

## Modeling of a sessile droplet with the curvature dependence of surface tension

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**Abstract:** In this paper, using the Gibbs dividing surface method, the formula that determines the curvature-dependent surface tension in a system with two phases is deduced. The well-known Tolman formula is a special case for this formula. The problem of a sessile droplet is considered. The Bashforth–Adams equation analogue in view of the curvature-dependent surface tension is obtained and the numerical solution of the equation is carried out. We show that if the droplet size is not so large compared to the thickness of the surface layer (micro- or nanodroplets), the dependence of the surface tension on the curvature is very important.

**Key words:** Sessile drop, surface tension, capillary pressure, Laplace equation, equilibrium capillary surface, size dependence, Tolman length, mean curvature, radius of curvature, nanodroplet

### 1. Introduction

In thermodynamics the surface tension is determined by the energy of isothermal interface formation and is a measure of the excess surface free energy compared to volumes of the coexisting phases [1,2]. Surface tension is an interface curvature function at any point. Surface tension depends on the Tolman length [1–3] and respectively on the interface layer thickness. The thickness of this layer depends on the temperature and when approaching the critical point can reach considerable values. Once the critical point is reached, both adjacent phases are transformed, forming one inhomogeneous intermediate phase, which is the reason for the thickening of the interphase layer. At the critical point, the intermediate phase extends all over the entire volume, causing the surface tension to vanish. Experimentally, this phenomenon manifests itself as critical opalescence. Consequently, with the temperature increase the curvature dependence of the surface tension should increase due to the interfacial region thickness increasing. In fluctuations of the surface tension this relationship apparently plays a key role. Surface tension also depends on the geometry of the interface of the coexisting phases [4]. Moreover, the smaller the interface surface area for a given condensed phase, the greater this dependence is.

Usually the dependence of surface tension on the surface curvature takes place for the small-sized condensed phase (for example, in microheterogeneous systems) and therefore it is often referred to as a size dependence of surface tension. Currently issues related to the study of size effects in solids and liquids are extremely important because of the intensive development of nanotechnologies. In particular, the surface tension is of great importance in nanofluidics [5]. To describe the surface of a spherical surface tension, the Gibbs–Tolman–Koenig–Buff (GTKB) equation has been used [1–3]. Exact analytical integration of this equation by different methods was presented in [4,6,7]. It can be concluded that a decrease of the condensed phase in

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size leads to the surface tension reduction. This conclusion is also supported by computer simulation [8] and calculations of the size-dependent surface energy for liquid inert gases within the technique involving interatomic potential [9]. In the case with a droplet (the curvature is positive) the surface atoms or molecules are “laid bare” and the interaction between them becomes weaker. As a result, the surface tension of the drop is reduced compared to a flat surface. In the case of a bubble (the curvature is negative), the situation is the opposite.

In [4] expressions for the surface tension of spherical, parabolic, cylindrical, and conical surfaces was obtained using the Gibbs dividing surface method. These expressions contain one geometric parameter. However, as is well known from [10–12], for an arbitrary surface it is necessary to introduce not one but two parameters – the principal radii of curvature at a point. This raises the question of the dependence of the surface tension and of the equilibrium capillary surfaces on these radii. Therefore, our paper is devoted to the solution of this important issue. The novelty of the work is that this problem has not been solved before.

### 1.1. Surface tension

Let us consider an isolated system in thermodynamic equilibrium, which consists of two bulk phases with different densities – vapor and liquid – and also the interface between them. The interfacial surface is a tension of surface [2,3]. Excess pressure is determined by the Laplace equation [10–12]:

$$\Delta p = \kappa \sigma, \quad (1)$$

where  $\sigma$  is the surface tension and  $\kappa$  is the mean curvature of the surface. The differential of excess pressure is:

$$d(\Delta p) = \kappa d\sigma + \sigma d\kappa. \quad (2)$$

To calculate the surface tension, let us apply the Gibbs equation, which can be written in the following form:

$$d\sigma = -\Gamma d\mu = -\delta d(\Delta p), \quad (3)$$

where  $\Gamma$  is the Gibbs adsorption,  $\mu$  is the chemical potential, and  $\delta \geq 0$  is a nonnegative parameter characterizing the thickness of the interfacial layer. In surface thermodynamics the Tolman length is used as a parameter  $\delta$ , which is equal to the distance between the surface of tension and equimolar surface. The numerical values of parameter  $\delta$  are in the range from 0.1 to 1 nm far from the critical point. In writing Eq. (3) we have taken into account that the differential for the chemical potential and the Gibbs adsorption are equal:  $d\mu = d(\Delta p)/\Delta n$  and  $\Gamma = \delta \Delta n$ , where  $\Delta n$  is the substance concentrations difference in interfacial phases. Eq. (3) holds for any smooth interfacial phase irrespective of its geometrical shape. In what follows we assume that  $\delta$  does not depend on the curvature radii. This assumption is considered acceptable if the curvature of the surface is not too large [1,2]; an analysis of the size dependence of the surface tension for the spherical surface shows that such an assumption is already acceptable when  $|\kappa| < 0.1/\delta$ . Substituting Eq. (2) into Eq. (3) we can obtain:

$$\frac{d\sigma}{\sigma} = -\frac{\delta}{1 + \delta \kappa} d\kappa. \quad (4)$$

Having integrated Eq. (4) we can find:

$$\sigma = \frac{\sigma^{(\infty)}}{1 + \delta \kappa}, \quad (5)$$

where  $\sigma^{(\infty)}$  is a flat surface tension as  $\kappa \rightarrow 0$ . For arbitrarily curved surface  $\kappa = 1/r_1 + 1/r_2$ , where  $r_1$  and  $r_2$  are the principal radii of curvature of the surface [10–12], from Eq. (5) we finally get:

$$\sigma = \frac{\sigma^{(\infty)}}{1 + \delta \left( \frac{1}{r_1} + \frac{1}{r_2} \right)}. \quad (6)$$

As can be expected, when  $r_1 = r_2$  from Eq. (6) the well-known Tolman formula is derived for small spherical droplets [3]; when  $|r_1| \gg |r_2|$  we have a formula for a long and thin-walled cylinder of radius  $r_2$  [4]. We also note that the above arguments are in accordance with the provision that at sufficiently high  $r_1$  and  $r_2$  in the thermodynamic equations the spherical surface curvature can be replaced by mean (Euler) curvature.

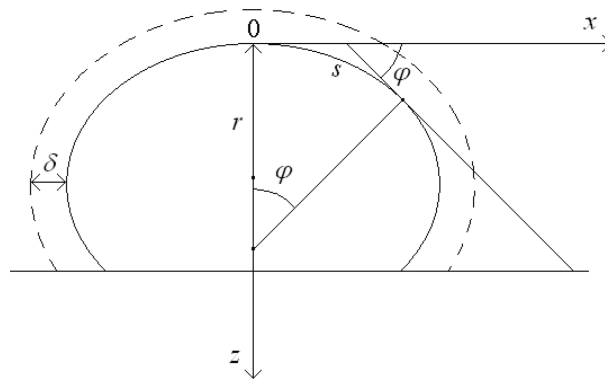
In [13] a comparison of simple size dependency for spherical and cylindrical surfaces resulted in the following interpolation formula:

$$\sigma = \sigma^{(\infty)} \left[ 1 - \delta \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \right]. \quad (7)$$

It is easy to verify that Eq. (7) can be derived using expansion of Eq. (5) into a series of  $\delta \kappa$  in view of zero and first member only.

## 2. The sessile droplet problem

As the most important application of the above results from a practical point of view, let us consider the problem of the sessile droplet (see Figure. 1). The droplet is on a nonwetable substrate, for example on a graphite atomically smooth surface. We use the Bashforth–Adams approximation [10–12] and, according to this, the influence of the substrate is not taken into account. In fact, this means that the interaction of atoms or molecules of the droplet with each other is much greater than their interaction with the substrate. As an example, we can consider a drop of a metallic melt on a graphite substrate. Note that the substrate impact was studied in [14–18], although ignoring the size dependence of the surface tension.



**Figure 1.** The sessile drop profile corresponding to surface of tension. The dotted line is the equipotential surface with the zero Gibbs adsorption ( $\Gamma = 0$ ).

From the standpoint of thermodynamics, a droplet is a macroscopic object. The solid–liquid interface is flat, so the size dependence of surface tension is not considered here. The point of origin is superimposed with a droplet vertex, which is on the surface of tension. The equilibrium droplet profile is determined in terms of

the constancy of the sum of hydrostatic and capillary pressure. In this case, the Laplace equation is:

$$\sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) = p_0 + \Delta\rho g z, \quad (8)$$

$$\frac{1}{r_1} = \frac{d\phi}{ds}, \quad \frac{1}{r_2} = \frac{\sin\phi}{x}, \quad \phi \in [0, \pi],$$

where  $p_0$  is the pressure of the droplet measured at the top ( $x = 0, z = 0$ ),  $\phi$  is the slope of the tangent at a point of the meridian,  $s$  is the arc length,  $x$  and  $z$  are the coordinates that define the droplet cross-section,  $\Delta\rho = m \Delta n$  is the difference in density between the liquid and vapor phases,  $g$  is the gravitational acceleration, and  $m$  is the mass of a single particle (atom or molecule). In this case the surface tension depends on the local curvature of radii  $r_1$  and  $r_2$ . Substituting Eq. (6) into Eq. (8), we obtain

$$\frac{d\phi}{ds} + \frac{\sin\phi}{x} = \frac{2\sigma^{(\infty)} + \Delta\rho g z (r + 2\delta)}{\sigma^{(\infty)}(r + 2\delta) - \delta [2\sigma^{(\infty)} + \Delta\rho g z (r + 2\delta)]}, \quad (9)$$

$$\frac{dx}{ds} = \cos\phi, \quad \frac{dz}{ds} = \sin\phi, \quad (10)$$

$$x(s = 0) = z(s = 0) = \phi(s = 0) = 0, \quad (11)$$

where  $r$  is the radius of curvature of the droplet vertices. When deriving Eq. (9) we took into account that because of the axial symmetry of the droplet on its top the following condition holds [12]:  $r = r_1 = r_2 = 2\sigma^{(\infty)}/p_0$ . As  $\delta = 0$  the surface tension dependence on the curvature is absent. In this case, the well-known Bashforth–Adams equation follows from Eq. (9) [10–12]. The Bashforth–Adams equation is reduced to various differential equations for the droplet profile or volume, which are solvable numerically.

If we introduce the dimensionless (related to  $r$ ) variables  $x$  and  $z$ , then Eqs. (9)–(11) are reduced to the Cauchy problem for a system of two nonlinear differential equations:

$$\frac{dx}{d\phi} = \frac{[1 - \alpha(\gamma + \beta z)] x \cos\phi}{(\gamma + \beta z)x - [1 - \alpha(\gamma + \beta z)] \sin\phi}, \quad (12)$$

$$\frac{dz}{d\phi} = \frac{[1 - \alpha(\gamma + \beta z)] x \sin\phi}{(\gamma + \beta z)x - [1 - \alpha(\gamma + \beta z)] \sin\phi}, \quad (13)$$

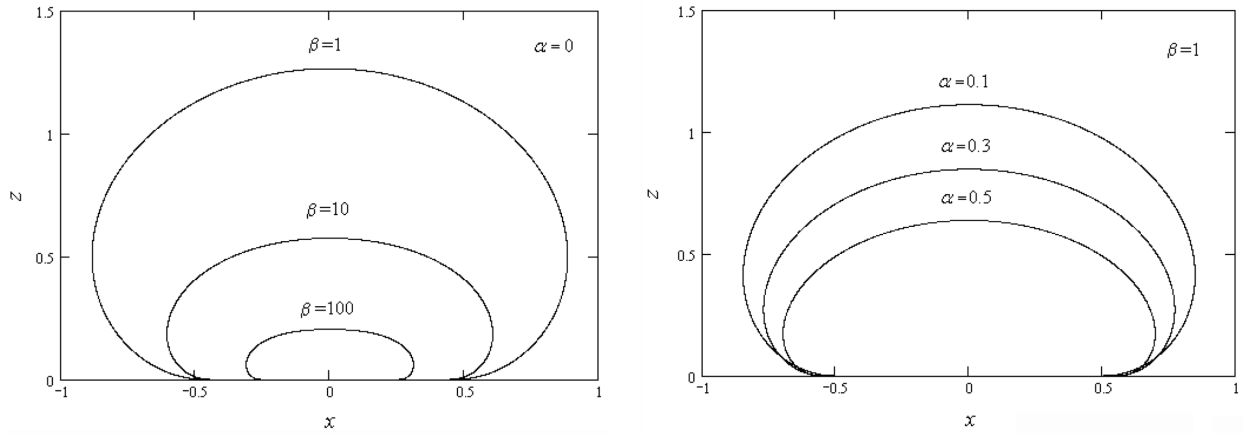
$$x(\phi = 0) = z(\phi = 0) = 0, \quad (14)$$

$$\alpha \geq 0, \quad \beta > 0, \quad 0 < \gamma \leq 2,$$

where  $\alpha = \delta/r$ ,  $\beta = \Delta\rho g r^2/\sigma^{(\infty)}$  and  $\gamma = 2/(1 + 2\alpha)$  are dimensionless parameters that define the physical properties for the droplet. These equations contain only two independent parameters,  $\alpha$  and  $\beta$ , which depend on the specific experimental conditions: parameter  $\alpha$  determines the dependence of the surface tension on the surface curvature and parameter  $\beta$  is linked to the capillary constant  $c = r^2/\beta$ .

Eqs. (12) and (13) with the initial conditions of Eq. (14) were solved numerically by the 4th order Runge–Kutta method with fixed step size. Graphs of the resulting solutions are shown in Figures 2a and 2b.

For clarity in these figures the origin is shifted to the droplet's bottom. The algorithm has been verified at  $\alpha = 0$  using the Bashforth–Adams table data partially presented in [10,12]. This reveals that the coincidence of the solutions is ensured at four significant digits. Since error in experimental measurements within the sessile drop method is, as a rule, higher than 0.1%, the accuracy achieved can be considered satisfactory for the solution of the equations.



**Figure 2.** The dimensionless profiles of sessile drops at various values of parameters  $\alpha$  and  $\beta$ .

Figure 2a shows that with the increase of the parameter  $\beta$  the droplet on the substrate surface becomes flatter. This may be due to a decrease in surface tension  $\sigma^{(\infty)}$  and/or increase in droplet density. Here the size effect of surface tension is not considered, which corresponds to the parameter values  $\alpha = 0$ ,  $\sigma = \sigma^{(\infty)}$ , and  $\gamma = 2$ . It follows from the above models under certain conditions that the dependence of the surface tension of the radii of curvature affects the equilibrium shape of the droplet and this is shown in Figure 2b. With the increase of parameter  $\alpha$ , the droplet flattened. This is due to a general decrease of surface tension and increase of the interface layer thickness. The change in the profile, in light of the above reasons, is not visible for larger drops. However, for micro- and nanosized droplets this could play a significant role at higher temperatures. It should be noted that nanodroplets, being common modern nanotechnology objects, are studied with transmission electron microscopy, which provides high resolution for studying the droplet shape.

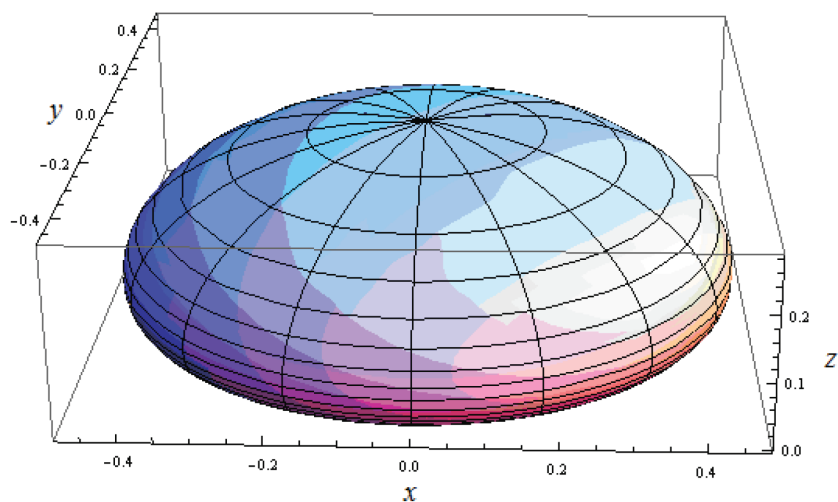
The droplet volumetric image is obtained by rotating the profile around the axis of symmetry (Figure 3). If the droplet profile is known, it is possible to calculate the droplet's equilibrium volume. In general, it is equal to:

$$V = \pi r^3 \int_0^{z_0} x^2 dz, \quad (15)$$

where  $z_0$  is the dimensionless meniscus height defined as a maximum value in the coordinate system. Our calculations showed that the sessile droplet volume can be well approximated by the following empirical formula:

$$V = \frac{4.73 r^3}{\beta^{0.941} + 1.028} \exp(-2.513 \beta^{0.398} \alpha). \quad (16)$$

For small values of the parameter ( $\beta \sim 0.1$ ) the calculated error in the sessile droplet volume according to Eq. (16) does not exceed 5%. Increase in the  $\beta$  parameter leads to this error's rapid decrease. Size effect of the surface tension can be neglected when  $\alpha \rightarrow 0$  and Eq. (16) remains valid.



**Figure 3.** Model image of sessile drop ( $\alpha = 0.2$ ,  $\beta = 10$ ).

### 3. Conclusion

With the decrease of the condensed phase in size the proportion of surface atoms increases, thus increasing the influence of the interphase boundaries. At the same time the size dependence of surface tension is determined by the Tolman length, i.e. the actual thickness of the interfacial (transition) layer. In the present work a formula for the surface tension dependence on the principal radii of curvature on an arbitrary surface (Eq. (6)) was correctly deduced. It was shown that curvature dependence of surface tension leads to a noticeable change in the equilibrium profile of sessile droplets on a flat nonwetting substrate. Note that the consequence resulting from the dependence of the surface tension on the surface curvature can be attributed to the capillary effect of the second kind [19].

Let us discuss briefly the possible application of the system of Eqs. (12) and (13). To determine the surface tension by the sessile drop method, taking into account the curvature dependence of surface tension, we can use an independent assessment of the surface layer thickness and the radius of curvature at the droplet apex obtained, for example, by using transmission electron microscopy. The thickness of the surface layer is taken as the maximum value of  $\delta$  [1]. Once the parameters  $\delta$  and  $r$  are determined the numerical solution of Eqs. (12) and (13) is required as well as its correlation with the sessile droplet profile to determine parameter  $\beta$ . Another method is easier to implement but, generally speaking, requires a mathematical foundation: by correlation of the droplet profile and numerical solution of Eqs. (12) and (13) the two parameters  $\alpha$  and  $\beta$  are extricated by this or that method. It is necessary to develop new algorithms as well as computational experiments. Methods for detailed determination of the surface tension without considering size effects were studied in [12]. For the above approximation these techniques are quite constructive. The next step in theoretical studies will be modification of Eqs. (12) and (13) taking into account the van der Waals forces between the droplet and the substrate.

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