SURFACE TENSION AND DYNAMIC CONTACT ANGLE ANALYSIS FOR LIQUID DROPLETS

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ABSTRACT
The methods of the surface tension measurement using the pendant or sessile drop profile are well known for their reliability and universality. The method procedures are well established but still require high quality drop images to measure the surface tension automatically, what may be the problem in difficult experimental conditions. In this paper, the highly automated methods of surface tension and dynamic contact angle measurement are presented. The usage of image processing techniques allows processing of images of different quality, acquired e.g. at high temperatures.

INTRODUCTION
Drop shape methods are widely used due to many advantages. They are easy to handle, require only small amount of the liquid and can be used in many difficult experimental conditions such as high pressure, temperature etc. The method can be used to measure the surface tension of various materials, from organic liquids to metallic melts and from pure solvents to concentrated solutions. Also, the experimental procedure allows capturing the evolution of dynamic systems to study time dependent properties.

The balance of gravity force and surface tension forms the distinct profile shape, which can be described using the Young-Laplace equation

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

where R_1 and R_2 are the two principal radii of curvature, and ΔP is the pressure difference across the interface.

For a general irregular drop form, the integration of the equation (1) is quite difficult. Fortunately, in the case of axially symmetric drop, the equation becomes two-dimensional, and efficient numerical procedures for this case have been developed.

The inverse problem of the surface tension determination from the drop shape is much more difficult. The first efforts in this problem were made by Bashforth and Adams [1], who composed the tables of drop profiles for different surface tension values and radius of curvature at the apex of the drop. Until the powerful computers became widely available, the number of methods using various simplifications was proposed, but their precision and range of applicability was significantly limited.

The major improvement over the existing methods was the introduction of the modern Axisymmetric Drop Shape Profile (ADSA) algorithm [2]. The Rotenberg's procedure fits the measured profile to a Laplacian curve using a nonlinear procedure. In ADSA, the objective function, which is used to evaluate the discrepancy between the theoretical Laplacian curve and the actual profile, is the sum of the squares of the normal distances between the measured points (i.e. experimental curve) and the calculated curve. In addition, the location of the apex of the drop is assumed to be unknown and the coordinates of the origin are considered as independent variables of the objective function. Thus, the drop shape can be measured from any convenient frame.

The second generation of ADSA, developed by del Río [3, 4] overcame the deficiencies of the numerical schemes of the first generation using more efficient algorithms. He used the curvature at the apex rather than the radius of curvature and the angle of vertical alignment as optimization parameters.

Today the numerical ADSA procedure is well established [5], with only known limitation to near spherical drops, where the algorithm hits the fundamental limitations of round-off errors and measurements precision.

Despite this fact, the development of the method is still not complete. In contrast to the development of the numerical procedure, the image acquisition and profile extraction step was not thoroughly considered. While this operation may be trivial in almost ideal case of professional laboratory equipment, in the case of difficult conditions and inexpensive setup, profile extraction may be tricky. For instance, a more sophisticated image analysis technique is required for poor quality images of bubbles, e.g. in a dispersion, than for pendant or sessile drop images in air. In this paper, a couple of improvements for the profile extraction step are proposed.

Also, the application of the ADSA method to the quasi-stationary drops is considered and the method of contact angle determination is proposed.

NUMERICAL PROCEDURE
In the case of axisymmetric drop, the equation for the drop profile shape (1) can be reduced to the system of ordinary differential equations

$$\begin{aligned}\ddot{y} &= -\dot{x}\left[-c(y-y_0)+\frac{\dot{y}}{x-x_0}+2b\right];\\ \ddot{x} &= \dot{y}\left[-c(y-y_0)+\frac{\dot{y}}{x-x_0}+2b\right],\end{aligned} \qquad (2)$$

with initial conditions $y(0)=y_0$, $x(0)=x_0$, $\dot{x}(0)=1$, $\dot{y}(0)=0$ and also, $\left.\frac{\dot{y}}{x}\right|_{t=0}=-b$. Here, b is the curvature at the drop apex and $c=\frac{\Delta\rho g}{\gamma}$ is the capillary constant ($\Delta\rho$

is the density difference between drop and the medium, g is the gravity acceleration).
To determine the surface tension it is needed to solve the inverse problem for the system (2) to find the parameters $\{x_0, y_0, c, b\}$. In practice, it is also needed to determine the camera tilt angle.
The solution is performed via minimization of the total error

$$E = \sum_i d\left(\{x_i, y_i\}, \{x(t), y(t)\}\right)^2 , \quad (3)$$

where $d\left(\{x_i, y_i\}, \{x(t), y(t)\}\right)$ is the distance between experimental point $\{x_i, y_i\}$ and the calculated line $\{x(t), y(t)\}$ (see fig. 1)

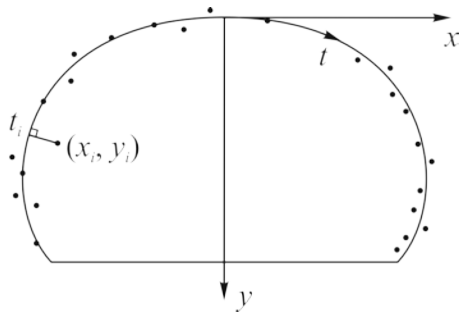

Fig. 1. Theoretical drop shape (solid line) and experimental points (dots).

Thus we need to calculate the distance between experimental points and the solution of (2). The system (2) does not have analytical solution, and it is solved numerically. So the distance

$$d\left(\{x_i, y_i\}, \{x(t), y(t)\}\right)^2 = \\ = \min_{t_i} (x_i - x(t_i))^2 + (y_i - y(t_i))^2 \quad (4)$$

has to be found by the minimization procedure. Due to efficiency reasons, the following procedure is performed.

The approximation error is evaluated simultaneously with the integration of (2). The experimental points $\{x_i, y_i\}$ are sorted by the image processing algorithm such that for each next point the corresponding arc length parameter t_i is increasing. Then, in the process of integration the last value of t_i can be used as initial estimate for t_{i+1}.
During the integration via Dormand-Prince method [6] at each step the values $\{x(t), y(t), \dot{x}(t), \dot{y}(t)\}$ are available, thus the t_i can be determined from the condition

$$(x_i - x(t))\dot{x} + (y_i - y(t))\dot{y} = 0 \quad (5)$$

using Newton method. It is only needed to track the value of the left side of (5) during the integration.

PRECISION EVALUATION

To estimate the precision of the developed method of surface tension calculation the numerical experiment was held. The theoretical profiles with parameter $1/b = R_0 = 2.4$, and different capillary constants $c = 3.7$ и $c = 1$ were generated. The method performance was evaluated for different levels of the total error δ

$$\delta^2 = \sum_{i=1}^{N} \rho^2 (X_i, \tilde{X}_i),$$

where X_i are coordinates of the theoretical profile points, $\tilde{X}_i$ are coordinates of the perturbed drop profile points, ρ is distance between points in direction of the normal to the theoretic drop profile (4). For the experiment, 100 points were taken. The perturbed values $\tilde{X}_i$ were calculated by adding uniformly distributed noise to the points X_i. In the Table 1 the results from 20 runs for each noise level are presented.

Table 1. Precision evaluation of the capillary constant determination by the Laplace method.

$R_0 = 2.4$						
	$c = 3.7$			$c = 1$		
δ	$c_{\min}$	$c_{\max}$	Δ_{rel}	$c_{\min}$	$c_{\max}$	Δ_{rel}
0	3.7190	3.7190	0.0190	0.9993	0.9993	0.0007
0.01	3.6625	3.7779	0.0211	0.9954	1.0029	0.0046
0.02	3.6091	3.7933	0.0252	0.9922	1.0073	0.0078
0.03	3.5664	3.8416	0.0383	0.9883	1.0110	0.0117
0.04	3.5239	3.8899	0.0513	0.9845	1.0147	0.0155
0.05	3.4823	3.9399	0.0648	0.9807	1.0184	0.0193
0.06	3.4417	3.9910	0.0787	0.9769	1.0222	0.0231
0.1	3.2847	4.2147	0.1391	0.9620	1.0375	0.0380

The values $c_{\min}$ и $c_{\max}$ represents minimum and maximum recovered values of c for each value of δ^2, also the table gives the relative errors of c determination:

$$\Delta_{\text{rel}} = \frac{\max\left\{|c_{\max} - c|, |c_{\min} - c|\right\}}{c}.$$

The examples of the determined drop parameters and drop profiles are given in figs 2, 3. The perturbed values of points $\tilde{X}_i$ are denoted with small circles and the recovered profile is denoted as solid line. In both cases $\delta^2 = 0.1$ was taken. The exact solutions are not given because they are visually matched almost exactly.

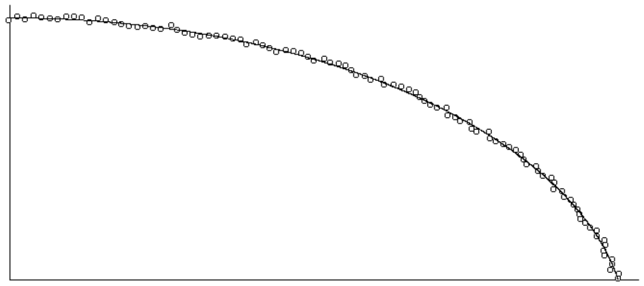

Fig. 2. The recovered profile for the parameter values $R_0 = 2.4$, $c = 3.7$, $\delta^2 = 0.1$

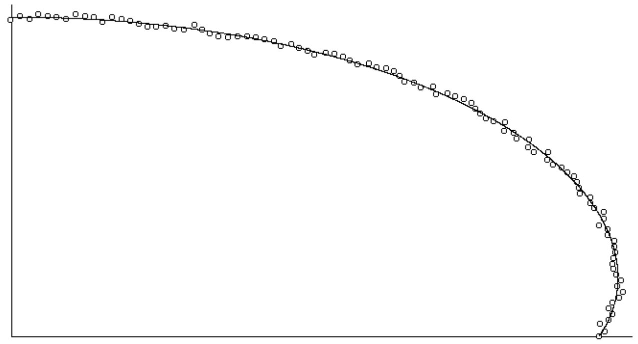

Fig. 3. The recovered profile for the parameter values $R_0 = 2.4$, $c = 1$, $\delta^2 = 0.1$

EXPERIMENTAL SETUPS

Two experimental setups were used in this study to test the efficiency of developed algorithm.

1. The goniometer LK-1 (OpenScience Ltd.) consisted essentially from horizontal microscope equipped with 4^x/0.10 objective, USB CCD camera (1280x1024, up to 25 fps) and mechanical substage for sample positioning (fig. 2). Drop of the liquid under investigation is deposited manually by means of the syringe on selected substrate surface, than the drop is positioned to the optical axis of the microscope and the system is focused. Individual images or image series are transferred to PC.

2. Special equipment was build up to study fast spreading of low viscosity alkali halide melts over ceramic substrates in air. Substrate is placed inside tubular furnace and heated up to desired experimental temperature. Substance to be melted is placed inside alumina crucible which is situated over substrate. When experimental temperature is reached, melt is extruded from the crucible through the capillary made of hexagonal BN and deposited on substrate. During deposition sequence of drop images is registered with special digital camera FastVideo 400 (400 fps at 640x480) and stored on PC.

Software package

The software package is designed to support the measurements of surface tension and contact angles in a wide class of conditions with a high amount of automation.

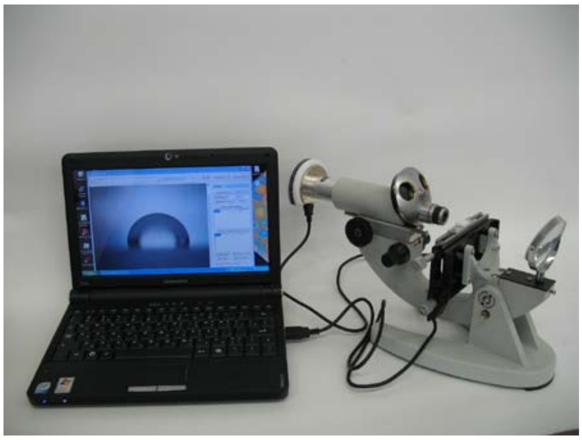

Fig. 4. Goniometer LK-1

The designed software includes universal video capture module working with any hardware supporting DirectShow video capture standard (almost any digital camera compatible with Microsoft Windows). This enables us to use widely available inexpensive digital cameras with different resolution; the adjustment to the hardware is performed via special calibration procedure.

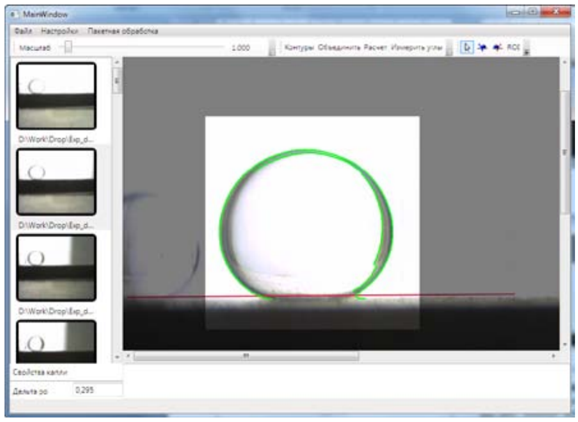

Fig. 5. An example of drop series processing developed program.

The software supports automated capture of frame series to study systems with dynamic parameters (as shown in fig. 5). For the case of rapidly changing systems, where the Young Laplace equation is not applicable, a special method of automated contact angle measurement can be used.

Image processing

As shown in [5], the most robust method of drop profile extraction is the Canny edge detection algorithm [7]. However, in difficult conditions even the Canny method extracts spurious edges due to lighting conditions, image noise and presence of foreign objects in the image.

To automate the process of drop profile extraction in such conditions the following procedure is used. First, the binary edge map acquired by edge detector is organized into lists of successive points using edge linking algorithm [8], based on the analysis of the pixel neighborhood. This stage is also essential for efficient error function (3) evaluation, as mentioned above. After this procedure, the drop contour is usually just the longest one, and can be found automatically. In rare cases drop contour can be edited manually to join broken contours or to remove obstacles.

To further refine the drop profile, the extension of the Canny method is applied, providing sub-pixel precision [9].

INTERFACIAL TENSION AND CONTACT ANGLE MEASUREMENT

The surface tension measurement was tested in application to stationary and quasi-stationary drops.

Interfacial tension measurement for quasi-stationary drops in lysozyme water solution / octane system

The developed algorithm has been applied to measure interfacial tension between water solution of lysozyme (10^{-4}M) and octane. Polytetrafluoroethylene (PTFE) substrate was placed on the bottom of optical glass cuvette. Than the cuvette was filled with octane and placed on substage of LK-1 goniometer.

The drop of lysozyme water solution was placed on PTFE surface by means of a sampler (fig. 6).

A sequence of drop images was recorded and interfacial tension during 400 seconds was evaluated (fig. 7). During ~50 s sharp decrease of interfacial tension to about 28 mN/m^2 was observed. Gradual decrease of interfacial tension from 28 to 24 mN/m^2 during next 350 s could be attributed to rearrangement of protein molecules in interfacial layer.

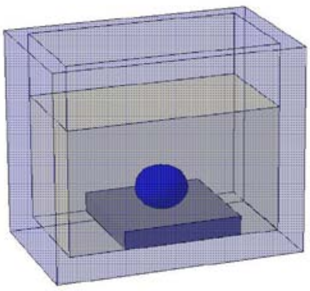

Fig. 6. Water drop on PTFE substrate immersed in octane.

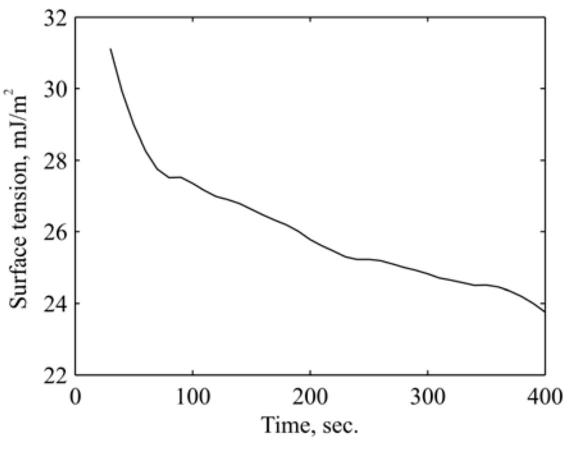

Fig. 7. Interfacial tension of octane/lysozyme water solution system.

Dynamic contact angle measurement for fast spreading drops (liquid NaCl / hydroxyapatite (HAP) system)

Low viscosity melts spreads fast over wettable substrates (for millimetric size drops triple line velocity up to 1 m/s could be observed [10]). Fast CCD recorders should be used to reveal details of spreading process. Although drop profile did not satisfy the Young-Laplace equation at such high spreading rates, it is important to determine dynamic value of contact angle $\theta(t)$ locally at triple line region. This allows to estimate driving force of spreading (per unit length of triple line):

$$F = \sigma_{lg}\left(\cos\theta(t) - \cos\theta_{eq}\right).$$

Thus, the contact angle has to be measured using different techniques.

In most cases drop profile remains quite smooth even when the drop is spreading rapidly. Moreover, when the contact angle is small, the drop is near spherical at the triple line region. Considering these facts we propose the following algorithm for measurement of the spreading drop contact angle.

First, the drop profile is extracted using the same procedure as for static and quasi-static drops i.e. Canny method with sub-pixel precision. It should be noted here, that the sub-pixel precision is necessary for this task, because of small resulting angles at the end of the spreading process.

Second, the drop left and right contact points are detected via the frame differencing.

Finally, the angle is evaluated using iterative fitting. Because the drop is assumed to be symmetrical, two parts from the both sides of the drop profile are taken and fitted by a circle. For the beginning, 5% of the drop profile is used (see fig. 8), and this percent iteratively increases while the fit remains “good”, that is the mean approximation error does not exceed 0,1 pixel (this is a precision of the used sub-pixel detection algorithm, according to [9].)

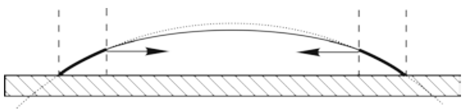

Fig. 8. Dynamic contact angle measurement scheme.

The example of the fitted circle for molten NaCl drop spreading over hydroxyapatite at 866°C is presented in fig. 9. The measured contact angles are given in fig. 10.

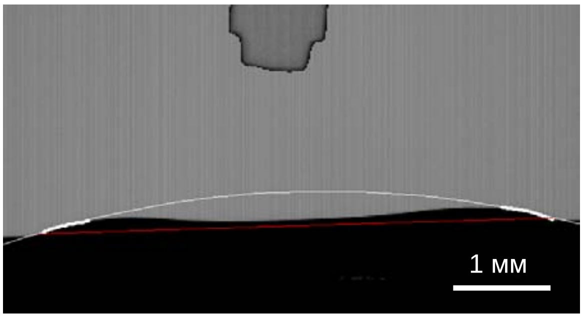

Fig. 9. Contact angle measurement of the spreading drop of molten NaCl

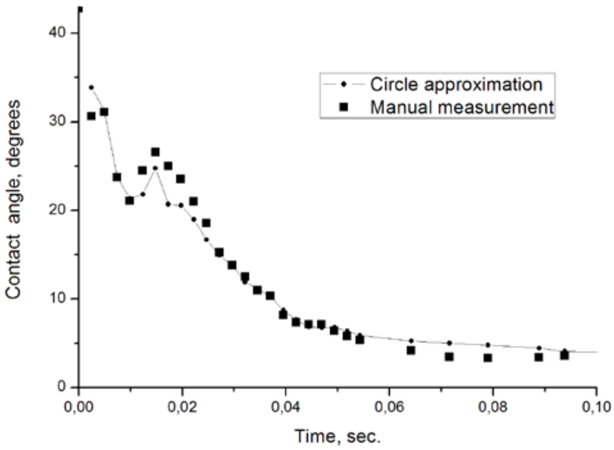

Fig. 10. Time dependence of contact angle for NaCl drop spreading over hydroxyapatite substrate.

CONCLUSION

In this work, the highly automated methods of surface tension and dynamic contact angle measurement are presented. The usage of advanced image processing techniques allows processing of images of different quality, acquired e.g. at high temperature and high pressure, in dispersions, etc. The developed software package allows using inexpensive experimental setups for express measurements of surface tension and contact angles.

The numerical and practical experiments revealed the high reliability and good precision of the developed methods.

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