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## A couple new ways of surface tension determination

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#### ABSTRACT

Axisymmetric liquid-fluid interface (ALFI) and axisymmetric drop shape analysis (ADSA) are the methods used in surface phenomena investigations. A photographed contour of a drop or a bubble is detected and fitted to numerically integrated Young-Laplace equation. However, ALFI fails in the stationery points, while ADSA gives the wrong surface tension value at the apex. An analytical expression for an interface shape overcome the weaknesses of the numerical models. It shows that pressure inside a drop is higher than outside, while a bubble encloses gas with negative gauge pressure. Since, the close-formed solutions origin from a force balance which preserves constant volume as well as temperature, entropy, and masses of ingredients are invariable the new formulas can be considered in the surface tension measurements. Hence, surface tension can be determined in the new ways. Each new method needs the measurements of two dimensions only and a solution of quite simple set of the equations. Moreover, the spare equations verify the solution. Then achieved surface tension is an input to obtain bubble shapes which are compared with experiment successfully.

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#### 1. Introduction

When heat exchange occurs between two fluid phases, e.g. liquid and gas (such as boiling) or two insoluble liquids, it is done through an interface where surface tension forces are applied. Thus surface tension phenomena have to be included into analysis of heat transfer through the interface, e.g.: [4,13,35,36,39,40,47].

Since, the new substances, e.g. polymers or liquid crystals, are increasingly synthetized their properties must be determined. Insomuch as, surface tension is important factor in heat or mass transfer processes, its proper and accurate measurement is important issue. There are two groups of measurement ways: dynamic methods and static ones. However, surface tension value are announced for static methods. The du Noüy ring method and Wilhelmy plate one based on measurement of a force applied when a body is taken out of a liquid. The former can be applied in liquidgas or liquid-liquid systems, while the latter only in liquid-gas system. However both of them needs, because of different causes, correction factors (cf. handbook [18]). The best measurement method would be one which satisfied all the assumption in a definition and inserts neither limitations nor interactions in an experiment additionally. Therefore, analysis of photographs of drops or bubbles far enough from a nozzle should fulfil these demands. The common feature of analysis of drop or bubble shape in photographs is Young-Laplace equation as beginning point of the calculations:

#### 1.1. Axisymmetric fluid-liquid interfaces

The group of methods based on drop shape analysis is being discussed wider. The source method presented by Hartland and Hartley [20] is derived from Young-Laplace equation

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right),\tag{1}$$

where

 $\Delta p$  – pressure difference between two sides of interface in the bulk phases,

 $\gamma$  – surface tension,

 $R_1$ ,  $R_2$  – main radiuses of curvature.

Initially, there are four unknown quantities at Eq. (1), hence the supplementary equations are added. To avoid measurement of pressure difference between two fluids separated by a surface the set of equations is extended by tension balance at the apex

$$\Delta p_0 = 2\gamma/R_0,\tag{2}$$

where  $\Delta p_0$  and  $R_0$  are determined at apex which is located in the origin in Fig. 1. Then, pressure at any point above the origin is obtained using hydrostatic pressure relationship, which leads to the expression:

$$\Delta p = \Delta p_0 + \Delta \rho g z = 2\gamma/R_0 + \Delta \rho g z, \tag{3}$$

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Fig. 1. Coordinate system and variables in Hartland and Hartley [20] method.

where

 $\Delta \rho$  – density difference between a heavier liquid and a fluid of lower density,

g – gravity acceleration,

z – the applicate.

The main curvatures  $1/R_1$  and  $1/R_2$  are defined as the quotients of radius  $d\Theta$  and arc length ds:

$$\frac{1}{R_1} = \frac{d\Theta}{ds},\tag{4}$$

and ratio of sine of angle between tangent to the surface and horizon  $\Theta$  and abscissa *x* 

$$1/R_2 = \sin \Theta / x. \tag{5}$$

where all the variables are defined in Fig. 1.

Substituting Eqs. (3)–(5) into (1) the force balance between two bulk phases separated by interphase surface is obtained

$$\frac{d\Theta}{ds} = \frac{2}{R_0} + \frac{\Delta\rho g}{\gamma} z - \frac{\sin\Theta}{x}.$$
(6)

The set of equations is extended by geometrical relationships:

$$\frac{dx}{ds} = \cos\Theta,\tag{7}$$

$$\frac{dz}{ds} = \sin \Theta, \tag{8}$$

and formulas for volume and surface of the investigated drop:

$$\frac{dV}{ds} = \pi x^2 \sin \Theta \tag{9}$$

$$\frac{dA}{ds} = 2\pi x \tag{10}$$

Eventually, the initial value problem, which is close to Bashforth and Adams (1883) equations, consists from Eqs. (6)-(10) and the initial conditions:

$$x(0) = z(0) = \Theta(0) = 0, \tag{11}$$

and

$$V(0) = A(0) = 0. (12)$$

The problem (6)-(8) with boundary condition

$$\frac{d\Theta}{ds} = \frac{\sin\Theta}{x} = \frac{1}{R_0},\tag{13}$$

and initial conditions (11) Hartland and Hartley [20] solve in dimensionless form with capillary constant a

$$a = \left(\frac{\gamma}{\Delta\rho g}\right)^{\frac{1}{2}} \tag{14}$$

as the length scale. It represents five first order differential equations and initial condition at the origin. It has been applied successfully by many researchers. However, Hartland and Hartley [20] announce the method fails when derivative of  $\Theta$  (angular inclination of the surface to the horizontal) is equal to zero. Volume and surface area are calculated using Eqs. (9) and (10) with initial conditions (12) after conversion into dimensionless form with capillary constant *a* as the length scale.

Hartland and Hartley [20] achievements were used by Loglio et al. [34] to investigate influence of vibrations on surface tension. Hanumanthu and Stebe [19] modified Hartland and Hartley's system of equation and researched liquid drop in equilibrium on axisymmetric conical surface of solid. Juza [24] replaced curvature with equatorial diameter. Berry et al. [3] named this method as pendant drop tensiometry. Li et al. [33] applied this method to investigate phospholipid DPPC. Alvarez et al. [2] applying Nelder-Mead algorithm (which calculates minimum of function), thus they determined surface tension in the case of low Bond number drops between fluids with similar density.

#### 1.2. Axisymmetric drop shape analysis

The above-mentioned method is named ALFI by August Wilhelm Neumann, who with co-researchers (cf.: [5,7,9-12,21-23, 25-27,30-32,37,41-43,48-51]) were developing it for decades intensely. As Neumann's research team has been focusing on drop investigations a term "axisymmetric drop shape analysis" (ADSA) was applied. The method to determine surface tension from a height and a diameter of a drop measurements was labelled as ADSA-HD by Del Rio and Neumann [11]. The only limitation is that solved equations have to be located below the infection point (cf. Fig. 1). Surface tension can be measured with 2% accuracy for sessile drop with contact angle less than 90° or pendant drops with narrowing. The method fails when drop widens without "a neck". Kwok et al. [30] applied the method to surface tension measurements during polymers' melting. Rotenberg et al. [41] determined the interfacial properties applying numerical fit of drop edge coordinates to Laplace equation (ADSA-P). The limitations of the method are the same as the former one.

Danov et al. [8] using Kralchevsky et al. [29] and Knoche et al. [28] achievements formulated a force balance in tangential and normal directions to the surface. They determined surface tension in two directions applying a method capillary meniscus dynamometry (CMD). The azimuthal surface tension was negative where ripples existed. Peters and Arabali [38] determined surface tension of oil in water. Their method bases on approximation shape of upper part of oil drop.

An idea of ADSA method to determine surface tension value is as follows. Del Rio and Neumann [11] rearrange Eqs. (6)-(8) as the function of *x* and convert curvature at apex *b* into variable:

$$b = 1/R_0.$$
 (15)

Eventually Young-Laplace and supplementary equations form the initial value problem as follows [11]:

$$\frac{dx}{d\Theta} = \frac{\cos\Theta}{2b + az - \frac{\sin\Theta}{x}},\tag{16}$$

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