and contact line roughness to the contact angle, we derive a new generalized Young's equation for the contact angle for a droplet on homogeneous and spherical rough solid substrates based on thermodynamics. In section 2, the

Helmholtz free energy 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 of the three-phase system

Let us consider the wetting of a droplet on a rough spherical solid substrate, refers to Fig. 1. The angle between the solid-liquid surface tangent and the liquid-vapor surface tangent is the contact angle θ . Let β be the angle between the substrates surface 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 $\alpha = \theta + \beta$. Let R be the radius of spherical liquid drop. R_O is the radius of spherical solid substrates. R_L is the radius of three-phase contact line.

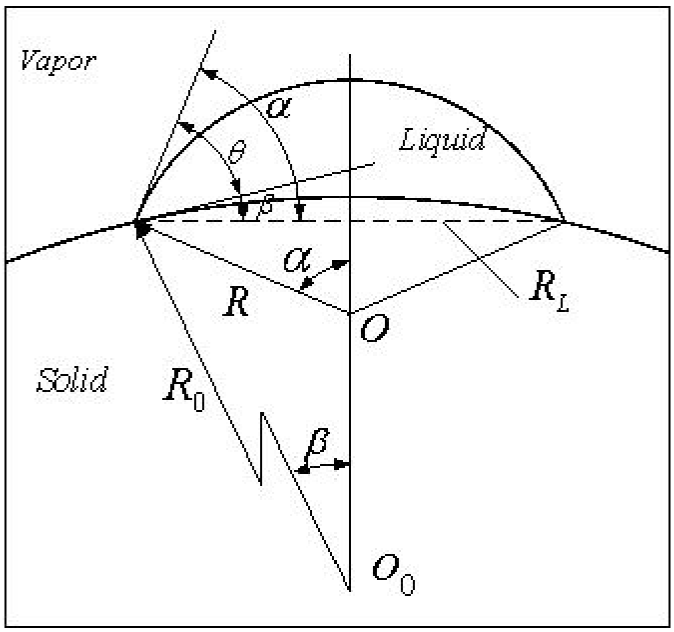

Fig. 1 An illustration of hydrophilic wetting of spherical liquid droplet on a spherical rough solid substrates

For simplicity, we ignore the gravitation in the following discussion. Thus, the equilibrium shape of a droplet on a spherical solid substrates has the shape of a spherical segment.

According to Gibbs concept of dividing surface [8] and dividing line[11], this solid-liquid-vapor system can be divided into six parts, i.e. liquid phase, vapor phase, the liquid-vapor interface, the solid-liquid interface, the solid-vapor interface and the three-phase contact line. Therefore, the total Helmholtz free energy F of the system is

$$F = F_L + F_G + F_{LG} + F_{SL} + F_{SG} + F_{SLG}, \quad (2.1)$$

where F is the total Helmholtz free energy, $F_L, F_G, F_{LG}, F_{SL} + F_{SG}$ and F_{SLG} are the Helmholtz free energies of the six parts respectively.

$$F_L = -p_L V_L + \mu_L N_L, \quad (2.2)$$

$$F_G = -p_G V_G + \mu_G N_G, \quad (2.3)$$

$$F_{LG} = \sigma_{LG} A_{LG} + \mu_{LG} N_{LG}, \quad (2.4)$$

$$F_{SL} = \sigma_{SL} A_{SL} + \mu_{SL} N_{SL}, \qquad (2.5)$$
$$F_{SG} = \sigma_{SG} A_{SG} + \mu_{SG} N_{SG}, \qquad (2.6)$$
$$F_{SLG} = \kappa L_{SLG} + \mu_{SLG} N_{SLG}. \qquad (2.7)$$

where p_L and p_G are the pressures of liquid phase and vapor phase, respectively. V_L and V_G are the volumes of liquid phase and vapor phase, respectively. μ_L, μ_G, μ_{LG}, μ_{SL}, μ_{SG}, μ_{SLG} are the chemical potentials 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} are their corresponding mole numbers, respectively. A_{LG}, A_{SL}, A_{SG} are the surface areas of the liquid-vapor interface, solid-liquid and solid-vapor interface, respectively. L_{SLG} is the length of the three-phase contact line, and k is the line tension.

The volume of liquid phase V_L is

$$V_L = \frac{\pi R^3}{3}(2+\cos\alpha)(1-\cos\alpha)^2 - \frac{\pi R_0^3}{3}(2+\cos\beta)(1-\cos\beta)^2 \qquad (2.8)$$

where R is the radius of the spherical liquid droplet.

The total volume V_t of the system is

$$V_t = V_L + V_G \qquad (2.9)$$

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

$$A_{LG} = 2\pi R^2(1-\cos\alpha) \qquad (2.10)$$

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

$$A_{SLa} = 2\pi R_0^2(1-\cos\beta) \qquad (2.11)$$

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

$$A_{SL} = r_S 2\pi R_0^2(1-\cos\beta) \qquad (2.12)$$

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

$$A_t = A_{SL} + A_{SG} \qquad (2.13)$$

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

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

$$L_{SLGa} = 2\pi R\sin\alpha \qquad (2.14)$$

and

$$L_{SLG} = 2\pi R r_L \sin\alpha \qquad (2.15)$$

respectively.

Based on the above relations, we have

$$F_L = -p_L \cdot \left[\frac{\pi R^3}{3}(2+\cos\alpha)(1-\cos\alpha)^2 - \frac{\pi R_0^3}{3}(2+\cos\beta)(1-\cos\beta)^2\right] + \mu_L N_L, \qquad (2.16)$$

$$\begin{aligned} F_G &= -p_G \cdot \left\{ V_t - \left[\frac{\pi R^3}{3}(2+\cos\alpha)(1-\cos\alpha)^2 \right.\right. \\ &\left.\left. -\frac{\pi R_0^3}{3}(2+\cos\beta)(1-\cos\beta)^2 \right] \right\} + \mu_G N_G, && (2.17) \\ F_{LG} &= \sigma_{LG} \cdot 2\pi R^2 (1-\cos\alpha) + \mu_{LG} N_{LG}, && (2.18) \\ F_{SL} &= \sigma_{SL} \cdot 2\pi r_S R_0^2 (1-\cos\beta) + \mu_{SL} N_{SL}, && (2.19) \\ F_{SG} &= \sigma_{SG} \cdot [A_t - 2\pi r_S R_0^2 (1-\cos\beta)] + \mu_{SG} N_{SG}, && (2.20) \\ F_{SLG} &= 2\pi\kappa r_L R \sin\alpha + \mu_{SLG} N_{SLG}. && (2.21) \end{aligned}$$

Therefore, putting above results into Eq. (2.1), the total Helmholtz free energy F Fcan be written as

$$\begin{aligned} F = &-(p_L - p_G) \cdot \left[\frac{\pi R^3}{3}(2+\cos\alpha)(1-\cos\alpha)^2 \right. \\ &\left. -\frac{\pi R_0^3}{3}(2+\cos\beta)(1-\cos\beta)^2 \right] \\ &-p_G \cdot V_t + \sigma_{LG} \cdot 2\pi R^2 (1-\cos\alpha) \\ &+(\sigma_{SL} - \sigma_{SG}) \cdot 2\pi r_S R_0^2 (1-\cos\beta) \\ &+\sigma_{SG} A_t + 2\pi\kappa r_L R \sin\alpha \\ &+\mu_L N_L + \mu_G N_G + \mu_{LG} N_{LG} + \mu_{SL} N_{SL} \\ &+\mu_{SG} N_{SG} + \mu_{SLG} N_{SLG} \end{aligned} \qquad (2.22)$$

3. Derivation of a new generalized Young's equation

It is convenient to introduce the grand potential to treat a system including some open subsystems. The definition of the grand potential Ω of a system is

$$\Omega = F - \sum_i \mu_i N_i, \qquad (3.1)$$

where N_i are the corresponding mole numbers of molecules of the subsystems.

From Eq. (2.22) and Eq. (3.1), the total grand thermodynamic potential Ω of the system is obtained

$$\begin{aligned} \Omega = &-(p_L - p_G) \cdot \left[\frac{\pi R^3}{3}(2+\cos\alpha)(1-\cos\alpha)^2 \right. \\ &\left. -\frac{\pi R_0^3}{3}(2+\cos\beta)(1-\cos\beta)^2 \right] \\ &-p_G \cdot V_t + \sigma_{LG} \cdot 2\pi R^2 (1-\cos\alpha) \\ &+(\sigma_{SL} - \sigma_{SG}) \cdot 2\pi r_S R_0^2 (1-\cos\beta) \\ &+\sigma_{SG} A_t + 2\pi\kappa r_L R \sin\alpha \end{aligned} \qquad (3.2)$$

The thermodynamic potential Ω is independent of the arbitrary choice of the position of the dividing surface, [6] we have the following restriction

$$\left[\frac{d\Omega}{dR}\right] = 0 \qquad (3.3)$$

Putting Eq. (3.2) into Eq. (3.3), we have,

$$\begin{aligned}
- &\ (p_L - p_G) \cdot \left[\frac{dV_L}{dR}\right] + \left[\frac{d\sigma_{LG}}{dR}\right] \cdot A_{LG} \\
+ &\ \sigma_{LG} \cdot \left[\frac{dA_{LG}}{dR}\right] + (\sigma_{SL} - \sigma_{SG}) \cdot \left[\frac{dA_{SL}}{dR}\right] \\
+ &\ \left[\frac{d\kappa}{dR}\right] \cdot L_{SLG} + \kappa \cdot \left[\frac{dL_{SLG}}{dR}\right] = 0.
\end{aligned} \qquad (3.4)$$

The dividing surface of liquid-vapor interface of a liquid droplet on homogeneous and spherical rough solid substrates should be parts of concentric and conformal spherical surface. These dividing surfaces are segmental. Therefore, we have the following relationships

$$R\sin\alpha = R_0\sin\beta, \quad R_0\cos\beta - R\cos\alpha = \overline{O_0O} = const, \qquad (3.5)$$

$$\frac{d\alpha}{dR} = \frac{cos(\alpha-\beta)}{Rsin(\alpha-\beta)}, \quad \frac{d\beta}{dR} = \frac{1}{R_0sin(\alpha-\beta)}. \qquad (3.6)$$

and

$$R_L = R\sin\alpha = R_0\sin\beta, \quad \frac{dR_L}{dR} = \frac{\cos\beta}{sin(\alpha-\beta)}. \qquad (3.7)$$

Now using Eq. (3.5-3.6), we have the following results,

$$\begin{aligned}
\left[\frac{dV_L}{dR}\right] &= \pi R^2(2+cos\alpha)(1-\cos\alpha)^2 \\
&\quad +\pi R^2\sin^3\alpha \cdot \frac{cos(\alpha-\beta)}{sin(\alpha-\beta)} \\
&\quad -\pi R_0^2\sin^3\beta \cdot \frac{1}{sin(\alpha-\beta)}, && (3.8) \\
\left[\frac{dA_{LG}}{dR}\right] &= 4\pi R(1-cos\alpha) + 2\pi Rsin\alpha\frac{con(\alpha-\beta)}{sin(\alpha-\beta)}, && (3.9) \\
\left[\frac{dA_{SL}}{dR}\right] &= 2\pi R_0 r_S\frac{sin\beta}{sin(\alpha-\beta)}, && (3.10) \\
\left[\frac{dL_{SLG}}{dR}\right] &= 2\pi r_L\frac{cos\beta}{\sin(\alpha-\beta)}. && (3.11)
\end{aligned}$$

It is known that a generalized Laplace's equation [12, 13]of a free spherical droplet in vapor is

$$p_L - p_G = \frac{2\sigma_{LG}}{R} + \left[\frac{d\sigma_{LG}}{dR}\right] \qquad (3.12)$$

Using $\alpha = \theta + \beta$ and putting Eqs. (3.8-3.12) into Eq. (3.4), we obtain

$$cos\theta = r_S \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}} - \frac{r_L \kappa cos\beta}{\sigma_{LG} R sin(\theta + \beta)} - \frac{sin\theta}{\sigma_{LG}} \left[\frac{d(r_L \kappa)}{dR} \right] \qquad (3.13)$$

Using the Young's equation Eq. (1.1) and Eq.(3.7), Eq.(3.13)can be written as

$$cos\theta = r_S \cos\theta_Y - \frac{r_L \kappa cos\beta}{\sigma_{LG} R_L} - \frac{\cos\beta}{\sigma_{LG}} \left[\frac{d(r_L \kappa)}{dR_L} \right] \qquad (3.14)$$

Eq. (3.14) is a generalized Young's equation for spherical droplets on a spherical homogeneous rough solid substrates for an arbitrary dividing surface between liquid phase and vapor phase.

If $r_S = 1$ and $r_L = 1$, then Eq.(3.14) reduces to our previous result Eq.(1.8).

If we suppose β=0, then, cos β=1 the spherical surfaces change to flat surfaces, Eq.(3.14) reduces to the generalized Young's equation, Eq. (1.7), obtained by Wang et al.[9]. Furthermore, if r_S=1 and r_L=1 then Eq. (3.14) reduces to the generalized Young's equation Eq. (1.4), obtained by Rusanov et al. [6].

4. Conclusion

Applying Gibbs' concept of dividing surface and dividing line, the wetting of spherical droplets on spherical rough solid substrates was studied by methods of thermodynamics. Considering the influences of line tension, a generalized Wenzel's equation for contact angle between droplets and spherical rough solid substrates is derived. Under some assumptions, this generalized Wenzel's equation reduces to Rusanov's equation.

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