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Measurement of the surface tension on a bubble wall

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Summary
The surface tension on a bubble wall is an essential parameter for many systems including air-sea gas exchange calculations and ultrasonic cleaning systems. However, most current methods cannot measure the surface tension on a bubble wall, but measure it elsewhere in the liquid, usually the flat air/liquid interface, and these values, as will be demonstrated here, can be different. Furthermore, chemical species or dopants at the bubble wall may also change the surface tension at the interface, which affects such calculations as the contribution of the oceans to the global carbon budget. This paper reports a bubble method for measuring the surface tension at the gas/liquid interface of a bubble wall by observing Faraday wave motion.

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1. Introduction

The question 'what is the surface tension on a bubble wall' is key to many environmental processes, including: the dynamics of bubble clouds under breaking waves and in ships wakes and their effect on sonar and air/sea gas transfer; and the formation of aerosols at the sea surface and their subsequent effect on climate; and the transport of pollutants.

However the actual meaning of the question 'what is the surface tension (σ) on a bubble wall' is less straightforward than might first be thought. This parameter is particularly important as it enters formulations for the physical processes which occur in a range phenomenon. These include the balance of forces when a liquid film breaks, the formation of liquid droplets when such films break, the coalescence and fragmentation of liquid drops and or gas bubbles in liquids, the motion of capillary waves on a gas/liquid interface, and many more. They enter these formulations because the 'surface tension' can be incorporated into the idealized physical model of the process through its twin abilities to equal the energy required to form a unit surface area of new interface, and to equal the force per unit length perpendicular to an imaginary line drawn in a flat interface. However these simple equalities leave out a wealth of detail that escapes the current physical models of these process, the most obvious being whether the process is done in static conditions (i.e. so slowly as to an equilibrium state to be established in the surface), or in dynamic conditions (i.e. so rapidly as to prevent equilibrium conditions from being established).

This difference means that a measurement of the 'value of the surface tension' undertaken by one accepted technique, may not be transferrable to another process. The implication is that textbook values of surface tension, or values of the surface tension of a particular water sample measured using accepted techniques in the field or the laboratory, may not be accurate to extrapolate to predict how that same water sample will behave when it participates in environmentally- and climatically-important processes.

This paper will report on the preliminary measurements made to explore these issues by comparison of single 'look-see' measurements (repetitions and statistical analysis will be made when enough data have been compiled) of the value of surface tension on a bubble wall using the threshold for the formation of Faraday waves, and measurement of the value of surface tension in the same liquid sample using a standard method.

2. Background

The well-known du Noüy ring tensiometer method is used in this paper to obtain values of surface tension that an accepted example laboratory method would produce. In this technique a ring is initially immersed in the liquid (Figure 1). The vertical separation between the ring and the liquid is then increased, and the force on the ring measured, until the ring finally separates from the liquid (Figure 2). The vertical separation is increased sufficiently slowly that equilibrium conditions exist on the surface.

To compare with this, we obtain an estimate of the surface tension that pertains to the threshold for the excitation of Faraday waves on the bubble wall [1,2]. Once the acceleration of a pulsating bubble exceeds a threshold value (which usually means that the amplitude or frequency of the sound field driving the bubble to pulsate has passed some critical value [3]), after a short transient period [4,5] that then leads to a steady-state pattern being formed on the bubbles wall [6,7], a perturbation is superimposed on the bubble wall motion which corresponds to that spherical harmonic which (i) had non-zero order, and cannot be 1 and (ii) has a natural frequency that is closest to half of the driving frequency. This is called the Faraday wave, first characterised by Faraday for flat air/liquid interfaces [8–10] and since studied on liquid drops [11]. If, say, the amplitude of the driving sound field continues to increase, additional spherical harmonic perturbations will be excited, and superimposed on the bubble wall motion [12].

The Faraday wave corresponds to that mode which has the lowest threshold pressure (the frequency of which is close to half that of the bubble pulsation resonance frequency), and if the excitation field exceeds that threshold but not that of any other mode, then only the Faraday wave and the pulsation motion will occur on the bubble [2]. The generation of a Faraday wave can be detected by electrochemical techniques [13–15], and by acoustical [16–24] and optical imaging [25], and it was proposed that these measurement points could be inverted to infer the value of surface tension, as it pertains to the threshold for Faraday waves. The mode natural frequency of a single bubble that is initially spherical in an infinite volume of liquid, and then has an axisymmetric mode excited upon its surface is

$$\omega_n = \sqrt{\frac{(n-1)(n+1)(n+2)\sigma}{\rho_0 R_0^3}}. \quad (1)$$

According to equation 1, surface tension σ can be calculated from ω_n, ρ_0, R_0 and n:

$$\sigma = \frac{\omega_n^2 \rho_0 R_0^3}{(n-1)(n+1)(n+2)}, \quad (2)$$

where ω_n is the driving frequency, ρ_0 is the liquid density, R_0 is the bubble equilibrium radius and n is the mode number. Liquid density is measured with a densitometer directly or calculated from $\rho_0 = m/V$, where m is the mass, and V is the volume; R_0 and n are determined from a frame of high-speed camera image; ω_n is the mode natural frequency. By adjusting the driving amplitude, while monitoring the surface wave activity using a high-speed camera, the acoustic pressure threshold required produce Faraday waves on bubble wall can be discovered. Additionally, tuning the driving frequency and repeating this procedure, while maintaining a certain order Faraday wave motion on the wall of a given bubble, a series of pressure threshold vs. driving frequency plots can be acquired. Such data can be plotted, and the curve should be 'U' shaped curve. The mode frequency ω_n can be determined form the high-speed video, and the mode order n can be estimated from the shape of the bubble imaged in three orthogonal directions. The only unknown in plotting the 'U' shaped curve is the surface tension. This allows the effective surface tension on the bubble wall to be measured if the other parameters in equation 2 are known.

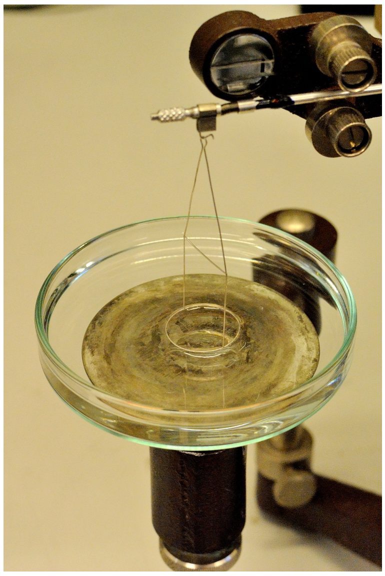

Figure 1. Photograph of the well-known du Noüy ring tensiometer method used for comparisons in this paper.

3. Experimental procedures

The apparatus shown in Figure 3 uses a 40 kHz sound field to trap the bubble at a pressure node within the cell. A piezoelectric transducer (resonance frequency = 40.0 kHz) was glued to the bottom of the water tank to generate the acoustic standing wave. It is assumed for the moment that this levitating field is sufficiently far from the bubble resonance that it does not contribute to the acceleration of the bubble wall sufficiently to affect the threshold for Faraday waves. Unless resources are available to conduct these experi-

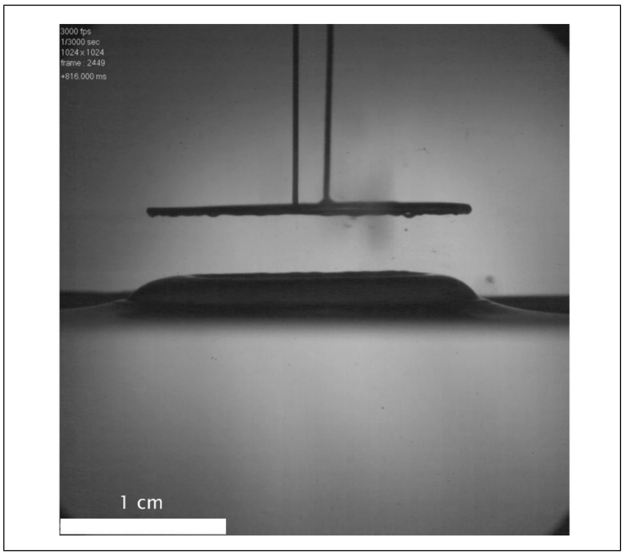

Figure 2. Frame showing the moment 4 ms after as the liquid film breaks away from the ring of the du Noüy ring tensiometer at room temperature (the white line at the bottom left of the frame is a 1 cm long scale bar). Frame rate was 3000 fps and the shutter speed was 1/3000 s.

ments in a microgravity environment [26–28], the bubble must be held at the focus (and in the field of view) of the camera, and the levitation method [29–34] is less invasive than tethering under glass bodies, or with hoops of fine wire to thread [35, 36].

The use of mirrors ensures that the bubble is properly illuminated and that images of it from top and side are simultaneously in focus in each frame of a high-speed camera (as is the ruler). Although manually tuning the frequency and amplitude of the sine wave that generates Faraday waves on a bubble wall and then recording the pressure threshold curve is practicable, it makes one measurement last up to 1 hour. However, the experiments must be done quickly to avoid rectified diffusion, and so a preprogrammed increments of increasing drive field amplitude are run until the Faraday wave is detected, and then the frequency is increased and the process repeated. A scanning program controlled the function generator and the high-speed camera simultaneously. It tuned the frequency and amplitude of the sine wave while sending trigger signals to the high-speed camera to capture sequences of photos of the bubble.

A monolayer of decane ($CH_3(CH_2)_8CH_3$) was placed on the surface of the previously fresh, purified water, and the value of the surface tension was measured in three ways: (i) using the du Noüy ring tensiometer; (ii) using the Faraday wave technique on a bubble injected into the body of the water; and (iii) using the Faraday wave technique on a bubble entrained into the body of the water through the upper liquid/air interface (and the decane monolayer) by a water droplet impacting the water body from above.

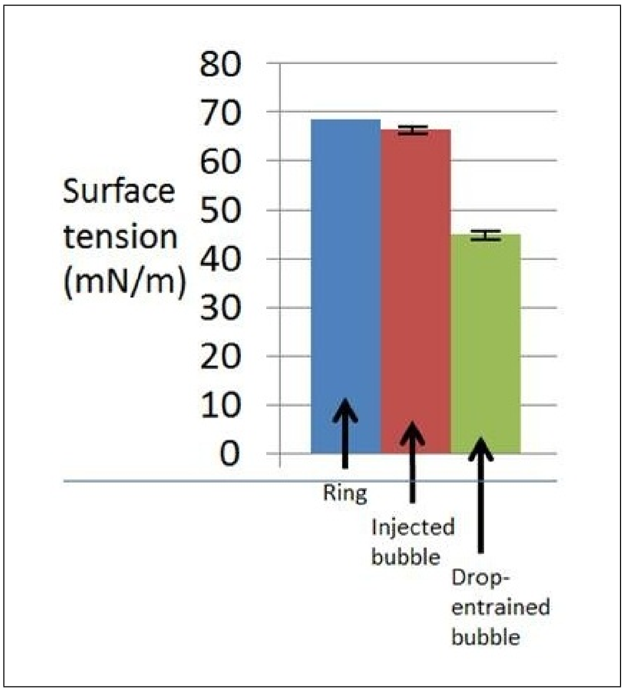

Figure 4. Comparison of the results obtained for the surface tension at the gas/liquid interface. Here the surface tension using the du Noüy tensiometer (blue column), the Faraday wave technique on a bubble injected into the body of the water (red column) and a bubble entrained through the decane layer by a water droplet (green column) are shown. These represent preliminary findings from a single experiment. The error bars reflect the estimated limits of precision of the measurement technique.

4. Results

Figure 4 shows that, under the conditions employed, the ring method is unable to detect the presence of the decane at the surface as the value of σ did not deviate from the ideal value for a pure air water interface (72.75 mN/m at 20 °C) in this case [37]. The bubble injected below into the bulk of the cell has a marginally lower surface tension, though more data is required to confirm the significance of this observation, while a bubble entrained by a drop through the decane layer has a significantly lower surface tension.

5. Conclusions

This paper records preliminary measurements that examine cases where a standard method of measuring surface tension (the du Noüy tensiometer) does not provide the complete story. To be specific, when a thin layer of decane floats upon the surface of test liquid, the surface tension measurement recorded by the du Noüy tensiometer was similar to that of clean water. However this contrasts with the much lower value of surface tension measured on the wall of a bubble that was entrained in the water by a water drop that fell through the decane layer. This indicates that

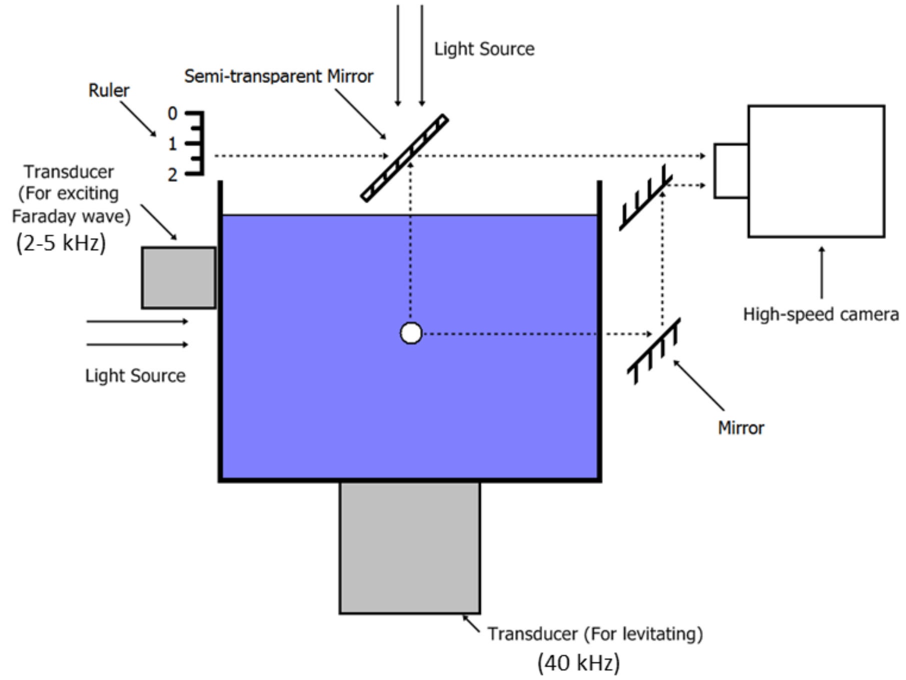

Figure 3. The apparatus used for measuring the Faraday wave threshold.

the measurement by the du Noüy tensiometer cannot safely be used to model the behaviour of the bubble that the drop entrained.

Furthermore, within a single liquid sample, which gives a single value of surface tension according to the du Noüy tensiometer, it was possible to create two bubbles (one by injection, one by liquid drop impact) that had markedly different values of surface tension. This is a cautionary tale against using the value of surface tension measured by the du Noüy tensiometer to model the behaviour of all bubbles contained within a liquid.

The fact that the value of surface tension from the du Noüy tensiometer agreed with the value obtained by the Faraday wave technique on the injected bubble, validates (as far as these preliminary tests can) the Faraday wave method, and indicates that the du Noüy tensiometer measurement is insensitive to the presence of the thin layer of decane. This is presumably because the liquid film rupture on which it makes its measurement depends on the stronger bond, which is dependent on the water rather than the decane.

The importance of these studies are as follows. If a value of surface tension is to be used in a model to predict, say, the formation of bubble clouds or the injection of aerosol droplets into the atmosphere, and used as input to predict the contribution these processes have to weather or climate, it is important that the value of the surface tension that is used is critically assessed to ensure that it is derived from a measurement process in which the same properties of surface tension are characterised, as are relevant to the physical mechanisms in play at sea. This extends to measurement of ‘surface tension’ for biomedical contrast agents, food and pharmaceutical manufacturing etc.

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