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2005 Europhys. Lett. 69 966

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## Aging of an antibubble

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received 14 October 2004; accepted in final form 17 January 2005

published online 16 February 2005

PACS. 47.55.Dz – Drops and bubbles.

PACS. 82.70.Uv – Surfactants, micellar solutions, vesicles, lamellae, amphiphilic systems (hydrophilic and hydrophobic interactions).

PACS. 83.80.Qr – Surfactant and micellar systems, associated polymers.

**Abstract.** – Antibubbles are unusual fluid objects consisting of a thin spherical air shell surrounding a liquid globule. Here we study and analyze the aging of these inverted bubbles. The lifetime is found to be distributed along an exponential law. Moreover, the breakdown of the air film is observed to be the analogue of dewetting by spinodal decomposition. We interpret the long lifetime of the antibubbles as resulting from the slow drainage of the air until the film reaches a critical thickness. Then, van der Waals forces act, leading to the collapse of the film.

*Introduction.* – A bubble is a thin film of liquid enclosing a gas pocket (see fig. 1a). The physics of bubbles is well established, and a large number of textbooks concerns this subject [1]. However, it is not so well known that the negative of this fluid object may exist: a thin air shell surrounding a liquid drop, the whole being contained in the same liquid (see fig. 1b). This unusual object was first reported by Hughes and Hughes [2], and it was thereafter coined antibubble by Connett [3]. More recently, it was found that antibubbles can be the consequence of the formation of microbubbles [4]. In that experiment, some air is injected around a drop of liquid through a hole in the bottom of a column of liquid. At a certain ratio of the air/liquid flow, antibubbles of radius  $R$  of about  $20\ \mu\text{m}$ , so-called microcapsules, are created. Antibubbles can also result from the coalescence of bubbles in particular experimental conditions [5]: a controlled air flow is injected at the bottom of a water/glycerol mixture column, which generates successive bubbles at a well-defined frequency. For this flow, consecutive bubbles coalesce and form antibubbles, of about 5 mm. Finally, we also saw similar objects (fluid shell surrounded by a more viscous liquid) when rotating a horizontal cylinder at the interface between ethanol and silicone oil. Ethanol is entrained in oil, and makes drops. As these drops come out of the oil bath, they get coated by a film of oil. In all these cases, authors report a lifetime often larger than 1 minute, and smaller than 1 h.

The long lifetime of antibubbles remains an open question. Even if similarities do exist between bubbles and antibubbles, the particular structure of the air shell does not allow to use the same arguments in both cases to explain the lifetime. In fig. 1 (bottom), the molecular structure of a soap film and of an air film is represented. The surfactant molecules are sketched by their hydrophilic head and their hydrophobic tail. Let us compare both situations. Firstly, the hydrophobic tails of surfactant molecules are in opposition for an antibubble. Secondly, the matter between the surfactant layers is air, which *a priori* suppresses the classical mechanism of stabilization of a thin soap film, which arises from the formation of two double layers of ions

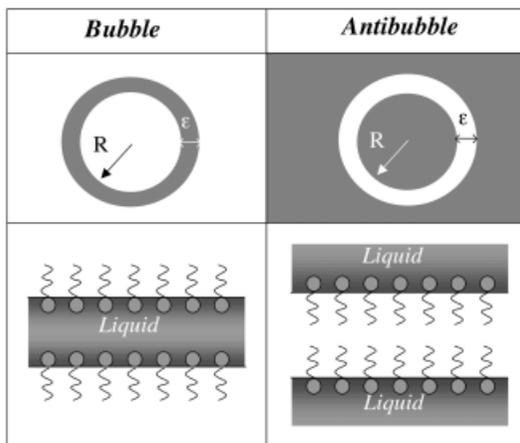


Fig. 1 – Comparison between a bubble and an antibubble of inner radius  $R$  and thickness  $\varepsilon$ . The molecular structures of soap and air films are displayed.

in the film. Consequently, two questions can be raised from the observation of antibubbles: i) how can we explain the order of magnitude of the antibubbles lifetime; ii) does a stabilizing process exist for the air films?

*Antibubble production.* – A plexiglass vessel is completely filled with a liquid mixture of water and  $C_{12}E_6$  hexa-ethyleneglycol mono n-dodecyl ether ( $10^{-3}$  M). This surfactant is stable and non-ionic, which considerably limits the presence of charges in the liquid. The CMC (critical micellar concentration) is estimated to be  $10^{-4}$  M; the considered concentration is thus far above the CMC. The rest of the mixture is placed in a tank equipped with a tap. A pipe drives the mixture 5 mm above the surface of the liquid contained in the vessel. By adjusting the speed and the flow of the incoming liquid, antibubbles are generated [6], with a radius between 5 and 15 mm. The air volume fraction can be estimated by measuring the ascent speed. The density of the antibubble is very close to that of the water. The stationary velocity (typically 1 cm/s) results from a balance between buoyancy and friction. Since the Reynolds number  $Re \approx 100$ , the Levich formula must be taken for the friction so that the force balance can be written [7]:

$$4\pi R^2 \varepsilon \rho g = 12\pi \eta_w R V, \quad (1)$$

where  $\rho$  and  $\eta_w$  are the water density and viscosity,  $V$  the ascent velocity and  $\varepsilon$  the film thickness. This yields an expression for the initial thickness, which was thus evaluated in our experiments to be about  $1 \mu\text{m}$ .

*Experiments.* – The study of the antibubbles lifetime is delicate because of the fragility of these objects. In order to avoid any external perturbations due to surface waves, flow or borders, the inner liquid was overweighted with a small amount of salt. These particular antibubbles sink. They are slowed down by a glycerol (density = 1.26) concentration gradient created at the bottom of the vessel. Hence, the antibubble stops in the container at the depth which matches its density, and the lifetime can be properly studied. Figure 2 presents in a semi-log plot the distribution of lifetimes for about 60 antibubbles. The solid line represents a fit by a decreasing exponential  $\exp[-t/\tau]$ , where  $t$  is the time and  $\tau$  the characteristic lifetime of the globule. The latter parameter was found to be around 240 s. The insert in fig. 2 shows the lifetime as a function of the size  $R$ , showing no significant correlation between both quantities.

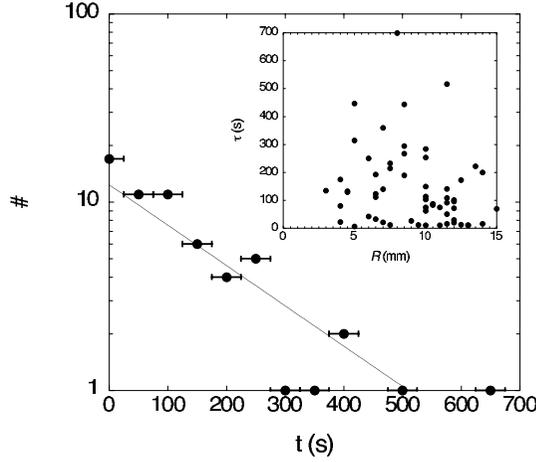


Fig. 2 – Distribution of antibubble lifetime displayed in a semi-log diagram. The solid line corresponds to a fit by an exponential law. The insert represents the size distribution of the characteristic lifetime.

*Film drainage.* – A first simple model can be proposed for explaining the long duration of the air film. This model is based on the gravity-driven drainage of air, from the bottom to the top of the antibubble, between which there is a hydrostatic pressure difference of  $2\rho gR$ . Air is driven from the bottom zone towards the antibubble top by this pressure difference. The characteristic time of drainage can be estimated as follows. We consider that air flows in a slot of thickness  $\varepsilon$  ( $\approx 10^{-6}$  m) and length  $\ell$  which scales as  $R$ . Let  $x$  be the axis along the length of the slot and  $z$  across the gap. The Navier-Stokes equation [8] applied to this slot reduces to

$$-\frac{\partial p}{\partial x} + \eta \frac{\partial^2 v}{\partial z^2} = 0, \quad (2)$$

where  $\eta$  is the air viscosity and  $v(z)$  the speed of air. Taking as boundary conditions  $v(0) = 0$  and  $v(\varepsilon) = 0$ , the mean speed is found after integration to be equal to  $\rho g \varepsilon^2 / (6\eta)$ . This yields a classical Reynolds thinning for the film:  $1/\varepsilon^2 = (\rho g t) / (3\eta R)$ , from which we can deduce a lifetime  $\tau$ : the film thins till it reaches a thickness  $\varepsilon_{\min}$  for which it bursts. In the absence of any stabilizing mechanism, this thickness should be given by the range of van der Waals forces (*i.e.* about 100 nm), which tends to rapidly squeeze the film. We thus get as a lifetime an expression which scales as  $3 R \eta / (\rho g \varepsilon_{\min}^2)$ . For  $R = 1$  cm,  $\eta = 10^{-5}$  Pa s,  $\rho = 10^3$  kg/m<sup>3</sup> and  $\varepsilon_{\min} = 100$  nm, we find a lifetime of about 1 h, in qualitative agreement with the largest reported values.

*Heterogeneous drainage.* – However, in many cases it is observed that the drainage time is significantly smaller than that. In addition, we did not report any correlation between the lifetime and the antibubble radius (fig. 2). This might result from a heterogeneous drainage of the air film, which was assumed above to flow with a constant thickness  $\varepsilon$ . Figure 3(a) shows the interference fringes that can be seen on the bottom of an antibubble illuminated by a low-pressure sodium lamp of wavelength 588 nm. It is first observed that close to the pole there is no fringe, indicating a thickness smaller than a quarter of light wavelength, *i.e.* 147 nm, in agreement with the argument about the possibility of reaching a van der Waals thickness for the film of air. In addition, the pattern shows that the thickness of the film is not constant along a latitude. Indeed, channels exist! They can be evidenced when the antibubble blows up (see fig. 3(b)). The air film collapse produces microbubbles which are aligned towards the

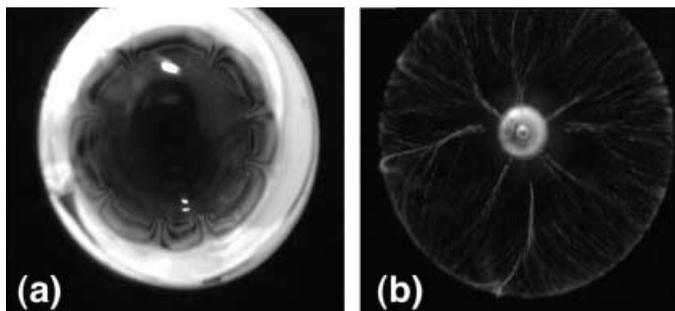


Fig. 3 – (a) Interference fringes at the bottom of the antibubble when lighted by low-pressure sodium lamp. A black zone (of thickness smaller than 150 nm) is observed at the center, and inhomogeneous patterns form radially. (b) Microbubbles generated after the explosion of the antibubble. These bubbles are aligned towards concentration of interference fringes, confirming the existence of radial air channels in the film.

high-concentration interference fringes where the film is known to be thicker.

The channels might originate from the van der Waals thinning. Once both surfaces start interacting, the interfaces fluctuate, which surface tension opposes. Balancing the van der Waals pressure ( $A/6\pi\epsilon^3$ , denoting  $A$  as the Hamaker constant) with the Laplace pressure (of the order of  $\gamma\epsilon/\lambda^2$ , with  $\lambda$  the typical wavelength of the interface fluctuation) yields a minimal wavelength scaling as  $\epsilon^2/a$ , where  $a = \sqrt{A/6\pi\gamma}$  is a microscopic length. This length (which classically appears in such a balance between van der Waals forces and capillarity [8]) is typ-

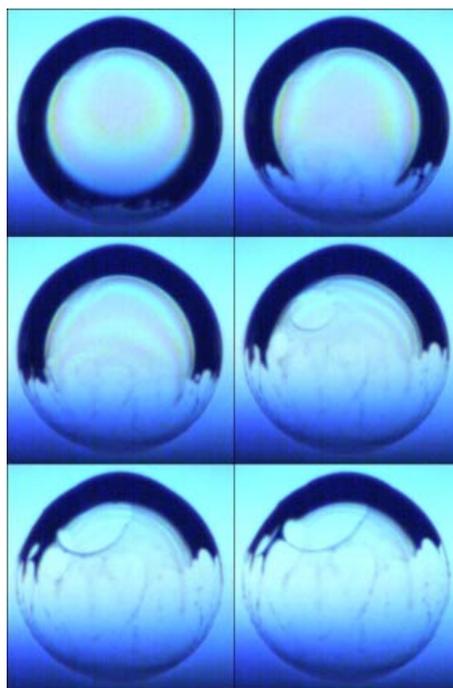


Fig. 4 – Spontaneous popping of an antibubble (from left to right and top to bottom). The images are separated by 1/800 s. The presence of multiple holes in the film can be observed as it starts collapsing.

ically of the order of 1 mm, for  $\varepsilon = 100$  nm. It defines the typical distance between thick and thin region in the region (close to the antibubble bottom) where van der Waals forces start to act. Once thicker regions form, they tend to rise, because of buoyancy, which eventually leads to radial channels along the antibubble. These channels act as Plateau borders in a foam: they efficiently drive air, which leads to a drainage time smaller than expected from a homogeneous scenario, since the film has only to thin at a smaller scale (the distance between two channels). This might also help understanding why the lifetime (in fig. 2) is not correlated to the antibubble size.

*Film collapse.* – Unlike soap films, air films should thus be intrinsically unstable. This can be confirmed by studying their collapse. This situation is very similar to the bursting of a liquid sheet and it is known that a spinodal collapse is expected if only attraction forces exist, since the evolution of the film then only depends on its thickness [8]. The air film breakdown was recorded using a high-speed camera. One of the results is represented in fig. 4 (from left to right, and from top to bottom), where the pictures are separated by 1/800 s. The film bursts at several positions at the same time. This situation is the opposite of a nucleation process for which a strong fluctuation at one point induces the retraction of the whole film. These movies suggest that the collapse dynamics is similar to a spinodal dewetting mechanism, as observed, for example, in nanometric PDMS films [9], and results from the amplification of thermal fluctuations of the surface, because of van der Waals forces, as assumed in the calculation of the lifetime.

*Conclusions.* – The antibubble lifetime can be understood as resulting from the gravitational thinning of the air film, till it reaches the critical thickness at which it bursts because of van der Waals forces. As a consequence of this drainage, a bump of air is observed to form at the top of the antibubble, which generally explodes at the bottom, where the film is the thinner. The figure of “dewetting” is characteristic of a spinodal “dewetting”, which arises from a pure van der Waals attractive force between the surfactant layers. The process of the antibubble aging has been identified to be the drainage of air. However, more advanced models should be proposed to take into account the existence of channels close to the end of antibubble life.

\* \* \*

SD would like to thank FNRS for financial support. This work has been also supported by the contract ARC 02/07-293. P.-G. DE GENNES and F. BROCHARD-WYART are gratefully thanked for their fruitful comments and encouragements. Special thanks are also due to H. CAPS (ULg) and J. MAGNAUDET (IMFT, Toulouse, France) for very valuable discussions.

## REFERENCES

- [1] WEAIRE D. and HUTZLER S., *The Physics of Foams* (Clarendon Press, Oxford) 1999.
- [2] HUGHES W. and HUGHES A. R., *Nature (London)*, **129** (1932) 59.
- [3] STONG C. L., *Sci. Am.*, **230**, April issue (1974) 116.
- [4] GANAN-CALVO A. M. and GORDILLO J. M., *Phys. Rev. Lett.*, **87** (2001) 274501.
- [5] TUFAYLE A. and SARTORELLI J. C., *Phys. Rev. E*, **66** (2002) 056204.
- [6] DORBOLO S., CAPS H. and VANDEWALLE N., *New J. Phys.*, **5** (2003) 161.
- [7] LEVICH V. G., *Physicochemical Hydrodynamics* (Prentice Hall) 1962.
- [8] DE GENNES P. G., BROCHARD-WYART F. and QUÉRÉ D., *Gouttes, bulles, perles et ondes* (Belin, Paris) 2002.
- [9] REITER G., *Science*, **282** (1998) 888.