One more approach to water-air interface studies

(Water droplets coalescence and air bubbles merge in water.)

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Abstract

One more approach to the water-air interface studies, using the idea of observations of water droplets and air bubbles in confined and semi confined space, is described. A narrow glass chamber with distance between walls of about 1 mm and glass surface, modified to obtain contact angle of 90 degrees, allows observation of water drops and air bubbles cross-section behavior. It is shown that reduction of one axis to 2-D space eases observation of water-air interface, promising simplification of hydrodynamic equations. Semi-confined space with only one glass surface with contact angle of 90 degrees also allows study of water drop dynamics, looking from drop inside. Visual observations under these conditions are described.

Introduction

Among other liquids water takes a unique position due to the role in the life and properties that makes water so unpredictable in the multiple manifestations. The purpose of this work was to develop an instrument that would enable detailed studies of water-air interface and water properties in stable environment allowing qualified changes of parameters and observations of derived changes of water-air interface behavior.

There were many attempts to observe water droplets coalescence and air bubbles in water merge that showed interesting and puzzling behavior of water-air interface. Initial observations of water drops coalescence are dated back to 1879 by Rayleigh[1] and the water drops floating on the water surface to 1881 by Reynolds[2,3]. Technological achievements of the 20th century allowed observing water drops behavior on the water surface using high frame-rate video camera. Very amazing observations were made by astronaut Donald Pettit in free space with zero gravity and described in his "Symphony of Spheres"[4,5]. There were even more sophisticated observations using Ultrafast X-Ray Phase-Contrast Imaging[6].

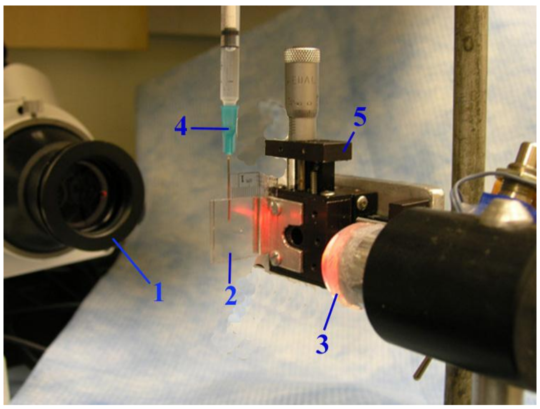
The major question that was attracting attention is the reasons of water drops hydrophobic behavior that makes them non-coalescing for a long period of time from millisecond to seconds. The major explanation that comes through many publications is air bubbles between drops in the coalescence region. In spite of the fact that this supposition was proven many times experimentally through observations of bubbles formation, still there are many questions that remain unanswered.

Modern theory tells that, while forming very complex structures through hydrogen bonding, water can exchange these formations on picosecond or even femtosecond scale of time. But droplets behavior shows that there should remain some stable formations in the air-water interface that might persist. Some odd speculations, coming from this feature, arise lately[7]. And though there are no clear evidences for such speculations it is evident that this question requires more precise attention and unifying approach that would allow studies of multiple influencing parameters and water properties, which can change very easily. There are no negligible parameters in the process due to very high sensitivity of water to outer influences. Everything should be taken into account.

This paper describes new approach to air-water interface study using cross-sections of water droplets and air bubbles in confined and semi-confined space of glass chambers made of glass with surface covered with sodium azide NaN_3 attached to self-assembling monolayer (SAM) of 11-bromo-undecyl-trichloro-silane (BUTS) formed on the glass surface. Such surface has a remarkable feature of being neutral to water so that the contact angle is close to 90^o. This allows observations of water droplets and air bubbles from inside with one additional parameter that is adsorption of water and air molecules to the glass walls, which certainly influence boundary behavior but still, can be measured and taken into account.

Experimental setup.

The experimental setup (fig.1) that was used in the described observations was very common and had no remarkable features except the dark field light source and the glass chamber with inside walls covered with sodium azide.



1. Microscope with video camera.
2. Glass chamber with variable distance between walls.
3. Source of monochromatic light of "dark field" type.
4. Syringe needle to inject water into the chamber.
5. Mechanism of distance variation.

Fig. 1.

The chamber.

There were two main types of chambers that were used in the experiments:

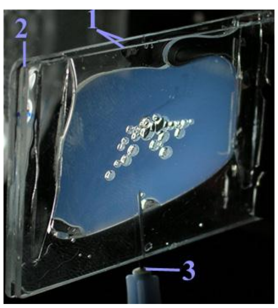


Fig.2

Chamber with fixed distance between walls

1. glass walls covered with NaN_3
2. PDMS layer of 1 mm thick
3. Syringe needle to inject bubbles.

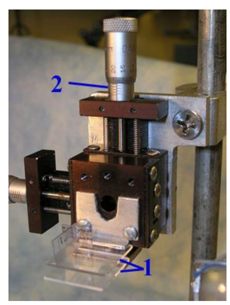


Fig.3.

Chamber with variable distance between walls

1. Glass walls covered with NaN_3.
2. Micrometric screw to change distance between the walls.

First type of chamber (Fig.2) with fixed distance between the walls was used to observe bubbles merge in water and water drops coalescence. This chamber was made of glass slides for microscope of 1 mm thick (Fisherbrand Microscope Slides Catalog #12-550C) and covered with NaN_3 on SAM of 11-bromo-undecyl-trichloro-silane (BUTS). The contact angle is very close to 90^o and this allows more precise observation of air-water boundary without remarkable distortion of reflected light. Distance between glass walls was formed using 1 mm thick poly-dimethyl-silane (PDMS) layer. One of PDMS features is its hydrophobicity.

Second type of chamber (Fig.3) with variable distance between glass walls was used to observe water droplets coalescence. This chamber was used for formation of both confined space between two walls and semi confined space used for observation of water drops cross-sections. In both cases the wall glasses were covered with sodium azide. Preparation of Selfassembling monolayer[8] was simplified to adjust to the laboratory possibilities.

The procedure of glass surface modifying was as follows:

1) Cleaning and activation of Si/glass surface:

To obtain an activating OH surface group on which the self-assembly can take place, the glass slides were sequentially cleaned with ethanol and demineralized water, oxidized by a mixture of concentrated H_2SO_4 and 40% aq. H_2O_2 (70:30 v/v, known as 'piranha solution') at 60 ºC, washed with demineralized water, and dried with compressed air.

2) Preparation of SAM with11-bromo-undecyl-trichloro-silane (BUTS):

The activated glass slides or Si wafers were immersed in a 1% v/v solution of BUTS in dry toluene under and stored in refrigerator for 45 min. The slides were then rinsed thoroughly with dry toluene and ethanol. The glass slides coated with SAM were baked in oven at 100 ºC for 10 min.

3) Surface modification by S_N2 reaction with Sodium azide:

Nucleophilic displacement of bromide by azide on SAM was carried out in DMF with sodium azide. The slides were immersed in a saturated solution of NaN_3 in DMF and stirred for 48h at room temperature. Then it was washed with demineralized water and dried with compressed air.

Special attention was devoted to the light source. First requirement was to use the light source that would allow paying more attention to observations of air-water boundary behavior with minimized distortion. To fulfill this requirement a dark-field light source was designed. The second requirement was to diminish chromatic aberrations. To fulfill this requirements monochromatic sources have been chosen that was Super Bright Luxeon 1Watt LED of different colors.

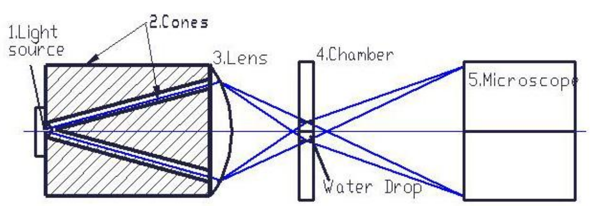


Fig. 4.

The diagram of the light source is represented on Fig.4. It consists of Super Bright Luxeon 1Watt LED (red or blue) (1). Two cones outer and inner (2) put one into another so that they form a light-guide. Both cones were glued to a lens (3) that focused a formed light ring on the chamber (4). Light from secondary light sources (light re-emitted from water droplet) in the chamber was coming to microscope (5) with video camera.
Sometimes a High frame rate video camera was used instead of microscope.

Results of observations.

There were two major types of observations made with this experimental setup.

<u>First.</u> Observations on modified glass surface. In this case water drops formed cross-sections as if they were divided into two halves by the glass surface (fig.5). The behavior of one half of the water drop could be observed from inside, using bottom views (fig.6), and dynamics of water flows studied, using contrastive particles (microspheres).

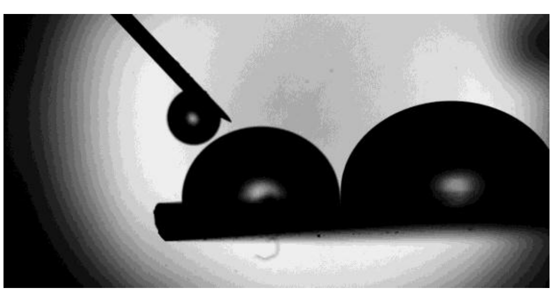


Fig.5

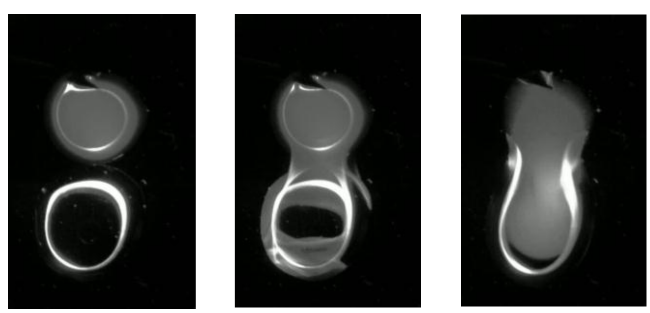


Fig.6

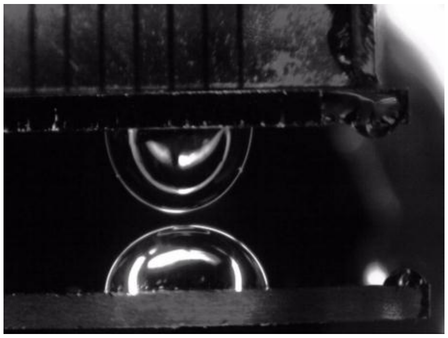


Fig.7

These observations were also combined with observations of two parallel modified glass surfaces with varying distance between them (fig.7). In this case studies of water drops coalescence events can be combined with influence of varying distance between walls.

<u>Second.</u> Observations on modified glass surface when two glasses form narrow chamber with distance between two parallel walls about 1 mm. (fig.2). The following images are all side views of the chamber. This chamber served as an instrument for observations of merger of air bubbles in water (Fig.8) and observations of water drops coalescence (Fig.9).

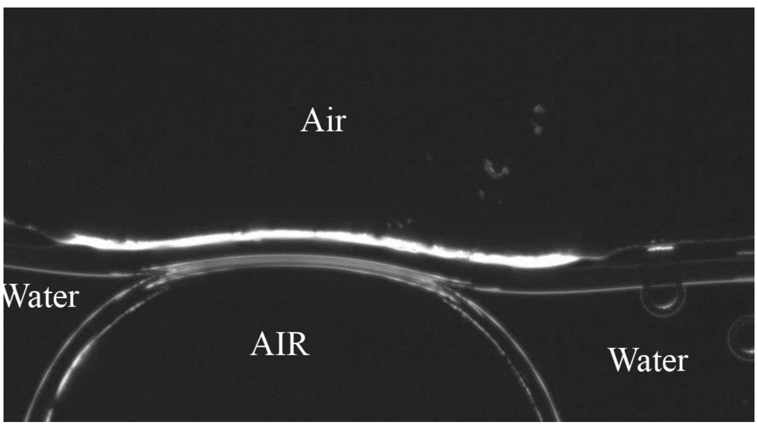
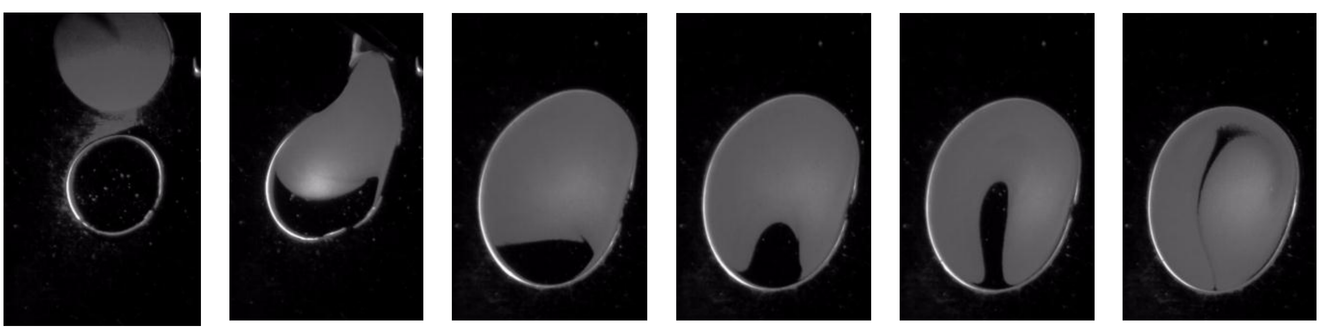


Fig.8

Fig.9

Addition of contrasting substance to the upper drop allowed observations of drops coalescence dynamics (Fig.10).



0 sec. | 1 sec. | 25 sec. | 2 min. | 5 min. | 15 min.

Fig.10.

In this series of pictures two water drops coalescence in the second type chamber is presented. The upper drop was a demineralized water of initial pH=6 with addition of polystyrene microspheres of 2 μ in diameter and concentration of 9 million per ml. (or 1 microsphere per about $3.7*10^{12}$ molecules of water). After addition of microspheres, water changed pH to 5.5. Bottom drop was a demineralized water of pH=6.

Such high concentration of microspheres has been chosen for the better visualization in this presentation only, since addition of solid particles into water changes its properties remarkably through formation of hydration shells that reduce system entropy[9]. In real experiments, for the purpose of water dynamics studies, concentration can be much lower.

The use of high frame rate camera also increases ability of this experimental setup allowing detailed observations of water-air interface behavior during the process of drops coalescence or merger of bubbles. Fig.11 represents a series of pictures of water drops coalescence. Upper drop was formed using demineralized water of initial pH=6 and filled with polystyrene microspheres of 2 μ in diameter and concentration of 9 million per ml. (or 1 microsphere per about $3.7*10^{12}$ molecules of water). After addition of microspheres, water changed pH to 5.5. Bottom drop was a demineralized water enriched with hydronium ions till the level of pH=3.

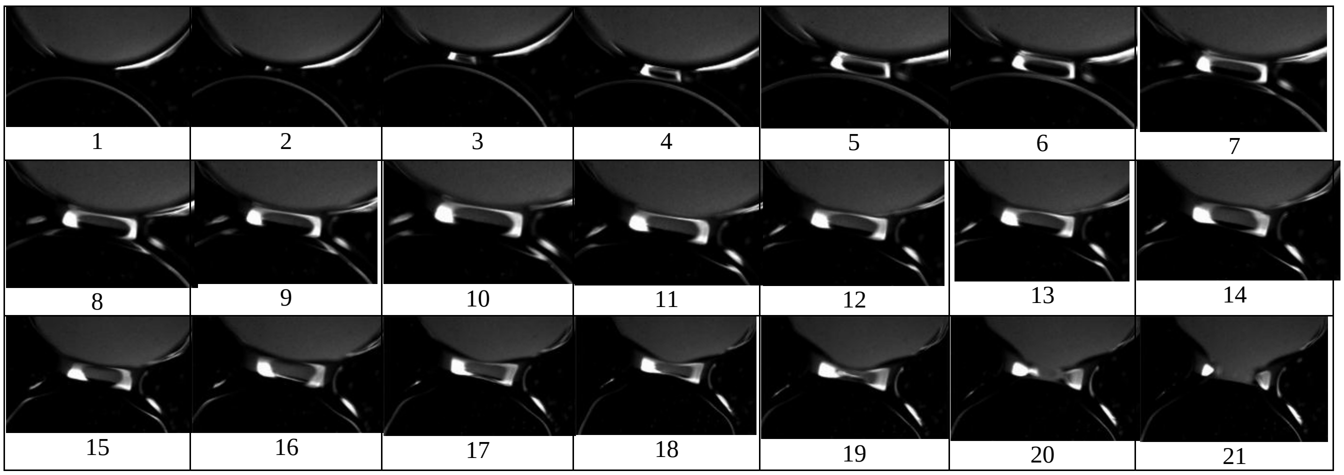


Fig.11.

Every next picture represents the state of water drops contact region with difference in time of 10^{-5} sec. As it is seen on this series, the wave formation begins in both drops with the starting point at the contact region. The video-clip that represents the process can be achieved from http://www. This clip allows determination of the wave parameters.

This chamber allows observation and study of the waves propagating along the borders of the drops. Measurements of the wave parameters enable calculation of water physical properties (such as viscosity). Reduction of space from 3D to 2D also simplifies hydrodynamic equations. Usage of this approach involves an additional parameter that should be taken into account, which is adsorption of water and air molecules to the glass walls. But this parameter can be measured.

Discussions

The heightened interest to water properties and avalanche of visual observations of different kinds reflects the shortage of our knowledge about water that can be explained with its high sensitivity to any influence of ambient conditions. It is necessary to admit that success in water structuring studies was achieved through computer simulations only (see summary at[10]). Thus limitation of influencing parameters, their stabilization and paying attention to, as well as attraction of mathematical approach and computer simulations, becomes important for extracting information from water.

Computer simulation of droplets coalescence for 3D space involves very complex equations (see for example[11]). Described approach represents an attempt to simplify hydrodynamic equations that would allow more steady approach to parameters variations.

Conclusion

Presented experiments do not offer new data that could be satisfactory for any conclusions about water properties, but designed experimental setup might be considered as a small step for further development of experimental observations in water hydrodynamics. Among other observations of water drops coalescence, described approach, using the idea of observations of water droplets and air bubbles in confined and semi confined space, is described. A narrow glass chamber with distance between walls of about 1 mm and glass surface, modified to obtain contact angle of 90 degrees, allows observation of water drops and air bubbles cross-section behavior. It is shown that reduction of one axis to 2-D space eases observation of water-air interface, promising simplification of hydrodynamic equations. Semi-confined space with only one glass surface with contact angle of 90 degrees also allows study of water drop dynamics, looking from drop inside.

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References

1. Rayleigh L., *Proc. R. Soc. London Ser. A* **1879**, *28*, 406–409.
2. Reynolds O., *Chem. News* **1881**, *44*, 211–212.
3. Reynolds, O. *Papers on Mechanical and Physical Subjects*; Cambridge University Press: Cambridge, U.K., 1900; Vol. 1.
4. Donald Pettit “Symphony of Spheres” http://spaceflightsystems.grc.nasa.gov/WaterBalloon/#ISS
5. Donald Pettit “Waves in a large free sphere of water”. http://www.freesciencelectures.com/video/waves-bubbles-and-reactions-in-a-free-sphere-of-water/
6. Kamel Fezzaa and Yujie Wang, Ultrafast X-Ray Phase-Contrast Imaging of the Initial Coalescence Phase of TwoWater Droplets, PHYSICAL REVIEW LETTERS 100, 104501 (2008)
7. I. S. Klyuzhin, F. Ienna, B. Roeder, A. Wexler, G. H. Pollack. Persisting Water Droplets on Water Surfaces. J. Phys. Chem. B, 2010, 114 (44), pp. 14020-14027
8. Natarajan Balachander and Chaim N. Sukenik, Monolayer Transformation by Nucleophilic Substitution: Applications to the Creation of New Monolayer Assemblies, *Langmuir*, 1990, 6 (11), pp 1621–1627
9. Chaplin M., Colligative properties of water. http://www1.lsbu.ac.uk/water/collig.html
10. Chaplin M., Interfacial water and water-gas interfaces, http://www.lsbu.ac.uk/water/interface.html
11. J. Eggers, J. R. Lister and H. A. Stone, Coalescence of liquid drops J. Fluid Mech. (1999), vol. 401, pp. 293-310