# Influence of bubble surface fluidity on collision kinetics and attachment to hydrophobic solids 

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## H I G H L I G H T S

- Adsorption of surface-active substances (SAS) retards bubble surface fluidity.
- Kinetics of bubble attachment to hydrophobic solid depends on solution composition.
- Attachment time is short in water and prolonged in higher SAS concentration.
- Kinetics of attachment is affected by air entrapped at hydrophobic surfaces.


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## GRAPHICALABSTRACT




#### Abstract

Influence of variations of the bubble surface fluidity on its rising velocity, kinetics of collisions, bouncing and attachment to hydrophobic solid surface was studied experimentally and modeled by means of numerical calculations. A theoretical model was elaborated to describe gradual retardation of the bubble surface fluidity as observed in surface-active substances solutions of increasing concentration. The model is described in details and validated against the experimental results. In experiments the ascending bubble collisions with solid wall, in surface-active substances solutions of gradually increasing concentration, were monitored using high speed photography, while in numerical simulations the bubble behavior (rising velocity, shape deformations, spatial displacement during collisions and bouncing) was determined by solving the governing equations describing conservation of momentum and mass of an incompressible viscous liquid. The results obtained in experiments and in numerical simulations were in a good agreement. Therefore, the model elaborated was used also to confirm that air presence at hydrophobic solid surfaces is responsible for the reported earlier effect of prolongation of time of the bubble attachment at higher concentrations of surface-active substances.


[^0]The results of numerical simulations showed similar trends as the experimental data, that is, with increasing degree of the bubble surface immobilization the calculated values of the bubble attachment time were prolonged.
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## 1. Introduction

Bubble rising velocity in liquids is determined mainly by the bubble's size, viscosities and densities of the liquid and of the gas phases, presence of surface-active substances and properties of the gas/liquid interface [1-5]. In pure liquids the bubble surface is fully mobile and therefore the bubble velocity is higher than that of a solid sphere of identical diameter and density [6-9]. In solutions of surface-active substances (SAS) the bubble rising velocity is lowered due to the adsorption layer formation, which retards fluidity of the liquid gas interface. As a result of the viscous drag exerted by continuous medium, uneven adsorption coverage along the interface of the rising bubble is developed [1-3]. When such adsorption layer, called the dynamic adsorption layer (DAL) [4], is formed the adsorption coverage (surface concentration) is at minimum at the upstream pole of the moving bubble, while at the rear pole is higher than the equilibrium one [1]. This uneven distribution of the adsorption coverage over surface of the rising bubble and the surface tension gradients induced (Marangoni effect) cause retardation of the bubble surface fluidity [ $1-3,10$ ]. Lowered fluidity means an increased hydrodynamic drag exerted at the moving bubble surface. This is a reason why velocity of the bubble rising in SAS solutions is lowered [ $3,4,11-15$ ]. Numerous theoretical approaches regarding various aspects of formation and properties of the dynamic adsorption layer and physicochemical hydrodynamics of the rising bubble have been described by Dukhin et al. [3,4]. Up to now, however, there is no direct experimental evidence of the DAL existence, but the results of indirect investigations show undoubtedly that the DAL is formed over surface of the rising bubble [13-16].

Presence of adsorption layer over the bubble surface affects not only the bubble rising velocity but also kinetics of the bubble collisions at various interfaces [17-22]. In solutions of surface-active substances the colliding bubble impact velocity is lowered, the bouncing is damped faster and the degree of bubble deformation is much smaller than in distilled water [18-22]. Moreover, the time needed for the separating liquid film to drain to its critical thickness of rupture is prolonged in sufficiently high SAS concentrations [23,24]. This effect was observed experimentally in the case of free solution surfaces [21] as well as for hydrophobic solid surfaces of different roughness [20-22,25]. This rather unexpected effect of prolongation of time of the three phase contact (TPC) formation at high SAS concentration was attributed [20-22,25,26] to air presence (nano- and/or micro-bubbles) at hydrophobic surfaces [25,27,28].

This paper presents a comparison of results of numerical simulations and experiments on influence of SAS on kinetics of the bubble collisions and the TPC formation at hydrophobic surfaces. A simple numerical model elaborated mimics (simulates) the gradual retardation of the bubble surface fluidity in solutions of surface-active substances via gradual increase of viscosity of the bubble/liquid interface (implies secondary tangential stresses near the interface). The results of simulations are compared with experimental data obtained for the bubbles rising, colliding and attaching to hydrophobic solid surfaces in SAS solutions of different concentrations.

## 2. Experimental

### 2.1. Methods

The experimental set-up used for monitoring the dynamic phenomena occurring during the bubble collisions with a solid wall was described in details elsewhere [22,25]. Briefly, a single bubble was formed at a capillary orifice (diameter 0.075 mm ) at the bottom of a square glass column ( $40 \times 40 \mathrm{~mm}$ ). Its motion was recorded using a high-speed video camera (SpeedCam MacroVis, 1040 fps ). A hydrophobic polytetfafluoroethylene (Teflon ${ }^{\circledR}$ ) plate was positioned horizontally beneath the liquid surface, at the distance $S=3$ or 250 mm from the capillary orifice. Sequences of recorded images of the colliding bubble were analyzed frame-by-frame using image analysis software (ImageJ, and/or WinAnalyze moving object tracking software).

The advancing contact angles $(\theta)$ at the Teflon ${ }^{\circledR}$ plates were determined by the sessile drop method (Kruss DSA100 tensiometer) and varied within the range ca. $100-115^{\circ}$.

The experiments were carried out at room temperature.

### 2.2. Materials

The polytetrafluoroethylene (Teflon ${ }^{\circledR}$ ) plates of $30 \times 30 \mathrm{~mm}$ dimensions were cut from the same piece of commercial Teflon ${ }^{\circledR}$. Prior to the experiment the plates were polished using the sand paper of grid number 600 (coarse) or 2500 (fine) to modify the plate's surface roughness. For convenience, these plates will be referenced further as Teflon2500 and Teflon600. Prior to experiments the plates were carefully cleaned using a chromic acid mixture and then rinsed thoroughly with water. Four-fold distilled water and Mili- $Q^{\circledR}$ water were used in the cleaning procedure, surfactant solution preparation and in the experiments.
$N$-Hexanol, $\alpha$-terpineol and $n$-octanol (Sigma-Aldrich) used in the experiments were commercial reagents of highest available purity ( $\geq 98 \%$ ).

## 3. Results and discussion

### 3.1. Theoretical model

Fig. 1A presents the schematic illustration of the model and computational domain. The dimensions of the liquid column were as follows: (i) height $H=40 \mathrm{~mm}$ or 6 mm , depending on the calculation effectiveness in respect to the computational time, and (ii) radius $L=2 \mathrm{~mm}$. The computational domain contained a gas bubble of radius $R_{\mathrm{b}}=0.74 \mathrm{~mm}$. Liquid column of $L=2 \mathrm{~mm}$ was chosen as a compromise between simulation accuracy with regard to socalled wall effects and computational time. The influence of the wall proximity on the bubble motion parameters obtained numerically was discussed elsewhere [29]. To minimize the influence of column wall proximity on the bubble motion, the slip boundary conditions at the side cylinder walls were assumed. The top cylinder wall was assumed to be a no-slip boundary (Dirichlet, $\mathbf{u}=0$ at the solid boundary), independently on the contact angle applied. The density of the liquid used in calculations was $1000 \mathrm{~kg} / \mathrm{m}^{3}$, while for gas $1.3 \mathrm{~kg} / \mathrm{m}^{3}$, i.e., was of an order of density of water and

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