# Derivation of generalized Young's equation for cylindrical droplets between the outer surfaces of two tangent cylinders

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## Abstract

The wetting properties of cylindrical droplets between the outer surfaces of two tangent cylinders are investigated by means of thermodynamics. For the three-phase system containing solid, liquid and vapor phases, a generalized Young equation for contact angles of cylindrical drops between the outer surfaces of two tangent cylinders has been thermodynamically derived. In fact, the theoretical foundation of the derived generalized Young's equation is based on Gibbs's capillary phenomena and the method of Rusanov's dividing line. 

***Keywords***: Cylindrical droplet, Contact angle, Generalized Young equation, Line tension, Tangent cylinder

## 1. Introduction

Wetting phenomena are essential and usual in a variety of natural and industrial processes [1-5]. Wetting of solids by liquids has attracted significant experimental and theoretical attention in past two decades [6-11]. In particular, the contact angle characterizing wetting behaviors not only indicate how well a fluid wets a solid surface, but also display the penetration of liquids in porous solids, as well as the description of solid surfaces treatments [12].

The contact angle is expressed as the angle between the liquid/gas and the solid/liquid interfaces, at the position where the three phases (solid, liquid, and vapor) meet. For a chemically homogeneous and smooth solid surface, the contact angle is presented by Young's equation [6]

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

where $\theta_Y$ is the equilibrium contact angle, $\sigma_{SV}$, $\sigma_{SL}$ and $\sigma_{LV}$ are the interfacial tensions that exist between the solid (S), vapor (V), and liquid (L), respectively.

In recent years a large number of investigations have been carried out regarding the wetting phenomena in capillaries. For the cylindrical drops on solid surfaces, N. Dumitrascu [13] studied the contact angle between liquids and cylindrical surfaces. Davide Mattia [14] carried out the conditions for the stability of liquid films on and inside cylindrical solid substrates, especially emphasizing on nanometre scale substrates. Vlado A. Lubarda

[15] investigated the stability of a cylindrical liquid bridge between two parallel plates and derived a closed expression with respect to the height of the bridge of cylindrical droplets.

However, to the best of our knowledge, there is still not the generalized Young's equation for cylindrical drops between the outer surfaces of two tangent cylinders. Therefore, in order to study the wetting properties of cylindrical drops between the outer surfaces of two tangent cylinders, in line with the principles of both Gibbs's dividing surfaces and Rusanov's dividing line, a generalized Young equation for contact angles is derived using the method of thermodynamics.

## 2. Calculating the systemic free energy

Considering a cylindrical droplet with single component, associated with its equilibrium vapor, placed between the outer surfaces of two tangent cylinders (see Figure 1).

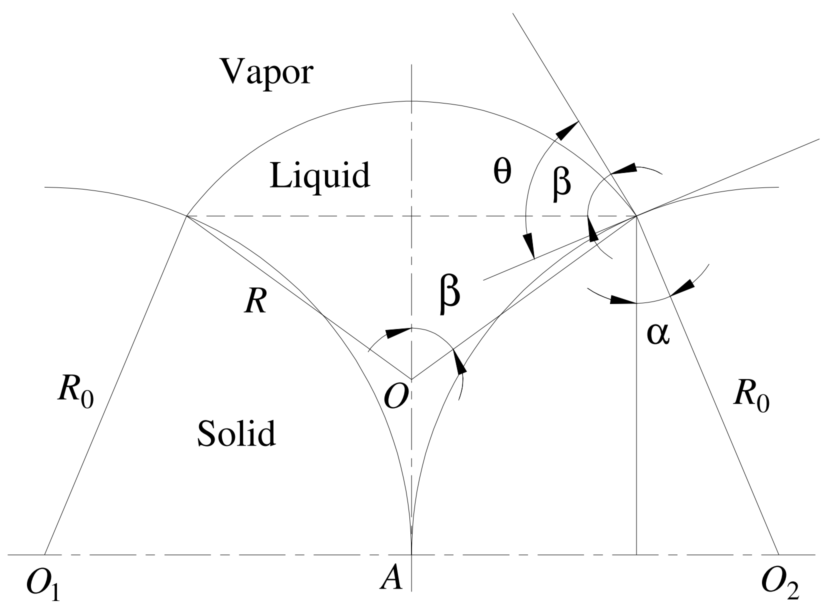


Figure 1. A cylindrical droplet between the outer surfaces of two tangent cylinders

According to the theory of Gibbs's dividing surfaces, the system, which is illustrated in figure 1, consists of six subparts, that is, liquid phase, vapor phase, solid/liquid interface, solid/vapor interface, liquid/vapor interface, as well as the triple phase line. And then, the Helmholtz free energy $F$ of this system is obtained by

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

where $F_L$, $F_V$, $F_{SL}$, $F_{SV}$, $F_{LV}$ and $F_{SLV}$ are the Helmholtz free energies of the liquid phase, the vapor phase, solid/liquid interface, solid/vapor interface, liquid/vapor interface, and the triple phase line, respectively.
The various free energies have the following forms

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

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

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

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

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

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

where $p_L$ and $p_V$ are the pressures of the liquid and vapor phases respectively, $V_L$ and $V_V$ are the volumes of the liquid and vapor phases, respectively, $\sigma_{SL}$, $\sigma_{SV}$ and $\sigma_{LV}$ are the surface tensions of the solid/liquid, solid/vapor, and liquid/vapor interfaces respectively, $A_{SL}$, $A_{SV}$ and $A_{LV}$ are the surface areas of the solid/liquid, solid/vapor, and liquid/vapor interfaces, respectively, $k$ is the line tension, $L_{SLV}$ is the length of the triple phase line, and $\mu_L, \mu_V, \mu_{SL}, \mu_{SV}, \mu_{LV}, \mu_{SLV}$, as well as $N_L, N_V, N_{SL}, N_{SV}, N_{LV}, N_{SLV}$ are the chemical potentials and the mole numbers of molecules of the corresponding phases, interfaces, and the triple phase line respectively.

For the purpose of simplicity, ignoring the gravity and the other forces or fields, and then, the equilibrium shape of a cylindrical droplet between the outer surfaces of two tangent cylinders is the combination of the prism same as a triangular prism and a cylindrical cap.

The volume $V_L$ of the liquid phase is given by

$$V_L = R^2 L(\beta - \sin\beta\cos\beta) + L\left\{R_0 R\cos\alpha\sin\beta + R_0^2\cos\alpha - \frac{\pi}{2}R_0^2 + R_0^2\alpha\right\} \tag{9}$$

Where $R$ and $L$ are the radius and height of the cylindrical drop, respectively $\alpha$ is the angle between the radius $R_0$ and the vertical line, and $\beta$ is the apparent contact angle.

The total system volume $V_t$ is given by

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

The liquid/vapor interfacial area $A_{LV}$ is expressed as

$$A_{LV} = 2R\beta L \tag{11}$$

The solid/liquid interfacial area $A_{SL}$ is written by

$$A_{SL} = 2R_0 L\left(\frac{\pi}{2} - \alpha\right) \tag{12}$$

The total interfacial area $A_t$ of the solid/liquid and solid/vapor interfaces is obtained as

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

The length of the three-phase line is written as

$$L_{SLV} = 2L \tag{14}$$

Based on the relations above, various free energies can be rewritten as

$$F_L = -p_L \cdot \left[R^2 L(\beta - \sin\beta\cos\beta) + L\left\{R_0 R\cos\alpha\sin\beta + R_0^2\cos\alpha - \frac{\pi}{2}R_0^2 + R_0^2\alpha\right\}\right] + \mu_L N_L \tag{15}$$

$$F_V = -p_V \cdot \left\{V_t - \left[R^2 L(\beta - \sin\beta\cos\beta) + L\left\{R_0 R\cos\alpha\sin\beta + R_0^2\cos\alpha - \frac{\pi}{2}R_0^2 + R_0^2\alpha\right\}\right]\right\} + \mu_V N_V \tag{16}$$

$$F_{SL} = \sigma_{SL} \cdot 2R_0 L\left(\frac{\pi}{2} - \alpha\right) + \mu_{SL} N_{SL} \tag{17}$$

$$F_{SV} = \sigma_{SV} \cdot \left[ A_t - 2R_0 L\left(\frac{\pi}{2} - \alpha\right)\right] + \mu_{SV} N_{SV} \tag{18}$$

$$F_{LV} = \sigma_{LV} \cdot 2R\beta L + \mu_{LV} N_{LV} \tag{19}$$

$$F_{SLV} = 2Lk + \mu_{SLV} N_{SLV} \tag{20}$$

Now putting the above Eqs. (15-20) into Eq. (2), the free energy $F$ of the total system is rewritten as

$$\begin{aligned} F =& -\left(p_L - p_V\right)\cdot\left[R^2L\left(\beta - \sin\beta\cos\beta\right) + L\left\{R_0 R\cos\alpha\sin\beta + R_0^2\cos\alpha - \frac{\pi}{2}R_0^2 + R_0^2\alpha\right\}\right] \\ & - p_V \cdot V_t + \sigma_{LV}\cdot 2R\beta L + \left(\sigma_{SL} - \sigma_{SV}\right)\cdot 2R_0 L\left(\frac{\pi}{2} - \alpha\right) + \sigma_{SV}\cdot A_t + 2L\cdot k \\ & + \mu_L N_L + \mu_V N_V + \mu_{LV} N_{LV} + \mu_{SL} N_{SL} + \mu_{SV} N_{SV} + \mu_{SLV} N_{SLV} \end{aligned} \tag{21}$$

## 3. Derivation of a generalized Young's equation

The grand thermodynamic potential $\Omega$ of a system containing a solid, a one component droplet as well as its vapor is expressed as

$$\Omega = F - \sum_i \mu_i N_i \tag{22}$$

where the subscript $i$ is the number of subsystems of the system.
Substituting Eq. (21) into Eq. (22) leads to

$$\begin{aligned} \Omega =& -\left(p_L - p_V\right)\cdot\left[R^2L\left(\beta - \sin\beta\cos\beta\right) + L\left\{R_0 R\cos\alpha\sin\beta + R_0^2\cos\alpha - \frac{\pi}{2}R_0^2 + R_0^2\alpha\right\}\right] \\ & - p_V \cdot V_t + \sigma_{LV}\cdot 2R\beta L + \left(\sigma_{SL} - \sigma_{SV}\right)\cdot 2R_0 L\left(\frac{\pi}{2} - \alpha\right) + \sigma_{SV}\cdot A_t + 2L\cdot k \end{aligned}$$

(23)

Because grand potential $\Omega$, the surface tensions $\sigma_{SL}$ and $\sigma_{SV}$ are independent of the choice of dividing surfaces [16], we get

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

$$\left[\frac{d\sigma_{SL}}{dR}\right] = 0, \ \left[\frac{d\sigma_{SV}}{dR}\right] = 0 \tag{25}$$

Using Eq. (23) to (25), one gets

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

From figure 1 we can obtain the following expressions

$$R_0 \sin\alpha + R\sin\beta = R_0 = const \tag{27}$$

$$R_0\cos\alpha - R\cos\beta = \overline{OA} = const \tag{28}$$

$$\theta = \alpha + \beta \tag{29}$$

and

$$\frac{d\beta}{dR} = \frac{\cos(\alpha+\beta)}{R\sin(\alpha+\beta)} \tag{30}$$

$$\frac{d\alpha}{dR} = -\frac{1}{R_0 \sin(\alpha+\beta)} \tag{31}$$

Using both Eqs. (9, 11, 12, 14) and Eqs. (30-31), we get

$$\left[\frac{dV_L}{dR}\right] = 2RL\beta \tag{32}$$

$$\left[\frac{dA_{LV}}{dR}\right] = 2\beta L + 2L\cdot\frac{\cos(\alpha+\beta)}{\sin(\alpha+\beta)} \tag{33}$$

$$\left[\frac{dA_{SL}}{dR}\right] = \frac{2L}{\sin(\alpha+\beta)} \tag{34}$$

$$\left[\frac{dL_{SLV}}{dR}\right] = 0 \tag{35}$$

It is well known that the Laplace' equation [17] of a free cylindrical liquid drop in vapor satisfies

$$p_L - p_V = \frac{\sigma_{LV}}{R} + \left[\frac{d\sigma_{LV}}{dR}\right] \tag{36}$$

It can be used for the droplet in figure 1.

Substituting Eqs. (32-35) into Eq. (26), we get,

$$\cos(\alpha+\beta) = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} - \frac{\sin(\alpha+\beta)}{\sigma_{LV}}\cdot\left[\frac{dk}{dR}\right] \tag{37}$$

Putting Eq. (29) into Eq. (37) yields

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

By comparing the classical Young's equation (1) with Eq. (38), we get

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

Hence, in terms of cylindrical droplets between the outer surfaces of two tangent cylinders, Eq. (39) is the generalized Young's equation applicable to arbitrary dividing surfaces between the liquid and vapor phases.

## 4. Conclusion

In this research, according to the concepts of Gibbs's dividing surfaces and Rusanov's dividing line, the wetting characteristics of cylindrical droplets between the outer surfaces of two tangent cylinders are investigated by method of thermodynamics. Taking the effects of the line tension into account, a generalized Young equation for contact angles of cylindrical droplets between the outer surfaces of two tangent cylinders, has been derived based on the method of Gibbs's dividing surfaces.

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