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Generalized Young equation for a spherical droplet inside a smooth and homogeneous cone involved by quadratic parabola

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Abstract
We thermodynamically investigate the wetting characteristics of a spherical droplet in a smooth and homogeneous cone rotated by the quadratic parabola $y = ax^2$ $(a > 0, x \geq 0)$ through the mechanisms of both Gibbs's dividing surfaces and Rusanov's dividing line. For the triple phase system including the solid, liquid and vapor phases, the derivation of a generalized Young equation containing the influences of the line tension is successfully carried out. Additionally, we as well analyze various approximate forms for this generalized Young equation by using the corresponding assumptions.

***Keywords*:** liquid droplet; generalized Young equation; line tension; quadratic parabola; contact angle; cone

1. Introduction
Wetting phenomena of liquids on solid surfaces have attracted considerable attention of many researchers in past two centuries [1-12], because of their extensive usefulness not only in our daily lives but also in numerous industrial applications, such as coating processes, lubricants, microfluidic devices, and boiling heat transfer. In terms of a closed equilibrium system, it is common to establish the relation between the contact angle and physical properties of the solid/liquid/vapor system by the principle of the force balance at the triple line. A more typical example with an equilibrium contact angle θ_Y is the Young's equation [1], which can be given by

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

Where σ_{SG}, σ_{SL} and σ_{LG} are the solid/vapor, solid/liquid and liquid/vapor surface tensions, respectively. The Young's equation could be used under several limitative conditions, where the solid surfaces are smooth and homogeneous, and the gravity force and the line tension are also neglected. Due to these shortcomings, the Young's equation for the equilibrium contact angle cannot be readily employed for practical applications, especially in this work about the cone rotated by the quadratic parabola around y axis.

Indeed, the line tension at the triple phase line, where the solid, liquid and vapor contact each other, has considerable impacts for contact angles that are formed by liquid drops on top of solid surfaces. The generalized Young equation depicts the dependence of the contact angle on the radius of the triple line. In 1977, Pethica [13] developed a generalized Young's equation describing liquid drops on smooth and homogeneous solid surfaces,

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

where θ is the contact angle, R_L and k are the radius of the contact line and the line tension, separately. In addition, Rusanov yet proposed a generalized Young's equation [14] considering the derivative term of the line tension by the radius of the triple line,

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

where the quantity in square bracket stands for the derivative of the line tension with respect to the radius of the contact line.

The concept of the line tension was first introduced thermodynamically by Gibbs in his theory about capillarity, but the more comprehensive study of this amount merely started a century later and is fully investigated in past decade. Rafael [15] studied the relationship between the drop size, the line tension along with the advancing and receding contact angles. Hie [16] established a theoretical model to estimate the contact angle of liquid droplets on rough solid substrates and compared both the theoretical and experimental results. Peng [17] calculated the effects of the line tension for the cylindrical and spherical droplets using the method of molecular dynamics simulation. More recently, Masao [18] performed the effects of the line tension on the heterogeneous nucleation of the convex and concave spheres.

Existing literatures give a large number of theoretical and experimental investigations [19-25] related to the generalized Young equation for contact angles of spherical drops on regular solid surfaces which provide information helpful to clearly understand the wetting properties of liquid droplets. However, to the best of our knowledge, the generalized Young's equation for a spherical droplet within a smooth and homogeneous cone revolved by the quadratic parabola has not been addressed until now. In this paper, on the basis of the principles of dividing surfaces mentioned by Gibbs and the dividing line proposed by Rusanov, we investigate the wetting characteristics of a spherical droplet in a smooth and homogeneous revolved cone. We successfully derive a generalized Young equation for spherical drops in a smooth and homogeneous cone, and this equation is suitable for arbitrary dividing surface between the liquid drop and solid substrate. Moreover, several simplified expressions of this generalized Young's equation are yet discussed under some assumptions.

2. Computing the entire free energy of the system

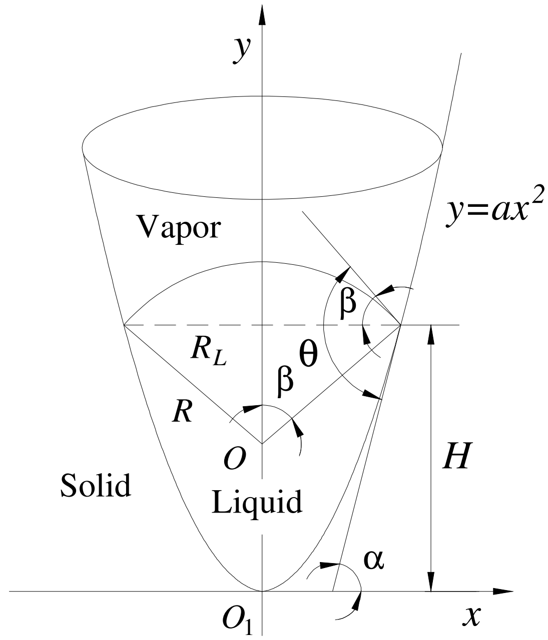

Figure 1. Representation of a spherical droplet within a smooth and homogeneous cone rotated by the quadratic parabola $y = ax^2\ (a > 0, x \geq 0)$ around y axis.

For the purpose of simplicity, we suppose that the quadratic parabola $y = ax^2\ (a > 0, x \geq 0)$ is used to generate the cone around y axis in Figure 1, whereas the case of the coefficient a smaller than zero is similar to this. As a result, in this work we will consider a single component spherical droplet (phase L) with its equilibrium vapor (phase G), placed within a smooth and homogeneous cone solid (phase S), as indicated in Figure 1.

On account of the principle of Gibbs's dividing surface, the triple phase system in this study is divided into six subsystems, namely, liquid phase, vapor phase, solid-liquid interface, solid-vapor interface, liquid-vapor interface, and the triple phase contact line. In this way, the Helmholtz free energy F of the system may be obtained

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

where F_L, F_G, F_{SL}, F_{SG}, F_{LG} and F_{SLG} are the free energies of various subsystems, respectively; subscripts are the symbols representing the corresponding phases, interfaces as well as the contact line (e.g., the indexes L and SLG stand for the liquid phase and the triple contact line, separately), respectively.

Various free energies of six subsystems are expressed as follows [2]

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

$$F_G = -p_G V_G + \mu_G N_G \tag{6}$$

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

$$F_{SG} = \sigma_{SG} A_{SG} + \mu_{SG} N_{SG} \tag{8}$$

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

$$F_{SLG} = kL_{SLG} + \mu_{SLG} N_{SLG} \tag{10}$$

where p the pressure, V the volume, μ the chemical potential, N the mole number of molecule, σ the surface tension, A the surface area, k the line tension, and L the length of the triple phase contact line.

To simplify the calculating of geometry quantities in the above equations, we neglect the gravity and other forces or fields. And then, the balance shape of a spherical droplet within the revolved cone is the combination of both a cone and a segment.

The volume V_L of the liquid phase is given by

$$\begin{aligned} V_L &= \int_0^H \pi \frac{y}{a} dy + \frac{\pi}{3} R^3 (1-\cos\beta)^2 (2+\cos\beta) \\ &= \frac{\pi}{2a} H^2 + \frac{\pi}{3} R^3 (1-\cos\beta)^2 (2+\cos\beta) \end{aligned} \tag{11}$$

Where H and R are the height and radius of the spherical droplet respectively and β is the apparent contact angle.

The whole volume V_t of the liquid-vapor system is given as

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

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

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

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

$$\begin{aligned} A_{SL} &= \frac{\pi}{a} \int_0^H \sqrt{1+4ay}\, dy \\ &= \frac{\pi}{6a^2} \left[(1+4aH)^{\frac{3}{2}} - 1 \right] \end{aligned} \tag{14}$$

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

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

The length of the three phase contact line may be obtained by

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

Based on the foregoing determined geometry amounts, a variety of free energies above have the following forms

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

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

$$F_{SL} = \sigma_{SL} \cdot \frac{\pi}{6a^2} \left[(1+4aH)^{\frac{3}{2}} - 1 \right] + \mu_{SL} N_{SL} \tag{19}$$

$$F_{SG} = \sigma_{SG} \cdot \left\{ A_t - \frac{\pi}{6a^2} \left[(1+4aH)^{\frac{3}{2}} - 1 \right] \right\} + \mu_{SG} N_{SG} \tag{20}$$

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

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

Put the preceding Eqs. (17-22) into Eq. (4) to get

$$
\begin{aligned}
F = & -\left(p_L - p_G\right)\cdot\left[\frac{\pi}{2a}H^2 + \frac{\pi}{3}R^3\left(1-\cos\beta\right)^2\left(2+\cos\beta\right)\right] - p_G\cdot V_t \\
& + \sigma_{LG}\cdot 2\pi R^2\left(1-\cos\beta\right) + \left(\sigma_{SL}-\sigma_{SG}\right)\cdot\frac{\pi}{6a^2}\left[\left(1+4aH\right)^{\frac{3}{2}}-1\right] \\
& + \sigma_{SG}\cdot A_t + 2\pi kR\sin\beta + \mu_L N_L + \mu_G N_G + \mu_{LG}N_{LG} \\
& + \mu_{SL}N_{SL} + \mu_{SG}N_{SG} + \mu_{SLG}N_{SLG}
\end{aligned}
\tag{23}
$$

3. Derivation of generalized Young equation

The grand potential Ω of the system which is composed of a solid, a single component spherical drop along with its vapor is defined to be

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

where the index i is the amount of subsystems of the system.
Substitute Eq. (23) into Eq. (24) to obtain,

$$
\begin{aligned}
\Omega = & -\left(p_L - p_G\right)\cdot\left[\frac{\pi}{2a}H^2 + \frac{\pi}{3}R^3\left(1-\cos\beta\right)^2\left(2+\cos\beta\right)\right] - p_G\cdot V_t \\
& + \sigma_{LG}\cdot 2\pi R^2\left(1-\cos\beta\right) + \left(\sigma_{SL}-\sigma_{SG}\right)\cdot\frac{\pi}{6a^2}\left[\left(1+4aH\right)^{\frac{3}{2}}-1\right] \\
& + \sigma_{SG}\cdot A_t + 2\pi kR\sin\beta
\end{aligned}
\tag{25}
$$

Since the grand potential Ω, the surface tensions σ_{SL} and σ_{SG} are independent of the radius R, we then have,

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

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

Let us put Eq. (25) into Eq. (26) and take Eq. (27) into account, we get

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

Note that we can obtain the following expressions from Figure 1

$$
R_L = R\sin\beta \tag{29}
$$

$$
H - R\cos\beta = \overline{OO_1} = const \tag{30}
$$

$$
H = aR^2\sin^2\beta \tag{31}
$$

Differentiating the variables β and R_L with respect to the radius R, we can write

$$
\frac{d\beta}{dR} = \frac{\cos\beta - 2aR\sin^2\beta}{R\sin\beta\left(1+2aR\cos\beta\right)} \tag{32}
$$

$$\frac{dR_L}{dR}=\frac{1}{\sin\beta\left(1+2aR\cos\beta\right)} \tag{33}$$

Applying Eqs. (11, 13, 14, 16) together with Eq. (32), we have

$$\begin{aligned}\left[\frac{dV_L}{dR}\right]&=2\pi aR^3\sin^4\beta+2\pi aR^3\sin^2\beta\cos\beta\cdot\frac{\cos\beta-2aR\sin^2\beta}{1+2aR\cos\beta}\\&\quad+\pi R^2\left(1-\cos\beta\right)^2\left(2+\cos\beta\right)+\pi R^2\sin^2\beta\cdot\frac{\cos\beta-2aR\sin^2\beta}{1+2aR\cos\beta}\end{aligned} \tag{34}$$

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

$$\left[\frac{dA_{SL}}{dR}\right]=\frac{2\pi R\sqrt{1+4a^2R^2\sin^2\beta}}{1+2aR\cos\beta} \tag{36}$$

$$\left[\frac{dL_{SLG}}{dR}\right]=\frac{2\pi}{\sin\beta\left(1+2aR\cos\beta\right)} \tag{37}$$

The Laplace's equation [6] of a free spherical drop yields

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

We can also obtain the following relations from Figure 1

$$\begin{cases}\sin\alpha=\dfrac{2aR\sin\beta}{\sqrt{1+4a^2R^2\sin^2\beta}}\\[2ex]\cos\alpha=\dfrac{1}{\sqrt{1+4a^2R^2\sin^2\beta}}\\[2ex]\theta=\alpha+\beta\end{cases} \tag{39}$$

Now we put Eqs. (34-38) into Eq. (28) and utilize Eq. (39) to get

$$\begin{aligned}\cos\theta&=\frac{\sigma_{SG}-\sigma_{SL}}{\sigma_{LG}}-\frac{\sin\beta\left(1+2aR\cos\beta\right)}{\sigma_{LG}\cdot\sqrt{1+4a^2R^2\sin^2\beta}}\cdot\left[\frac{dk}{dR}\right]\\&\quad-\frac{k}{R\sin\beta\cdot\sigma_{LG}\cdot\sqrt{1+4a^2R^2\sin^2\beta}}\end{aligned} \tag{40}$$

Further, we substitute the Young's equation (1) into Eq. (40) to obtain

$$\begin{aligned}\cos\theta&=\cos\theta_Y-\frac{\sin\beta\left(1+2aR\cos\beta\right)}{\sigma_{LG}\cdot\sqrt{1+4a^2R^2\sin^2\beta}}\cdot\left[\frac{dk}{dR}\right]\\&\quad-\frac{k}{R\sin\beta\cdot\sigma_{LG}\cdot\sqrt{1+4a^2R^2\sin^2\beta}}\end{aligned} \tag{41}$$

By using Eqs. (29, 33), Eq. (41) becomes

$$\cos\theta=\cos\theta_Y-\frac{1}{\sigma_{LG}\cdot\sqrt{1+4a^2R_L^2}}\cdot\left[\frac{dk}{dR_L}\right]-\frac{k}{R_L\cdot\sigma_{LG}\cdot\sqrt{1+4a^2R_L^2}} \tag{42}$$

Therefore, in terms of the spherical droplet inside a smooth and homogeneous cone revolved by the quadratic parabola $y=ax^2$ $(a>0,\, x\geq 0)$, Eq. (42) is the generalized Young's equation suitable for random dividing surfaces between the liquid and vapor phases.

If we initially suppose that the limiting case $\lim_{a \to 0} y = \lim_{a \to 0} ax^2 = 0$, then the quadratic parabola $y = ax^2 \ (a > 0,\ x \geq 0)$ changes to x axis, i.e., the rotated cone surfaces reduce to planar surfaces, Eq. (42) correspondingly becomes the generalized Young's equation (3) established by Rusanov. Go a step further, if we assume that the line tension is hold constant, Eq.(42) further reduces to the equation (2) proposed by Pethica. Finally, without considering the effects of the line tension, Eq. (42) decreases to the classical Young equation (1).

4. Conclusions

Based on the theorems of Gibbs's dividing surfaces and Rusanov's dividing line, by using the method of thermodynamics we research the wetting properties of a spherical droplet within a smooth and homogeneous cone spun by a quadratic parabola $y = ax^2 \ (a > 0,\ x \geq 0)$. Considering the impacts of the line tension, we successfully derive a generalized Young equation depicting the contact angle between a spherical drop and the inner wall surface of a rotated smooth cone on the basis of the principle of Gibbs's dividing surfaces. In addition, this generalized Young equation can simplify as the Rusanov's equation, the Pethica's equation as well as the usually used Young's equation under some hypotheses.

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