Experimental setup for determining the surface tension of highly curved interfaces by static and dynamic methods

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Abstract. Experimental devices and techniques for determining surface and interface tensions of low-melting metals bordering with vacuum, liquid mediums and solid substrates have been described. Dynamic method is discussed for the gallium microliter sessile droplet immersed in water and a static method is considered for the tin microdroplet pending on a conical tip of a cantilever needle.

1. Introduction
Thermophysical properties of nanoparticles have a pronounced dimensional dependence, which must be taken into account when developing structural nanomaterials [1]. In this regard, experimental and theoretical study of size effects is an important and actual task [2–5]. Microdrops of low-melting metals and their alloys have great potential for use in reconfigurable electronics, conductive composite materials, electrochemical sensors, photocatalysis, and other high-tech areas of technology [6]. Micro- and nano droplets of various metals were visualized using a transmission electron microscope (TEM) in [3]. At the same time, however, there was no possibility of manipulating micro-objects, which is implemented in modern scanning probe microscopy. The purpose of this study is to develop an experimental method for determining the wetting angle, surface and interface tension of metal microdroplets bordering with vacuum, other liquids and substrate.

2. Dynamic method for measuring the surface tension of microliter drops of liquid metals
The dynamic method we used to determine the surface properties of low-melting metals is based on the analysis of the frequency spectrum of capillary oscillations of a liquid drop [7–9]. A schematic diagram of an experimental setup for studying capillary and rheological properties of microliter droplets of various liquids is shown in figure 1.

It includes a system for forming microliter drops of a given size in a gaseous medium or other liquid, a furnace for heating a cuvette with the test liquid and recording unit for the capillary oscillation and geometrical parameters of microliter droplets. In this study, capillaries
Figure 1. The experimental setup for studying the capillary properties of microliter drops (side view): 1a—microliter droplet on the end of the capillary; 1b—microliter droplet on the substrate; 2—milliliter glass cuvette; 3—capillary for formation microliter droplets; 4—substrate; 5—heating element with a thermocouple to maintain a predetermined temperature of the glass cell; 6—a microscope that forms a droplet contour image enlarged 100–200 times on the active area of the photodiode; 7—photodiode; 8—light-emitting diode (LED) for illumination of the microliter droplet; 9—digital oscillograph recording capillary oscillations microliter droplets.

Figure 2. The microliter gallium droplet on a copper substrate immersed in water.

of stainless steel with a diameter of 0.35–0.6 mm were used. In the process of research, the microliter droplet can remain on the end of the capillary (“pendant drop”) or be placed on the substrate 4 (“sessile drop”). A second microscope (not shown) with an additional illuminator and a digital image recording system is used to record the geometrical parameters of the microliter droplets necessary for calculating surface and interfacial tensions, as well as wetting angles. The optical axes of the first and second microscopes intersect at a right angle in the center of the microliter droplet under study.

The measurements were carried out with a gallium drop placed on a copper substrate. The drop with the substrate is immersed in distilled water at $T = 310 \text{ K}$ (figures 1 and 2).
Figure 3. Capillary oscillation of a sessile droplet corresponding to a standing wave (3) with \( n = 2 \): (a) the schematic view of the perturbed droplet profile; (b) the dependence of profile deviation coordinates \( \zeta \) on the arc length coordinate \( s \) along the unperturbed contour. Nodes are marked with points A, B, C, D.

The maximum radius of the sessile drop is \( R = 1.3 \) mm. The length of the contour of the vertical section of the droplet passing through its top is \( l = 5.55 \) mm. The capillary constant for gallium:

\[
a = \sqrt{\frac{\sigma}{\rho g}},
\]

(1)

where \( \sigma \) and \( \rho \) are the surface tension and density of the fluid, \( g \) is the free fall acceleration. For pure gallium \( \sigma = 715 \) dyn/cm, \( \rho = 6.1 \) g/cm\(^3\) and \( a = 0.35 \) cm. In the case we are considering, \( R/a = 0.37 \), and necessarily account is taken of gravity. For the capillary oscillations frequencies of the fluids interface one can use the relation [8]:

\[
\omega^2 = \frac{\rho - \rho_1}{\rho + \rho_1} g k + \frac{\sigma_{12} k^3}{\rho + \rho_1},
\]

(2)

where \( \omega \) and \( k = 2\pi/\lambda \) are the frequency and the wave vector of a capillary wave with a length \( \lambda \), \( \rho_1 \) is the density of outer liquid, \( \sigma_{12} \) is the interface tension.

To assess the interface tension we use the Antonov rule \( \sigma_{12} = \sigma - \sigma_1 \), where \( \sigma_1 \) is the surface tension of the outer liquid, which in the case of water equal to 72 dyn/cm. Thus, the interface tension below is taken to be \( \sigma_{12} = 643 \) dyn/cm. We have to consider two cases for behavior of droplet horizontal contour on substrate during oscillations. The first case takes place for small oscillations amplitudes when the droplet contour on the substrate does not shift and one can assume that an odd number of half-waves fit on the vertical contour length \( l \), which can be written as in [9]:

\[
(2n - 1) \frac{\lambda}{2} = l.
\]

(3)

The mode \( n = 2 \) corresponds to \( l = 3\lambda/2 \) is shown in figure 3.

The second case can be realized for higher excitation amplitudes when the droplet-substrate contact line tears off from initial position and freely move along substrate as shown in figure 4. This situation was considered in [9] and named “mobile contact line”. In this case the relation between wavelength and vertical contour length has the form [9]:

\[
m\lambda = l.
\]

(4)

The experimental oscillogram of light intensity scattered by gallium sessile droplet is shown in figure 5, corresponding frequency spectrum is presented in figure 6.
Figure 4. The same as in figure 3, but for “mobile contact line mode”: (a) droplet contour at \(m = 1\) in (4); (b) deviation coordinate \(\zeta\) from arc length \(s\); \(A, A_1, D, D_1\) and \(B, C\) are edges and nodal points of the contour respectively.

Figure 5. Time dependence of the photodiode signal intensity for a gallium microliter droplet oscillating on a copper substrate in water at \(T = 310\) K.

The main peak in the spectrum falls at \(v = 64\) Hz and can be interpreted as corresponding to the mobile mode \(m = 1\). In this case, formula (2) with \(\lambda\) from (4) gives a frequency \(v_1 = 59.8\) Hz. In the same spectrum, a weakly pronounced peak is observed at a frequency of \(v = 102\) Hz. It can be explained as the oscillation mode of a droplet with a fixed wetting contour and a wavelength corresponding to \(n = 2\) in formula (3). In this case, one can get from formula (2) a frequency equal to \(v_2 = 108\) Hz. The fact that two different modes of oscillations of the droplet contour are observed in one measurement can be explained by the fact that, upon damping of vibrations, the initially mobile droplet contour is pinned on the substrate.

The damping decrement of capillary oscillations amplitude due to viscosity is estimated by the formula [7]:

\[
\gamma \approx \frac{2\eta k^2}{\rho},
\]
where $\eta$ is the dynamic viscosity of the fluid. For gallium, $\eta = 2.2$ cP, which corresponds to $\gamma = 3.15$ s$^{-1}$. With decreasing drop size, the role of viscous dissipation increases, and when the drop radius is less than the critical one,

$$a_c \approx \frac{2\eta^2}{\rho \sigma},$$

vibrations become impossible. For gallium, $a_c = 0.34$ $\mu$m at $T = 310$ K, which determines the range of applicability of the method described above.

3. Static methods for determining the capillary properties of liquid metal microdroplets

To determine the surface tension and wetting angle by a static method, we used a two-cascade projector based on an electron microscope TESLA BS-250, which allows placing micro-objects and visualizing them with an increase from 500 to 2500 (two-cascaded shadow mode) [4]. It is possible to achieve an increase of up to 40 000 with a three-stage projector [5]. A scheme of the main components of an experimental setup is shown in figure 7.

Combining the projector with an ultra-high vacuum (UHV) chamber, shown in the diagram, significantly increases the analytical capabilities of the installation due to the additional equipment installed on the it free flanges. In particular, electron beam passing through the object can be turn towards the energy analyzer in order to measure the electron energy losses. The heating element is equipped with a thermocouple to keep a sample temperature stability in the range $T = 300$–$550$ K. The object of study, which is a metal microdroplet, with the help of four built-in micromanipulators can be placed both on the cantilever beam and on the conical tip of its needle. Both options are shown in photographs in figure 8.

The surface tension of a tin drop waiting on the conical tip of an AFM needle at the melting point temperature was determined by measuring its profile. The scheme for measuring the electron image of a micro droplet is shown in figure 9. The surface of the silicium needle is covered with a platinum island film. It was found that platinum covered only 17% of cantilever surface. Assuming the additive character of interfacial energy in the heterogeneous system under...
Figure 7. Scheme of an experimental setup based upon a TEM TESLA BS-250: 1—electron-optical column of the microscope; 2—ultra-high vacuum chamber; 3—luminescent screen; 4—energy analyzer of electrons passing through the sample.

Figure 8. Electron microscopic photographs of tin droplets placed on the cantilever beam (a) and the conical tip of the needle (b) of the AFM probe.

consideration and using the experimental value of the contact angle for droplet with needle, we obtain $\sigma_{\text{tin}} = 490 \text{ dyn/cm}$.

4. On the possibility of implementing a dynamic method for metal microdroplets using an electronic projector
When using an electronic projector, there are possibilities of applying dynamic methods for measuring the capillary properties of liquid metals micro droplets. The general view of the sample chamber and the scheme for implementing the dynamic method are shown in figure 10.

The use of the capillary dynamics method for micron-sized droplets becomes possible with the use of heat-resistant optic light guides, which allow transferring an image of an oscillating microdroplet from sample chamber to a photodiode. There is also the possibility of analyzing
Figure 9. The scheme of measuring the electronic image of a liquid tin micro droplet pending on the conical tip of the needle of an AFM probe.

Figure 10. The sample chamber: (a) general view; (b) the scheme (1—microdroplet of liquid metal; 2—AFM probes on micromanipulators; 3—laser LED; 4—two arms of a flexible fiber optic light guides introduced into the object camera; 5—photodiode; 6—heating element with a thermocouple).

the oscillations of the intensity of the electron beam after scattered by object of submicron sizes. In this case, the long-focus lens of microscope is placed immediately after the projection lens in order to collect the electron beam inside the UHV chamber by Faraday cup.
5. Conclusions
An experimental setup was assembled combining a TEM with an UHV chamber. The installation allows one to visualize micro-objects, manipulate them and measure their capillary properties by static methods. The modification of the electron-optical microscope scheme is proposed, which makes it possible to apply the discussed above dynamic method to submicron objects.

The interpretation of our experiment on measuring the frequencies of capillary vibrations of sessile droplet using the dispersion relation [8] shows its applicability with an accuracy of about 6%. That is may not be sufficient to detect fine effects for smaller droplets. For correct interpretation of the frequency spectrum and further developing the dynamical method described above one have to improve this dispersion relation. This can be done by comparing the numerical solutions of the hydrodynamic equations [10] and the experimental resonance dependences $\zeta(s)$ for different immiscible liquids.

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