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An Attempt to Analyze Axisymmetric Sessile and Pendant Droplets

by

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Abstract

An attempt was made to accomplish shape analyses on axisymmetric sessile and pendant droplets using the modified Laplace equation. It was demonstrated that the minimum interfacial energy condition can conveniently derive Young-Dupre's equation with the aid of Lagrange's multiplier method for a sessile droplet under zero-gravity. On the other hand, under gravity, a simple computer calculation showed that the minimum energy condition in which the sum of the interfacial energy and the potential energy of the sessile drop becomes a minimum, demonstrates the consistency of the calculated contact angle with Young-Dupre's equation. The pendant droplet calculation was also accomplished in a similar manner. Under gravity, the shape analysis revealed that the center of gravity of the droplet moves both upward and downward as its volume increases, implying that energy compensation is occurring with the variation in the interfacial areas.

Keywords: surface tension, sessile drop, pendant drop

1. Introduction

Surface properties of materials including surface tension, interfacial tension, wettability, etc. are very important for various usages in our real world. On the other hand, surface tension and interfacial tension become more significant under weightless microgravity environment. In any case, to enhance the knowledge of surface/ interfacial tension is essential. There are several methods to measure surface tension. Among those are sessile drop method, pendant droplet method, drop weight method, maximum bubble pressure method, etc.[1,2] Most of these methods are based on the exact shape of droplets or bubbles. In the old days, Bashworth and Adams' table[3] played a significant role in this field. Nowadays, detailed digitized data points are obtained through the sophisticated equipments and the curve fitting methods have taken place of the Bashworth and Adams' table to find out the objective values of surface tension. Accordingly, it is very important to develop an understanding on the precise shape of the droplets or bubbles during the measurement. A number of detailed analyses with sophisticated mathematical application[4,5] have been published until now. However, it has to be possible to apply another simple amd convenient way of demonstration to clarify the droplet shape properties.

The purpose of this study is to develop a basic understanding of the shape for axisymmetric sessile and pendant droplet based on Laplace equation in order to be of help for more precise and accurate measurement of surface tension. In this study, analytical and calculational results under zero gravity and under gravitational acceralation are presented.

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2. Principle

With a Laplace equation, the difference in pressure exerted on the interface can be calculated, where the curved interface separates two bulk phases with a sufficiently large curvature radius:

$$\gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=\Delta P \quad (1)$$

Here, γ is the interfacial tension (or surface tension), R_1 and R_2 are the two principle curvature radii that are perpendicular with each other, and ΔP is the difference in pressure between the two bulk phases. Initially, the influence of an external force such as gravity is not taken into account in this equation. In case when gravity is applied, the pressure difference can be expressed as a function of the elevation:

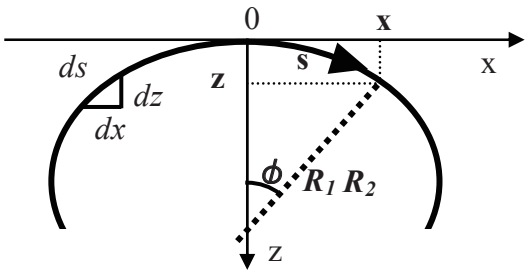

Figure 1: Calculation configuration for a sessile drop

$$\Delta P = \Delta P_0 + (\Delta\rho)gz \quad (2)$$

Here ΔP_0 is the pressure difference at the selected datum plane, $\Delta\rho$ is the difference in densities of the two bulk phases, g is the gravitational constant, z is the vertical distance from the datum plane.

As shown in Fig. 1, the x-axis is tangent to the curved interface and normal to the symmetrical axis and the origin of the coordinates axes is placed at the apex,

Combining Eq. (1) and Eq. (2) gives

$$\gamma\left(\frac{1}{R_1}+\frac{\sin\phi}{x}\right)=\frac{2\gamma}{R_0}+(\Delta\rho)gz \quad (3)$$

Here, following a similar manner to Roetenberg et al,[6] R_1 turns in the plane of the paper and $R_2 = x/\sin\phi$ rotates in a plane perpendicular to the plane of the paper and about the axis of symmetry; R_0 is the radius of curvature at the origin of the x-z coordinate system (i. e., $R_1 = R_2 = R_0$ at the origin), and ϕ is the turning angle measured between the tangent to the interface at the point (x, z) and the datum plane.

In the mathematical consideration, the interface should be described completely as $u = u(x, y, z)$. Due to the symmetry, only the description of the meridian section is enough to solve the equation. If one takes s as the arc length measured from the origin, o, the following parametric form becomes possible:

$$x = x(s) \text{ and } z = z(s),$$

and the geometrical consideration gives the differential identities

$$\frac{dx}{ds}=\cos\phi \quad (4)$$

$$\frac{dz}{ds}=\sin\phi \quad (5)$$

By definition

$$\frac{1}{R_1}=\frac{d\phi}{ds} \quad (6)$$

Combination of eqs. (6) and (3) yields

$$\frac{d\phi}{ds}=\frac{2}{R_0}+\frac{(\Delta\rho)g}{\gamma}z-\frac{\sin\phi}{x} \quad (7)$$

Accordingly, eqs. (4), (5) and (7) and the boundary conditions

$$x(0) = z(0) = \phi(0) = 0$$

finally give the x, z and ϕ as a function of the argument s. For given R_0, $\Delta\rho$ and γ, the complete shape of the curve can be obtained by integrating these three equations simultaneously. In a realistic calculation, one more parameter to decide the droplet height is required; i. e., the contact angle between droplet and substrate or the volume of the droplet (otherwise the mass). Under these conditions, a curved line for the drop shape is calculated with increasing the argument s. An effort made in the numerical analysis used a Fortran compiler in Bosei calculation server set at Tokai University Information Technology Center. In case when the minimal value should be obtained, a simple bisection scheme as an iterative method was adopted for a relatively small Fortran program in double precision.

3. Results and Discussion

3.1 *Relatioship with the Young-Dupre equation*

As a liquid surface becomes spherical under zero gravity, one can derive Young-Dupre equation under a minimal condition of total surface/interfacial energy of the system based on the fact of the spherical surface (Fig. 2). With this configuration, the interfacial areas between the liquid and the gas S_{gl} and between the liquid and the solid S_{sl} are expressed in the following:

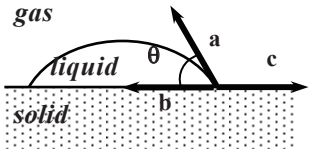

Figure 2: Young-Dupre equation at a planar surface

$$S_{gl} = 2\pi r^2(1-\cos\theta) \quad (8)$$

$$S_{sl} = \pi r^2 \sin^2\theta \quad (9)$$

where r is the curvature radius of the interface between the liquid and the gas and θ is the contact angle. The volume of the liquid V is given as

$$V = \frac{\pi}{3}r^3(1-\cos\theta)^2(2+\cos\theta) \quad (10)$$

Accordingly, the total surface/interfacial energy of the system G on the selected solid surface area S_0 that contains the liquid is written as

$$G = aS_{gl} + bS_{sl} + c(S_0 - S_{sl}) \quad (11)$$

Here, a, b and c stand for the interfacial tension (or interfacial energy) between the liquid and the gas, between the liquid and the solid, and between the solid and the gas,

respectively. Inserting eqs. (8) and (9) into the above equation gives

$$G = 2a\pi r^2(1-\cos\theta)+(b-c)\pi r^2\sin^2\theta + cS_0 \quad (12)$$

The essential condition required here is to obtain the minimal value of total surface/interfacial energy of the system under a constant volume of the liquid and such a requirement can be satisfied by means of the Lagrange' multiplier method that is written with the partial differentials of G and V:

$$\frac{G_r}{G_\theta} = \frac{V_r}{V_\theta} \quad (13),$$

where each partial differential is presented as follows:

$$G_r = 2\pi r(1-\cos\theta)\{2a+(b-c)(1-\cos\theta)\}$$
$$G_\theta = 2\pi r^2\sin\theta\{a+(b-c)\cos\theta\}$$
$$V_r = \pi r^2(1-\cos\theta)^2(2+\cos\theta)$$
$$V_\theta = \pi r^3\sin^2\theta(1-\cos\theta)(1+\cos\theta)$$

By inserting each differential parameter into eq. (13) gives

$$\frac{(b-c)(1-\cos\theta)}{a+(b-c)\cos\theta}+\frac{\cos\theta}{1+\cos\theta}=0 \quad (14)$$

and rearranging the above equation finally yields the Young-Dupre equation.

$$a\cos\theta+(b-c)=0 \quad (15)$$

Thus, as expected, the Young-Dupre equation can be demonstrated from the minimal condition of the total surface/interfacial energy of the system.

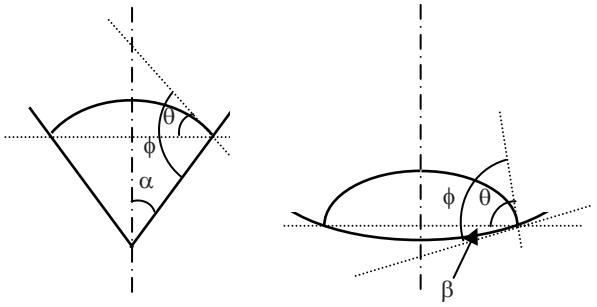

Figure 3: Cross sectional configurations of contact for a conical (left) and spherical (right) substrate

Even in cases where the solid surface has a conical or spherical configuration (Fig. 3), the Young-Dupre equation can be derived through the similar process. For the case of conical surface as shown in the figure, the contact angle of the liquid on the conical solid ϕ is given as

$$\phi = \frac{\pi}{2}-\alpha+\theta \quad (16)$$

$$\cos\phi = \sin(\alpha-\theta) \quad (17)$$

Along the similar demonstration process with Lagrange' multiplier method, the corresponding partial differentials are

$$G_r = 2\pi r(1-\cos\theta)\left\{2a+(b-c)\frac{1+\cos\theta}{\sin\alpha}\right\}$$

$$G_\theta = 2\pi r^2\sin\theta\left\{a+(b-c)\frac{\cos\theta}{\sin\alpha}\right\}$$

$$V_r = \pi r^2(1-\cos\theta)\left\{(1-\cos\theta)(2+\cos\theta)+(1+\cos\theta)\sin\theta\frac{\cos\alpha}{\sin\alpha}\right\}$$

$$V_\theta = \pi r^3\sin^2\theta\left(\sin\theta+\cos\theta\frac{\cos\alpha}{\sin\alpha}\right)$$

and a similar calculation using eq. (13) can be rearranged into

$$a\sin(\alpha-\theta)+(b-c)=0 \quad (18)$$

and then

$$a\cos\phi+(b-c)=0.$$

For the case of spherical surface (with R as radius), the relationship among the angles shown in Figure 3 is written as

$$R\sin\beta = r\sin\theta \quad (19).$$

the contact angle of the liquid on the spherical solid ϕ is given as

$$\phi = \theta+\beta \quad (20)$$

Based on this relation, the following partial differentials can be derived:

$$\frac{\partial\beta}{\partial r}=\frac{\sin\theta}{R\cos\beta} \quad \text{and} \quad \frac{\partial\beta}{\partial r}=\frac{r\cos\theta}{R\cos\beta}$$

Accordingly, each partial differential factor to be utilized in Lagrange' multiplier method is in the following:

$$G_r = 2\pi r(1-\cos\theta)\left\{(1-\cos\theta)(2+\cos\theta)+(1+\cos\theta)\sin\theta\frac{\sin\beta}{\cos\beta}\right\}$$

$$G_\theta = 2\pi r^2\sin\theta\left\{a+(b-c)\frac{\cos\beta}{\sin\beta}\right\}$$

$$V_r = \pi r^2(1-\cos\theta)\left\{(1-\cos\theta)(2+\cos\theta)+(1+\cos\theta)\sin\theta\frac{\sin\beta}{\cos\beta}\right\}$$

$$V_\theta = \pi r^3\sin^2\theta(\sin\theta+\cos\theta\frac{\sin\beta}{\cos\beta})$$

Further calculation and a similar rearrangement of the equation gives

$$a\cos(\theta+\beta)+(b-c)=0 \quad (21)$$

and then

$$a\cos\phi+(b-c)=0.$$

As realized, it is successfully demonstrated that such a simple analytical process can perfectly derive the Young-Dupre equation based on the minimal surface/interfacial energy requirement.

3.2 *Shape analysis on sessile drop under gravity*

In the field where a gravitational acceleration is being exerted, it is not easy to derive the Young-Dupre equation with a simple analytical process described in the above. Thus the author made an attempt to calculate contact angle and realize the relationship as the calculational fact on the

Young-Dupre equation.

The model adopted here is the system where liquid pure iron is placed on a solid alumina surface with a contact at temperature 1550℃. The values of parameter (surface/ interfacial energy) *a*, *b* and *c* are 1.915, 1.8494 and 0.750 (N/m), respectively. [7,8] With these surface and interfacial energy values, the contact angle of liquid iron on the solid alumina is calculated to be 125° [8,9], which is close to the literature data.

In the calculation, the point of interest is whether calculation gives the exact contact angle value of 125 degrees, based on the surface/ interfacial tension data. As it is well known in the gravity field, the height of liquid droplet varies with varying its contact angle even for a droplet of an identical mass and surface tension.[7]

Here, the equilibrium drop shape of liquid iron is obtained for the given contact angle, mass, density and surface tension data. Therefore, one has to take the potential energy of the droplet into account. It is called a potential method for this kind of calculation.

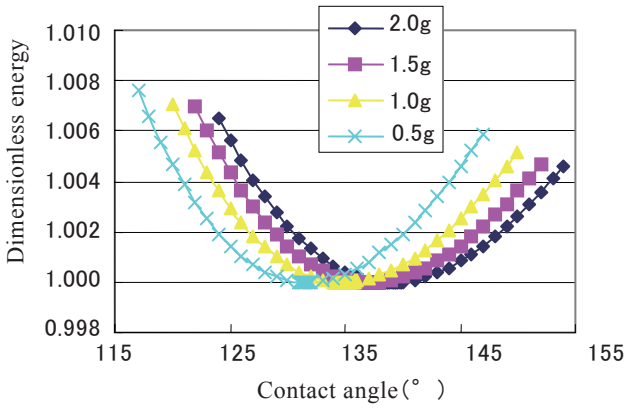

Figure 4: Calculated contact angle between liquid iron and alumina by means of minimal interfacial energy condition (Sessile drop mass: 0.5, 1.0, 1.5 and 2.0 g)

If one accomplishes a simple calculation under the condition that only requires the minimum energy for the system, anomalous and completely mistaken results will be given where wrong contact angle values are calculated and the calculated contact angle even increases with increasing the liquid iron mass, as shown in Figure 4.

On the other hand, the contact angle calculation can be accomplished correctly to attain a 125 degree contact angle for the liquid iron on the solid alumina in case when the minimal energy condition is adopted through a combination of total surface/interfacial energy of the system and the potential energy of the liquid iron droplet, as shown in Figure 5.

Similar calculation results can be presented in Tables 1 and 2, where the contact angle of liquid iron placed on solid alumina with a conical shape and a spherical shape are calculated, respectively. For the computation on conical substrate, opening angles α were given as the initial value for the system, and the horizontal angle θ was calculated. From this value the contact angle for the case was obtained following the configuration. Although the calculated values are rounded off at an appropriate decimal place in the tables, the significant figure can be improved with increasing the precision of the computing system.

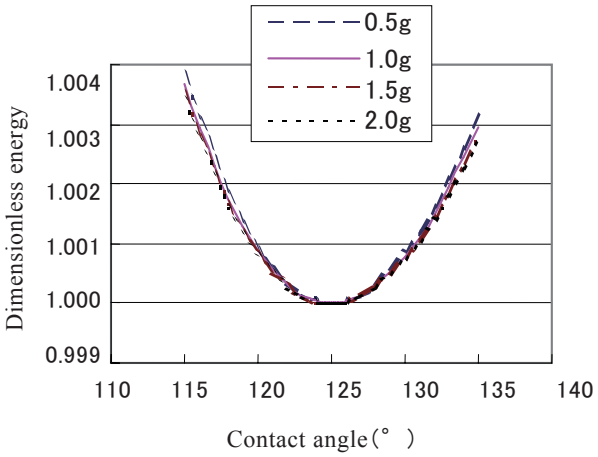

Figure 5: Calculated contact angle between liquid iron and alumina by means of minimal sum of interfacial energy and potential energy (Sessile drop mass: 0.5, 1.0, 1.5 and 2.0 g)

Table 1. An exampleof calculation results for a droplet of 1 g liquid iron placed on the conical surfaces of alumina (Configuration on the angles α and θ refered in Fig. 3.)

Given opening angle α (°)	Calculated horizontal angle θ (°)	Calculated contact angle $\phi = 90 - \alpha + \theta$ (°)
30	65	125
45	80	125
60	95	125
75	110	125
90	125	125

Table 2. An example of calculation results for a droplet of 1 g liquid iron placed on the spherical surfaces of alumina (Configuration on the angles β and θ refered in Fig. 3.)

Given surface curvature radius (cm)	Calculated angle for tangent plane β (°)	Calculated horizontal angle θ (°)	Calculated contact angle $\phi = \beta + \theta$ (°)
1	21.48	103.52	125
2	9.75	115.25	125
5	3.71	121.29	125
10	1.79	123.21	125

As a conclusion for this chapter, a successful calculation can be demonstrated even for the numerical analyses if one adopts the minimal energy condition that is straightened up

with both total surface/interfacial energy of the system and the potential energy of the droplet. The calculation can be applied to a variety of substrate configurations such as planar, conical, spherical, etc.

3.3 *Application to pendant drop under gravity*

In order to calculate the shape of pendant droplet, a very minor revision is necessary in eq. (7); only modification is to put minus to the gravitational acceleration g, because the direction of gravitational force is opposite to the case of sessile drop. Comparing with the case of sessile drop, calculation is substantially difficult for pendant shape. For the calculation of sessile drop, solution gives a realistic configuration whatever the case may be, because the droplet mass is always supported by the substrate. However, one should be very careful for pendant drop because the numerical solution does not necessarily express a realistic situation. Care should be also taken about the point of contact: accurate information on how the contact is occurring between the liquid and the substrate. In the present study, it is adopted as a starting point for convenience that a completely wettable situation where contact angle is equal to zero, such as water wetting to ice or a window pane. For this situation it can be imagined that water is about to drip from the surface of ice or glass. The density of water is set to 1 g/cm^3.

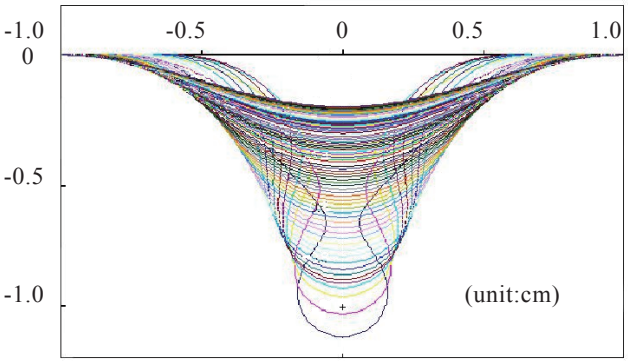

Figure 6: Variation in the calculated pendant drop shape as a function of the curvature radius at the apex which varies from 0.15 to 1.0 cm; Both axes give the scale size for each droplet in cm.

Figure 6 shows a typical example of calculation result where the curvature radius at the apex of the pendant drop is varied from 0.15 to 1.0 cm, which corresponds to the R_0 in eq. (7). Each shape gives the variation at a quasi-static state.

Along with this calculation process, the volume and the center of gravity for each liquid mass are obtained. Figure 7 plots the volume as a function of curvature radius at the apex, which gives the maximum volume value at the curvature radius at the apex ca. 0.33 cm. This implies that, under the conditions on the density and the contact angle, the liquid mass is not allowed to increase its volume; if an excessive amount of water flows into the mass, the liquid mass cannot exist, i. e., the liquid mass breaks and falls down. Moreover, a series of calculation reveals a fact of great interest that

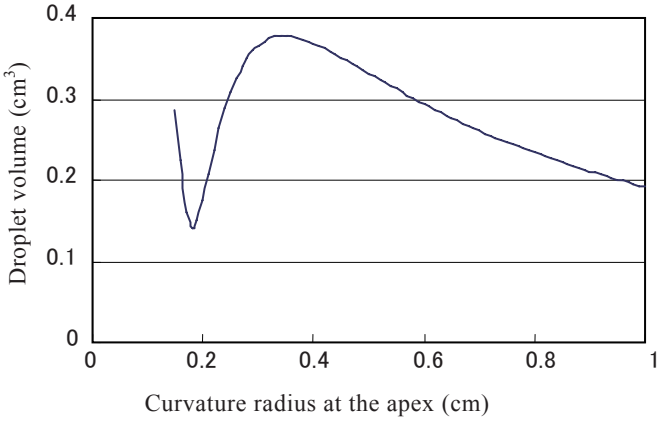

Figure 7: Pendant drop volume as a function of curvature radius at the apex

there are both cases where the center of gravity moves upwards and downwards with increasing the volume of the liquid mass as realized in Figure 8. It is suggested from this finding that there should be a kind of compensation between the surface/interfacial energy and the potential energy of the system if the center of gravity moves upwards though it is natural for the center of gravity to move downwards. In case when the center of gravity of the liquid mass moves upwards to increase its potential energy, it becomes possible for the system to increase its volume on conditions that the corresponding interfacial areas decrease to the sum of the surface/interfacial energy, which can compensate the increase in the potential energy.

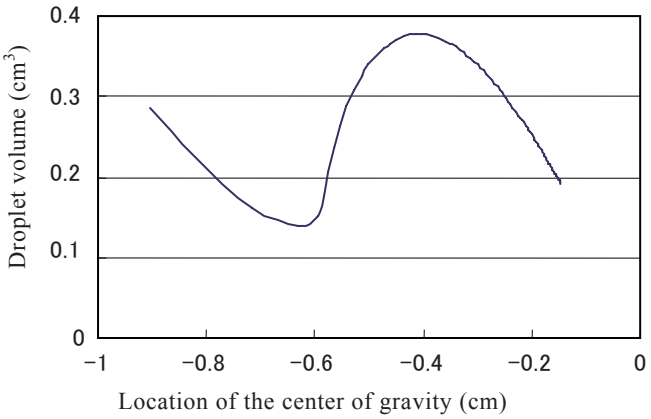

Figure 8: Relationship between pendant drop volume and the location of its center of gravity

4. Conclusion

Analyses are accomplished for the shapes of axisymmetric sessile and pendant droplets. As for sessile drop, the analytical consistency can be clearly revealed by means of Lagrange' multiplier method for zero-gravity shape. Relating to the gravitational field, the modified Young-Dupre equation can also demonstrate the consistency of the wetting configuration. Calculation for pendant drop gives a complicated behavior in the relation between the volume and the gravity center of the droplet; the center of gravity can move both upwards and downwards. It is demonstrated that this calculation scheme can consistently treat the droplet shape variation and be of great help for the shape-related consideration.

5. References

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