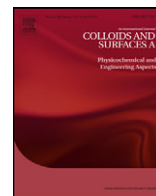




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# Antibubble lifetime: Influence of the bulk viscosity and of the surface modulus of the mixture

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### ABSTRACT

Lifetime of antibubbles has been measured for different liquid mixtures. The life duration of an antibubble is governed by the air drainage from the bottom to the top of the antibubble. We show that their lifetime is influenced by both bulk and surface properties of the liquid mixture used to create the antibubble. When the viscosity is increased, the stability of the antibubbles during the first seconds of their life is enhanced. By changing the surface modulus by a factor 100, the mean antibubble lifetime is doubled. Surfactants can affect the mobility of the film surface and, thereby, the rate of air film thinning.

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## 1. Introduction

An antibubble is the negative object of a soap bubble. Instead of having a thin shell of liquid that separates the air inside and outside the bubble, the antibubble is a thin air shell that separates two liquids. The principle for generating an antibubble is very simple. It consists in pouring delicately a soapy water mixture at the surface of the same mixture contained in a tank. The poured liquid first forms a globule at the surface of the liquid. By gently increasing the flow, the globule manages to pass through the surface to form a cylinder of liquid inside the tank liquid. This cylinder of the poured liquid is separated from the remaining by a thin air layer. Due to Rayleigh–Plateau instability, the cylinder collapses into some antibubbles. The picture of an antibubble can be seen in Fig. 1(right).

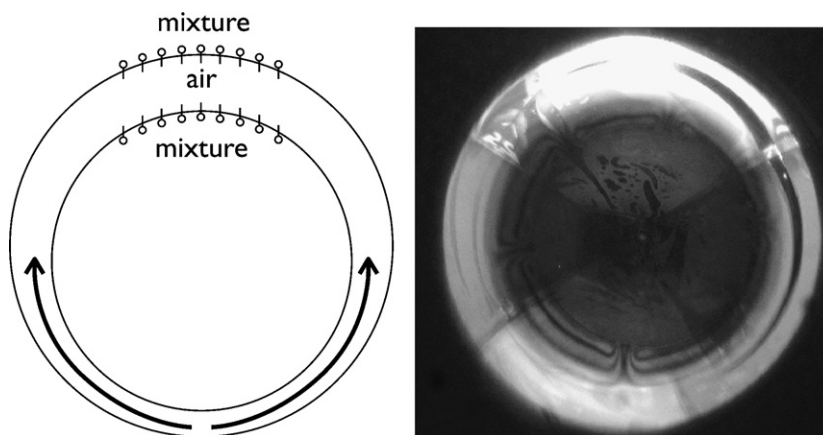
While the discovery of this fluidic object is rather ancient [1], the object was considered as a scientific curiosity that could be found in popular works like [2]. On the other hand, the works concerning the antibubbles are no older than 5 years [3–8]. Most of these studies are concentrated on the mechanism that allows the antibubble to be generated [3,7,8]. The mystery was to understand why such an object can be observed since, contrary to soapy bubble, no stabilization mechanism exists. Indeed, the stability of a soap film is ensured by the existence of a repulsion force (positive disjoining pressure). In the so-called common black film, the repulsive force is created by the charges on the film surfaces brought with the ionic surfactant molecules, adsorbed on the film surfaces [9]. The molecular

structure of the antibubble air shell is schematized in Fig. 1(left). The surfactant molecule hydrophobic tails are in opposition; the interaction between the walls is fundamentally different from the soapy bubble situation because the electrostatic field is closed in the aqueous phase, so that no electrostatic repulsion between the film surfaces is expected. That means that the antibubble can not be a stable object since the attractive van der Waals forces are dominant. In [6], the lifetime of the antibubble has been studied. It follows an exponential distribution. A maximum lifetime has been determined by considering the characteristic time to drain the air from the bottom to the top of the antibubble under the action of the hydrostatic pressure gradient. The air film collapses at the bottom when the thickness of the air film becomes of the order of the distance for which van der Waals forces are significant (about 100 nm).

In this paper, we are interested in determining the role of the liquid mixture in the formation and the lifetime of the antibubble. It has been shown that the antibubble can be created with different kinds of surfactant: anionic or non-ionic, commercial soap, pure surfactant, beer protein. . . it is to note that the role of the surfactant is not taken into account in the drainage theory in [6]. However, it is observed that the mixture does play a role, e.g. it is very difficult to generate an antibubble with a solution of SDS only; the addition of glycerol increases the probability to obtain an antibubble. Despite the different observations, no work has been dedicated to the influence of the surfactant, which is known to be very important for soap bubbles. In the present study, we propose to explore the influence of two parameters: the bulk viscosity and the surface modulus of the surfactant mixture. Firstly, we show that an increase of the viscosity prevents the early popping of the

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**Fig. 1.** (Left) Structure of the antibubble. The air film is thinner at the bottom than at the top of the antibubble due to the slow drainage of the air driven by the hydrostatic pressure gradient. The surfactant molecule orientations are presented only at the top of the sketch. Surfactant hydrophobic tails are in opposition. (Right) Picture of an antibubble having a diameter of 10 mm. Interference fringes can be observed. Moreover, the border appears brilliant due to total reflection of light on the air shell.

antibubble by the damping of capillary waves. Secondly, we show that the surface modulus plays an important role: when the surface modulus is low, the film surfaces could be partially mobile which leads to somewhat faster film thinning and shorter bubble lifetime.

## 2. Experimental details

The antibubbles are created by gently pouring a part of the considered liquid contained in a becher onto the surface of a tank containing the same liquid. It is very important to control the flow rate of the pouring and the size of the jet as explained in [8]. The antibubble is created when the incoming jet of liquid that is surrounded by a thin layer of air decomposes into liquid pockets. These pockets form antibubbles. In [8], the proposed technique to create antibubbles is based on the control of the jet using a pump. This pump injects the liquid through a 2 mm diameter tube that turns towards the liquid perpendicularly to the surface of the bath. The control parameters are the speed and the distance between the nozzle and the surface of the bath. They find that for a speed of 20 cm/s and a height of 11 mm, the probability of generating an antibubble is maximum. Here, we chose to create the antibubble manually in order to generate antibubble one by one. The gesture to pour the liquid and obtaining an antibubble is very simple but need some training. As soon as the antibubble is generated, the lifetime of the antibubble is measured using a clock (the lifetime precision is therefore about 3 s). We estimate that the diameters of the studied antibubbles are equal to  $10 \pm 5$  mm. The size of the antibubble does not influence the lifetime as shown in [8].

Two kinds of mixtures have been investigated in order to evidence the influence of the bulk viscosity. The first one is composed by 3 L of tap water mixed with 18 mL of Dreft (dishwashing liquid by Proctor and Gamble) (MIX1). The second is the same mixture but 1 L of glycerol is added. A 4 L solution is obtained and called MIX2. The surfactant concentration has changed but remains above the CMC.

To evidence the effect of the surface modulus, two mixtures have been prepared using deionised water. The components are an anionic surfactant sodium lauryl-dioxyethylene sulfate (SLES), zwitterionic surfactant cocoamidopropyl betaine (CAPB) and myristic acid (MAc) (see [10]). First a stock solution is prepared (MIX3). It is composed by 6.6 wt% SLES and 3.4 wt% CAPB. The second mixture is composed by the stock solution plus 0.4 wt% of MAc (MIX4). This stock solution is diluted 20 times with pure water to prepare the working solution. The reagents used are the following: SLES (product of Stepan Co., Northfield, IL; commercial name STEOL CS-170), CAPB (product of Gold-Schmidt, Essen, Germany;

commercial name Tego Betaine F50), and MAc (Carl Roth GmbH, Karlsruhe, Germany; >98% for Biochemistry).

The characteristics of the four mixtures can be found in Table 1. The viscosity is doubled between MIX1 and MIX2 while the surface modulus of MIX4 is two orders of magnitude larger than for MIX3.

## 3. Results and interpretation

### 3.1. Influence of the viscosity

The cumulated distribution of function (CDF) of the antibubble lifetime  $\tau$  is reported in Fig. 2(left) for the mixtures MIX1 and MIX2. The average lifetime does not change with the viscosity: 85.5 s and 85.4 s for MIX1 and MIX2 respectively. On the other hand, the variance is decreased when the viscosity increases. From 61.3 s for MIX1, the standard deviation decreases to 45.5 s for MIX2.

The viscosity is known to damp the capillary waves. When the antibubbles forms, the air film pinches off. This sudden change of topology generates capillary waves at the surface of the antibubbles. As they are damped by the viscosity, they cannot destabilize the antibubble. This explains the decrease of the standard deviation of the lifetime when the viscosity is increased. Moreover, since early death antibubble proportion is decreased when the mixture viscosity is increased, that shows that the viscosity enhances the probability of generating a stable antibubble.

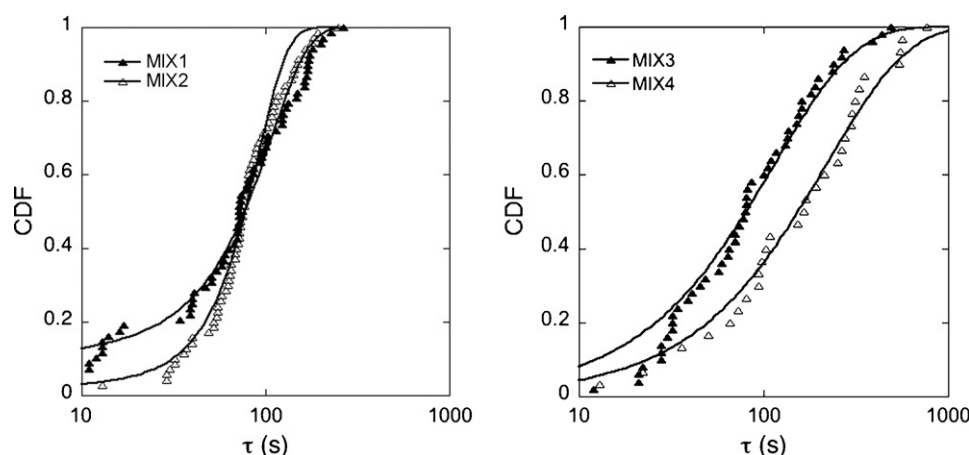
### 3.2. Influence of the surface modulus

The CDF of the lifetime of antibubbles generated with MIX3 and MIX4 is plotted in Fig. 2(right). For MIX3, the lifetime average  $\bar{\tau}$  and the standard deviation  $\sigma$  are found to be equal to 116 s and 107 s respectively. On the other hand,  $\bar{\tau}$  and  $\sigma$  are found to be 218 s and 187 s for MIX4. The average and the standard deviation are of the

**Table 1**

Composition of the different tested liquid mixtures, named MIX1, MIX2, MIX3 and MIX4. The mixtures MIX1 and MIX2 have been used to evidence the influence of the viscosity. On the other hand, MIX3 and MIX4 have the same viscosity and surface tension. The surface modulus of MIX4 is 75 times larger than for MIX3. Dreft is a trademark by Proctor and Gamble. The composition proportions of the different mixtures are described in the text.

Name	Composition	$\mu$ (mPa s)	$\sigma$ (mN/m)	$E_d$ (mN/m)
MIX1	Dreft	1	–	–
MIX2	Dreft + glycerol	2	–	–
MIX3	SLES + betaine	0.9	28.5	4.2
MIX4	SLES + betaine + MAc	0.91	23.8	305



**Fig. 2.** (Left) Influence of the bulk viscosity on the lifetime cumulative distribution function. The circles and the squares correspond to MIX1 (low viscosity, 68 events) and MIX2 (high viscosity, 70 events) respectively. (Right) Influence of the surface modulus on the lifetime cumulated distribution function. The circles and the squares correspond to MIX3 (low surface modulus, 50 events) and MIX4 (high surface modulus, 30 events) respectively. The curves are saturating exponential fits.

same order of magnitude for both mixtures. This is a signature of an exponential distribution. That is the reason why both distributions are well fitted by saturating exponential function

$$F(\tau) = 1 - \exp\left(-\frac{\tau}{T}\right) \quad (1)$$

where  $T$  being the characteristic time of the process that provokes the air film rupture. One finds  $T = 117$  s and 223 s for MIX3 and MIX4 respectively. These values are in very good agreement with the lifetime average and standard deviation.

For an antibubble, no repulsion force has been found (except for a possible steric repulsion between the opposing surfactant tails that has not been evidenced to be important). The van der Waals force is the only force that acts between the film walls. The air is consequently squeezed in the film and the sudden collapse of the air film is delayed by the air located in the shell. As the bottom of the antibubble is submitted to a larger hydrostatic pressure than the top, the air is slowly drained to the top. An upper limit for the drainage time is found by considering that the air shell thickness is the typical distance for which van der Waals forces are predominant (100 nm). The air film is thinned at the bottom till a perturbation is amplified by the van der Waals forces which provokes the spinodal collapse of the air film. It is possible to calculate the maximum lifetime of the antibubble considering the following assumptions: (i) the air flow is a Poiseuille-like flow, (ii) the film thickness  $\varepsilon$  is 100 nm. Using Navier–Stokes equation at 1 dimension, the mean velocity of the flow can be evaluated. The air has to move from the bottom to the top of the antibubble that has a radius  $R$ . The maximal drainage time for the air to run this distance with the characteristic calculated mean velocity is found to scale as  $3R\eta_{air}/(\rho g \varepsilon^2)$  where  $g$  is the gravity,  $\eta_{air}$  is the viscosity of the air and  $\rho$  the density of the water. The estimation of the upper boundary for the lifetime is found to be one hour that is coherent with the measurements [6].

The experiments presented in the current paper, clearly evidence the influence of the chemical composition of the liquid mixture. Especially, we find that the antibubble lifetime is decreased when the surface modulus is low. From the drainage theory point of view, that signifies that the mean speed of the air in the spherical air shell is higher when the surface modulus is lower. We can interpret this fact by claiming that the flow is not a pure Poiseuille flow for low surface modulus mixture since the boundaries are not rigid. More precisely, the origin of mean speed

difference is probably due to a change of the boundary condition at the interface. The speed of the air cannot be considered as being zero at the interface when the surface modulus is low. That means that the interfaces are mobile, part of the flow can be considered as being a plug flow.

#### 4. Conclusion

We show that the viscosity and the surface modulus of the mixture used to generate antibubbles play an important role. First, increasing the bulk viscosity of the mixture enhances the chance of surviving of an antibubble during its life beginning. A high viscosity helps in stabilizing the new born antibubble by damping capillary waves. Second, the surface properties of the air–liquid interface determine whether the air flow from the bottom to the top of the antibubble is more *Poiseuille-like* or more *plug flow*. Modifying the surface modulus changes the boundary conditions of the air flow. A Poiseuille flow is found when the surface modulus is large. On the other hand, a plug flow superposed to a Poiseuille flow when the surface modulus is low. When the flow is more characterized as a Poiseuille flow, the air drainage is slow and the lifetime of the antibubble large.

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