

MODELING OF MICRO- AND NANODROPLETS

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Abstract

In this review, a formula that determines the curvature-dependent surface tension in a droplet with two phases has been discussed. Taking into account the dependence of the surface tension on the system size, nonlinear differential equations describing the droplet profile have been derived. It has been shown that, if the droplet size is not too large compared with the thickness of the surface layer (micro- or nanodroplets), the dependence of the surface tension on the curvature is extremely important.

Keywords: nanodroplet, surface tension, Gibbs adsorption, Tolman length.

Rezumat

În această lucrare se examinează formula care determină dependența tensiunii superficiale de curbură într-o picătură cu două faze. Ținând cont de dependența tensiunii superficiale de dimensiunile sistemelor, au fost obținute ecuațiile diferențiale neliniare care descriu profilul picăturii. S-a demonstrat că, atunci când dimensiunea picăturii nu este prea mare în comparație cu grosimea stratului de suprafață (micro- sau nanopicături), dependența tensiunii superficiale de curbură este foarte importantă.

Cuvinte cheie: nanopicătură, tensiune superficială, adsorbție Gibbs, lungime Tolman.

1. Introduction

A nonwetting liquid takes the form of a drop on the surface of a body. Young suggested measuring contact angle θ between the liquid and the surface. The mechanical equilibrium of a droplet lying on a flat hard surface under the constraints of three surface tensions is referred to as the Young equation. The surface tension (Young's equation) for large droplets (see Fig. 1) is determined as follows [1–9]:

$$\sigma_1 = \sigma_2 + \sigma \cos \theta, \quad (1a)$$

where σ_1 is the tension at the solid–liquid interface, σ_2 is the tension at the solid–vapor interface, and σ is the tension at the liquid–vapor interface.

The drop volume is determined from angle θ from the formula [1–9]

$$V = \frac{4}{3} \pi r_s^3 \varphi(\theta) \quad (1b)$$

where r_s is equilibrium radius of the drop, and

$$\varphi(\theta) = \frac{1}{4} (1 - \cos \theta)^2 (2 + \cos \theta) \quad (1c)$$



Fig. 1. Dimensionless profiles of a sessile microdrop.

Let us consider an isolated system in thermodynamic equilibrium, which consists of two bulk phases with different densities—steam and liquid—and the interface between them.

Here, the surface tension acts as a separating surface with a *minimum value* [1–3]. Excess pressure is provided by the Laplace equation [4–10]

$$\Delta p = \kappa \sigma, \quad (2a)$$

where σ is the surface tension and κ determines the mean curvature of the surface. Differential of excess pressure is as follows:

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

To determine the surface tension, let us apply the Gibbs equation written in the following form:

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

where Γ is the Gibbs adsorption, μ is the chemical potential, $\delta \geq 0$ is a non-negative parameter characterizing the interfacial layer thickness. In surface thermodynamics, the Tolman length is used as a parameter δ , which is equal to the distance between the surface of tension and the equimolar surface. The numerical values of parameter δ lie in a range of 0.1–1 nm far from the critical boiling point. While writing equation (3), we took into account that the differential for the chemical potential and the Gibbs adsorption are $d\mu = d(\Delta p) / \Delta n$ and $\Gamma = \delta \Delta n$, where Δn is the substance concentration difference in interfacial phases. Equation (3) holds for any smooth interfacial phase regardless of its geometrical shape. Hereinafter, we assume that δ does not depend on the curvature radii. This assumption is considered acceptable, if the surface curvature is not too large compared with $1/\delta$ [1, 2]; analysis of the size dependence of the surface tension for the spherical surface show that this assumption is acceptable at $|\kappa| < 0.1/\delta$. Substituting (2) into (3), we can obtain the equation

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

Having integrated (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 an 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 [9]; therefore, from (5) we finally obtain

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

It is reasonable to expect that, at $r_1 = r_2$ the well-known Tolman formula for small spherical droplets is derived from (6) [3].

In [9], comparison of simple size dependences for spherical and cylindrical surfaces resulted in the following interpolation formula [9, 10]:

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

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

2. Theoretical Remarks for the Rekhviashvili–Sokurov`s Model

Let us consider the problem of a sessile droplet as the most important application of the above results from a practical point of view. The droplet lies on a poorly wettable substrate, for example, on an atomically smooth graphite surface.

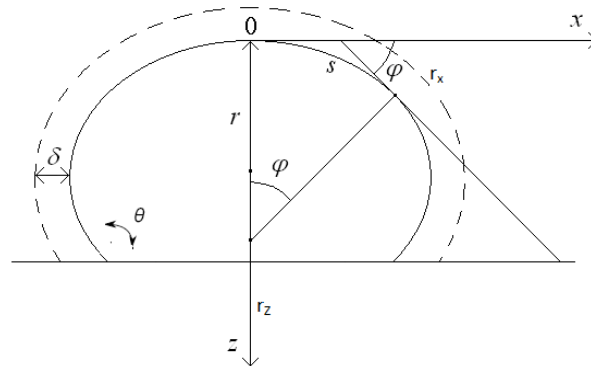


Fig. 2. Sessile drop profile corresponding to the surface of tension.

The dotted line denotes the equimolar surface with the zero Gibbs adsorption ($\Gamma = 0$).

We use the Bashforth–Adams approximation (see [6–9]); according to it, the effect of the substrate is not taken into account. From the standpoint of thermodynamics, a droplet is a macroscopic object. The solid–liquid interface is flat; therefore, the size dependence of surface tension is not considered here. The origin is superimposed with the droplet vertex, which is localized 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 as follows [9, 10]:

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

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

where p_0 is the pressure of the droplet measured at the top ($x = 0, z = 0$), φ 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 gaseous phases, g is the gravitational acceleration, 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 (6) into (8) we obtain [9, 10]:

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

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

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

where r is the radius of curvature of the droplet vertices. While deriving equation (9) we took into account that, owing to the axial symmetry of the droplet on its top, the following condition is hold [9]: $r = r_1 = r_2 = 2\sigma^{(\infty)} / p_0$. Since $\delta = 0$, the surface tension does not depend on the curvature. In this case, exactly the well-known Bashforth–Adams equation follows from (9) [9, 10]. The Bashforth–Adams equation is reduced to various differential equations for the droplet profile or volume, which can be solved numerically.

If we introduce the dimensionless (related to r) variables x and z , then (9)–(11) are reduced to the Cauchy problem for a system of two nonlinear differential equations [9, 10]:

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

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

$$\begin{aligned} x(\varphi = 0) = z(\varphi = 0) = 0, \\ \alpha \geq 0, \quad \beta > 0, \quad 0 < \gamma \leq 2, \end{aligned} \tag{14}$$

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 α and β that depend on the specific experimental conditions: the α parameter determines the dependence of the surface tension on the surface curvature; the β parameter is linked to the capillary constant $c = r^2 / \beta$.

Equations (12) and (13) with initial conditions (14) were solved numerically by the *4th order Runge–Kutta* method with a *fixed step* size. Graphs of the resulting solutions are shown in Figs. 2a and 2b. For clarity, in these figures, the origin is shifted to the droplets bottom. The algorithm was verified at $\alpha = 0$ using the Bashforth–Adams table data partly presented in [9]. This approach reveals that the coincidence of the solutions is provided at four significant digits. Since the error in experimental measurements within the sessile drop method is typically higher than 0.1%, the achieved accuracy can be considered satisfactory for the solution of the equations.

Figure 3a shows that, with an increase in the β parameter, the droplet on the substrate surface becomes flatter. This effect can be attributed to a decrease in surface tension $\sigma^{(\infty)}$ and/or an increase in the droplet density. Here, the size effect of surface tension that corresponds to the parameter values of $\alpha = 0$, $\sigma = \sigma^{(\infty)}$, and $\gamma = 2$ is not considered.

However, it follows from the above models that, under certain conditions, the dependence of the surface tension of the radii of curvature affects the equilibrium shape of the droplet; it is shown in Fig. 3b. With an increase in the α parameter, the droplet flattened. This effect is attributed to a general decrease in the surface tension and an increase in the interface layer thickness. In view of the above reasons, the change in the profile is not visible for larger drops. However, for micro- and nanosized droplets, it can play a significant role at higher temperatures. It should be noted that the nanodroplets, which are common modern nanotechnology objects, are studied by transmission electron microscopy providing a high resolution for studying the droplet shape.

If the droplet profile is known, it is possible to calculate the droplets equilibrium volume. In general, it is equal to [9, 10]:

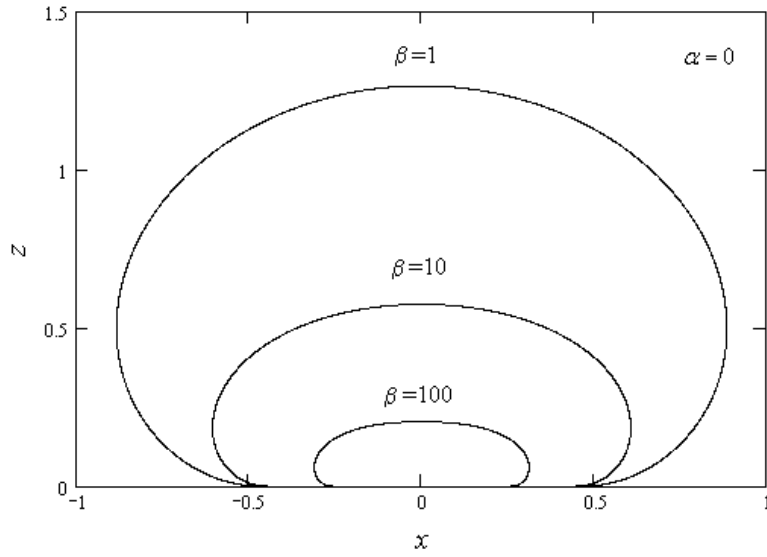
$$V = \pi r^3 \int_0^{z_0} x^2 dz, \tag{15}$$

where z_0 is the *dimensionless meniscus height* defined as a maximum value in the coordinate system.

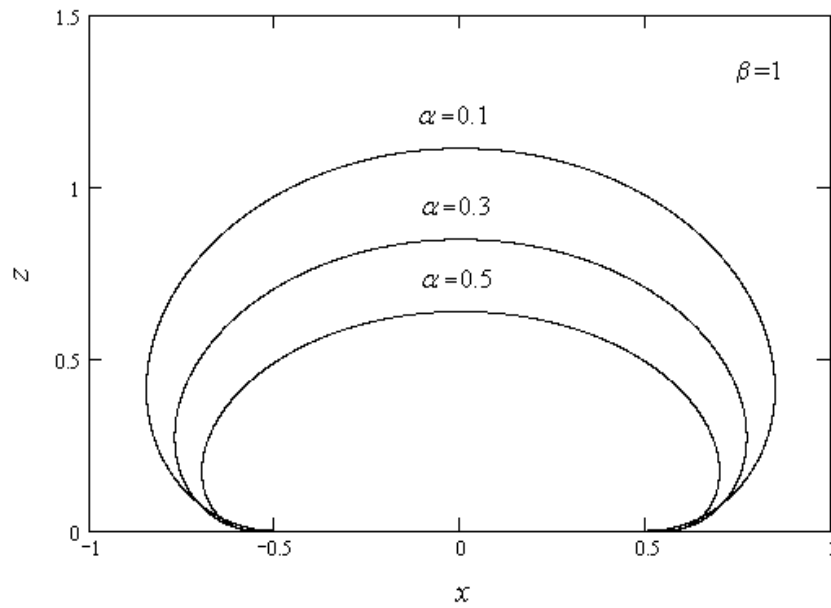
Our calculations show that the sessile droplet volume can be well approximated by the following empirical formulas [9, 10]:

$$V \sim \frac{4,7 r^3}{\beta^{0,9} + 1,03} \exp(-2,5\beta^{0,4} \alpha), \tag{16a}$$

$$V \sim \frac{9r^3\beta^{-2}}{\alpha^{1,1} + 0,2\beta^{-1,1} + 0,2} \quad (16b)$$



(a)



(b)

Fig. 3. Dimensionless profiles of sessile drops at various values of the α and β parameters [9].

For small values of the parameter ($\beta \sim 0.1$), according to formula (16a), the calculated error in the

sessile droplet volume does not exceed 5%. An increase in the β parameter leads to a rapid decrease in this error. The size effect of the surface tension can be neglected at $\alpha \rightarrow 0$, and formula (16a) remains valid. We use formula (16b), if $\beta > 1$.

3. Computational Experiment for the Rekhviashvili–Sokurov`s Model

Let us briefly discuss the possible application of the system of equations (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 determined, for example, by transmission electron microscopy.

We show the calculated nanodroplet models.

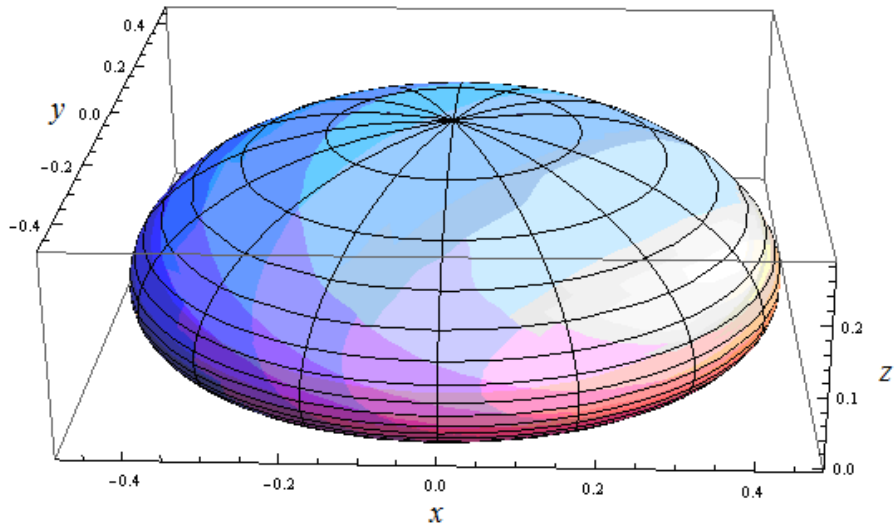


Fig. 4a. Model image of a sessile nanodrop ($\alpha = 0.2$, $\beta = 10$) [9].

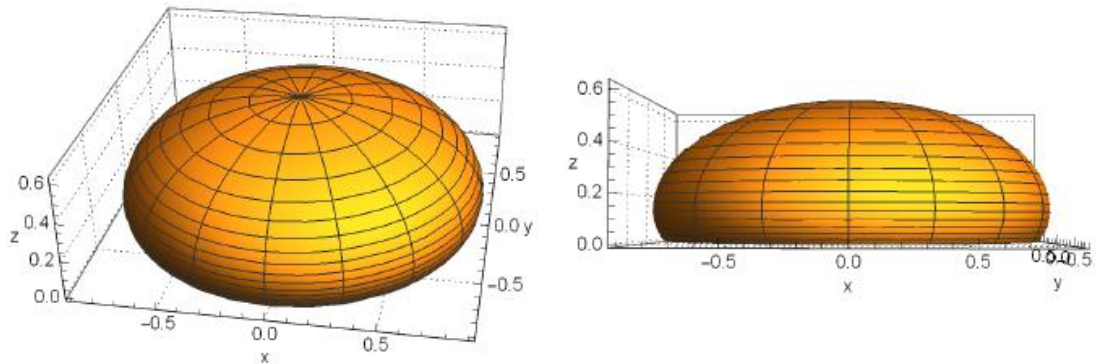


Fig. 4b. Model image of a sessile nanodrop at $\alpha = 0:1, \beta = 5$ [10].

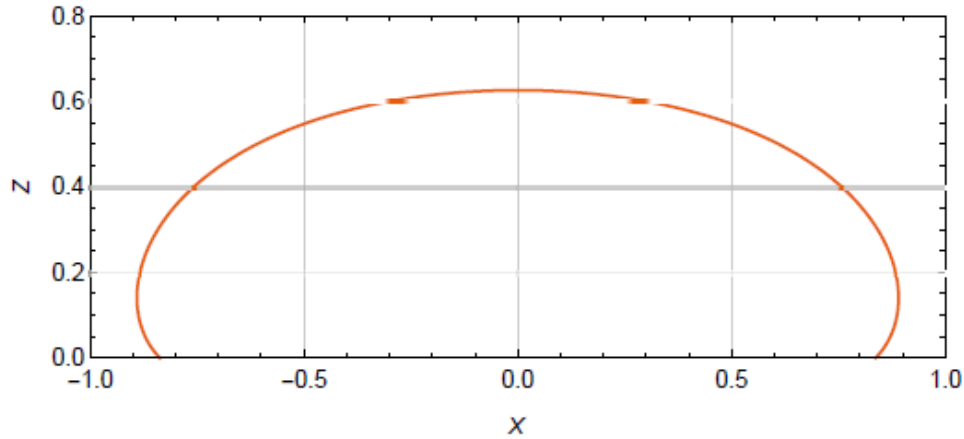


Fig. 4c. Model of a sessile nanodrop at $\alpha = 0:1, \beta = 5$ [10].

The thickness of the surface layer is taken as the maximum δ value [1]. Once the δ and r parameters are determined, the numerical solution of equations (12) and (13) is required along with its correlation with the sessile droplet profile to determine the β parameter.

This method is easier to implement; however, generally speaking, it requires a mathematical foundation: by correlation of the droplet profile and the numerical solution of equations (12) and (13) two parameters α and β are extricated by this or that method.

We will develop new algorithms and computing experiments.

Methods for a detailed determination of the surface tension without considering size effects are studied in [5–8]. For the above approximation, these techniques are quite constructive.

The next step in the theoretical studies will be modification of equations (12) and (13) taking into account the van der Waals forces between the droplet and the substrate.

4. Analytical Remark

From formulas (10), (12), and (13), the following asymptotic dependence can be obtained:

$$\tan(\varphi) \sim \frac{1}{\rho_r}, \quad (17)$$

where $\rho_r \sim \frac{r_z}{r_x}$ (see **Fig. 2**). Radius r_z is an analog of r_1 , and r_x is an analog of r_2 .

On the other hand, we got the following formula (see formula (22) in [9]):

$$\tan\left(\frac{\theta}{2}\right) = \frac{1}{\rho}, \quad (18)$$

These formulas have the same analytic structures.

5. Conclusions

(a) With a decrease in the condensed phase in size, the proportion of surface atoms increases thus increasing the effect 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.

(b) In this study, a formula for the dependence of the surface tension on the principal radii of curvature on an arbitrary surface (equation (6)) has been correctly deduced. It has been shown that the curvature dependence of surface tension leads to a noticeable change in the equilibrium profile of sessile droplets on a flat non-wetting substrate. Note that the consequence of the dependence of the surface tension on the surface curvature can be attributed to the capillary effect of the second kind [9, 10].

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References

- [1] S. Ono and S. Kondo, *Molecular Theory of Surface Tension in Liquids*, in *Structure of Liquids*, V. 3/10 of the series *Encyclopedia of Physics*, Berlin, Heidelberg, Springer, 1960, pp. 134–280.
- [2] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity*, Oxford University Press, 1989.
- [3] R. C. J. Tolman, *Chem. Phys.* 17 (3), 333 (1949).
- [4] S. Sh. Rekhviashvili and E. V. Kishtikova, *Tech. Phys.* 56 (1), 143 (2011).
- [5] A. W. Adamson, A. P. Gast, *Physical Chemistry of Surfaces*, Wiley-Interscience Publication, John Wiley & Sons, 1997.
- [6] M. J. Jaycock and G. D. Parfitt, *Chemistry of Interfaces*, Halstead Press, John Wiley and Sons, 1981.
- [7] A. I. Rusanov and V. A. Prokhorov, *Interfacial Tensiometry*, Elsevier, 1996.
- [8] M. Miyahara, H. Kanda, T. Yoshioka, and M. Okazaki, *Langmuir* 16 (9), 4293 (2000).
- [9] S. A. Baranov, S. Sh. Rekhviashvili, and A. A. Sokurov. *Surf. Eng. Appl. Electrochem.* 55 (3), 286 (2019).
- [10] A. A. Sokurov, *Vestnik KRAUNC, Ser. Fiz.-Mat. Nauk* 23 (3), 140 (2018).