Tellus (1990), *42B*, 200–205

Surface-active monolayers, bubbles, and jet drops

By DUNCAN C. BLANCHARD, *Atmospheric Sciences Research Center, State University of New York at Albany, Albany, NY 12222, USA*

(Manuscript received 28 November 1988; in final form 22 March 1989)

ABSTRACT

High-speed motion picture films (about 3000 frames per second) of bubbles of 0.7 and 1.3 mm diameter bursting at a seawater surface covered with an oleic acid monolayer show that the formation and behavior of the jet drops are profoundly influenced by the monolayer. It is doubtful, however, that monolayers on the surface of natural bodies of water exert as high a surface pressure as does an oleic acid monolayer. Natural monolayers probably affect film drop production more than that of the small jet drops that are important in atmospheric processes.

1. Introduction

Some 35 years ago, in this journal, we published (Kientzler et al., 1954) a series of photographs of bursting bubbles taken both with a high-speed motion picture camera (about 3000 frames per second) and with a 35-mm camera equipped with a short duration flash ($\sim 30\ \mu s$). These photographs confirmed Stuhlman's (1932) contention that the bursting of an air bubble at a water surface produced a jet of water that rose rapidly from the bottom of the collapsing bubble cavity to become unstable and break up into a number of drops. Since our purpose in this early paper was to show evidence of the formation of the jet and the production of jet drops, which we believed contributed significantly to the marine sea-salt aerosol (Woodcock et al., 1953), we did not publish photographs that showed the effect of surface-active monolayers on the water in bringing about profound changes in the production of jet drops. It is the purpose here to present these photographs and discuss briefly some work on bubble bursting that has evolved over the years.

2. The photographs

Details of the photography with the high-speed motion picture camera are discussed in Kientzler et al. (1954) and need not be repeated here. Fig. 1, 12 consecutive frames from the camera running at 3300 frames/s, shows the collapse of a 0.7 mm diameter air bubble at a seawater surface covered with an oleic acid surface-active film. The first of about 7 jet drops can be seen rising rapidly from the collapsing bubble cavity (frame 4) about 0.6 ms after bubble bursting (frame 2). More interesting, however, is what happens to the last 4 jet drops. In frame 9, about 2 ms after bubble bursting, these 4 drops are seen rising close together above the meniscus that obscures the view just above the surface of the water. The bottom drop is rising faster than the others, and 0.9 ms later (last frame) has collided with and coalesced with the two drops above it. Though not shown in Fig. 1, within another ms this drop caught up with and coalesced with the remaining drop to produce a single large drop from what originally had been four.

Some of the old high-speed movie films were recently examined, and it was found that 5 out of 8 cases of the 0.7 mm bubble bursting beneath an oleic acid surface monolayer showed that 2 to 4 of the lowest jet drops collided and coalesced into a single drop. This curious coalescence occurred in none of the 5 cases when the oleic acid monolayer was absent.

Figs. 2 and 3 show examples of the effect of an oleic acid surface film on the formation of jet drops from bubbles of 1.3 mm diameter bursting

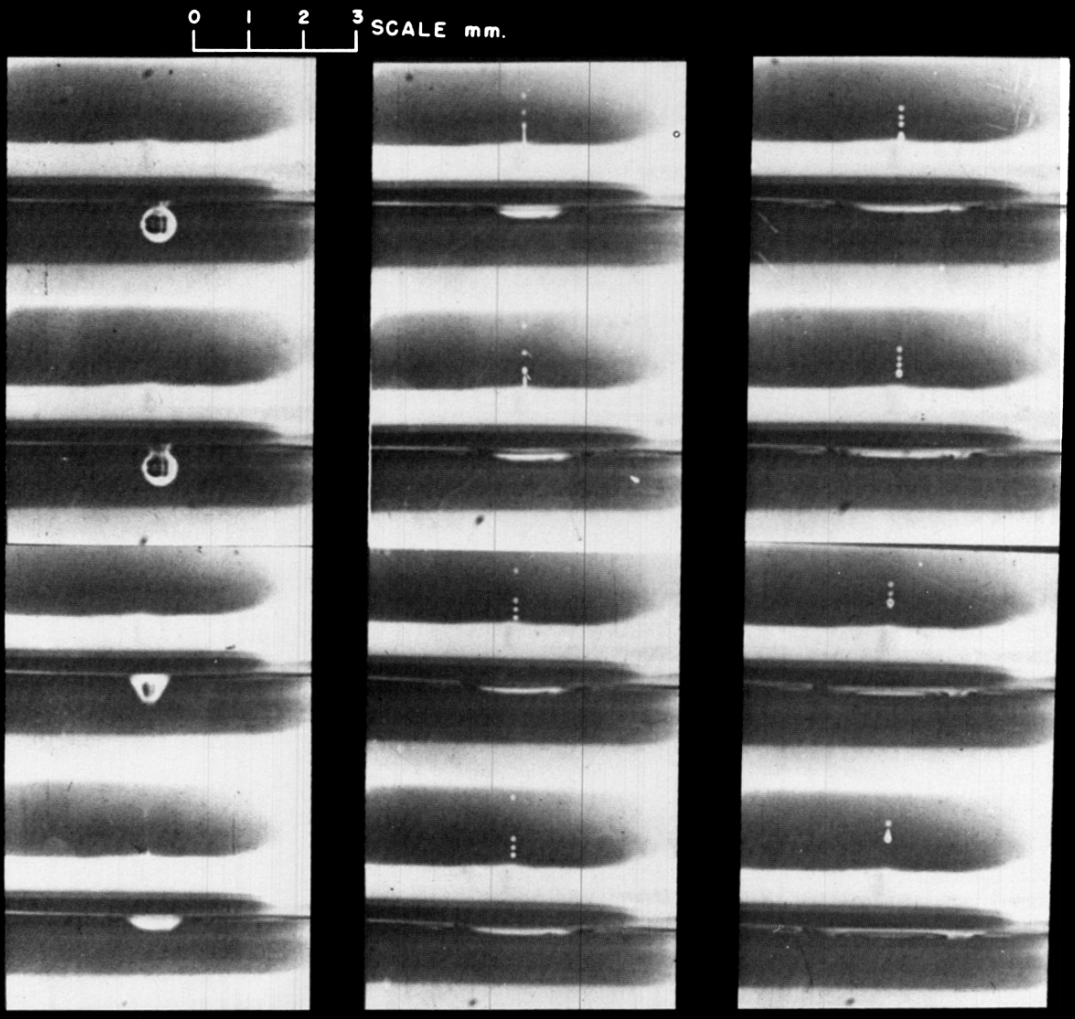

Fig. 1. High-speed motion pictures (3300 frames per second) of the formation of jet drops from a 0.7-mm diameter air bubble bursting in seawater whose surface is covered with an oleic acid monolayer. The dark line running horizontally through each frame is caused by a meniscus between the surface and the glass wall of the container. Note coalescence of jet drops in the last 4 frames.

in seawater. Here the camera is looking down on the surface of the water at an angle of about 10° above the horizontal. In the first frame of each sequence, the bubbles are just beneath the surface, and because of light refraction appear elliptically-shaped and shortened in the vertical direction. Normally, at a clean surface the reproducibility in the formation of jet drops is quite remarkable, but as shown here this is not necessarily the case with an oleic acid surface film. In Fig. 2, the jet rises as a long, narrow cylinder of water that appears to become unstable and break up into a number of jet drops after the cylinder breaks away from the bubble cavity. In Fig. 3, the behavior is quite different; the jet is short and relatively thick and produces only one jet drop. In both cases the time from bubble bursting to the end of the sequence is <4 ms.

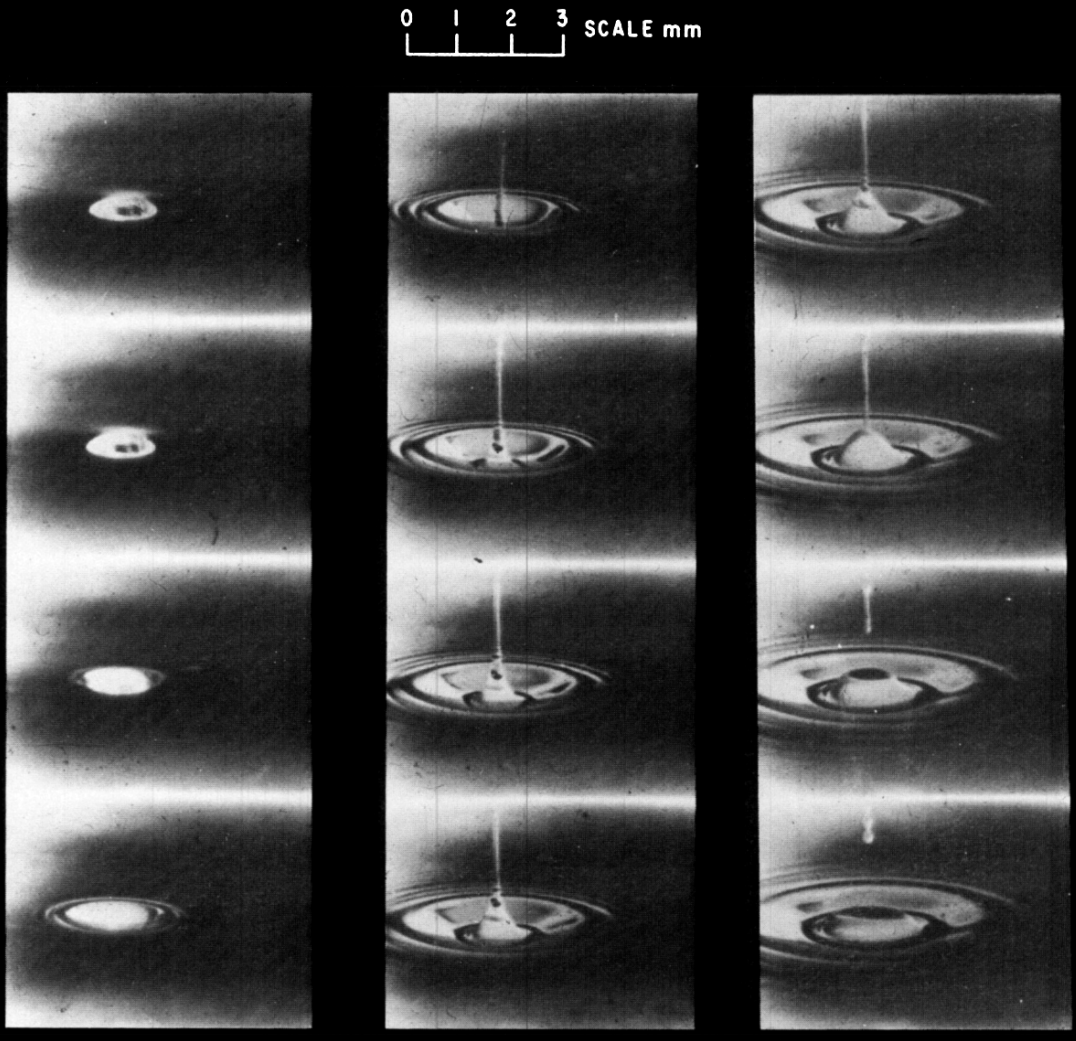

Fig. 2. High-speed motion pictures of a 1.3-mm diameter air bubble bursting in seawater covered with an oleic acid monolayer. Angle of view is 10° above the horizontal. Camera speed was 2600 frames per second.

3. Discussion

Our findings of the effects of surface-active films or monolayers on jet drop formation were the result of serendipity. We had no intention to study the effect of monolayers on jet drops. Rather, our use of the monolayers was primarily an attempt to get the bubbles to burst during the brief 1 or 2 s that the high-speed camera was running. Bubbles of the size we wanted to photograph typically persist at a clean seawater surface for several seconds before bursting, but we knew from experience that an oleic acid monolayer reduced the surface life to a small fraction of a second. Thus, with several bubbles per second bursting at a fixed spot on an oleic acid-covered surface, we knew that we could obtain a number of sequences of bubble bursting with the high speed camera.

It should be pointed out in passing that the 4-photograph sequence that has often been used to illustrate the formation of jet drops (e.g.,

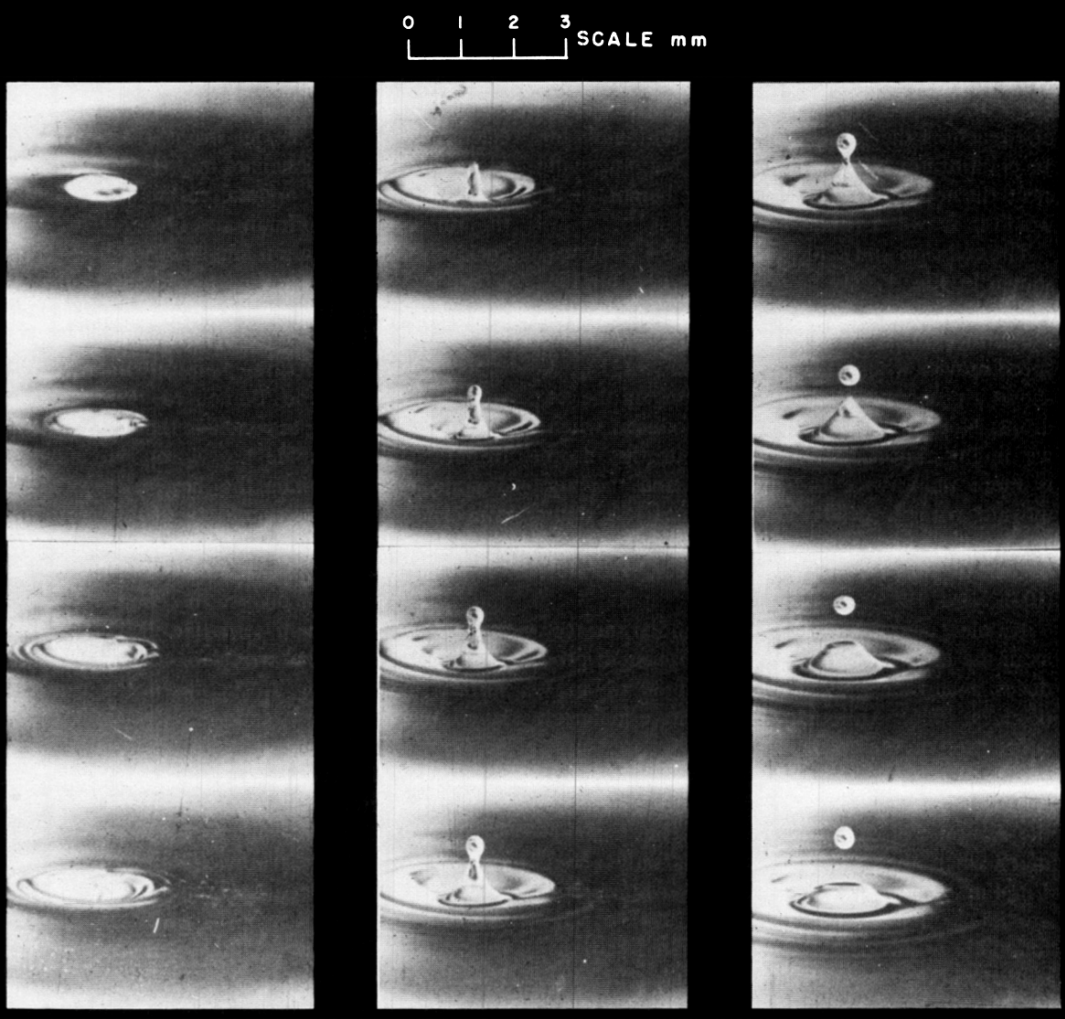

Fig. 3. Same as Fig. 2 except that the camera speed was 3000 frames per second.

Woodcock et al., 1953; Blanchard, 1963, 1975) from the collapse of air bubbles at the surface of the sea is actually that of a bubble bursting in freshwater. Here, unlike the seawater case, the bubbles have a short surface life that makes for relatively easy high-speed photography. There is no reason to believe, however, that the dynamics of bubble collapse are different for the two types of water. For a given temperature, the surface tension and viscosity are essentially the same, and observations show that the height of ejection of the top jet drop is the same for a given bubble size in both types of water for all bubbles <1-mm diameter. For larger bubbles bursting in distilled water, and sometimes in freshwater, the top drop ejection height is less than that for the same bubble bursting in seawater. This, however, is because in distilled water the larger bubbles usually burst before they reach an equilibrium position. Upon arriving at the surface, their momentum carries them about half a bubble diameter above the surface where they burst. Had they not burst, surface tension forces would pull them back down to an equilibrium position. When bursting occurs in the non-equilibrium position, there is relatively less of a bubble cavity,

and thus less surface free energy is available for jet drop ejection (Blanchard, 1963), and the jet drops are consequently ejected to a lower height. But if the bubble persists for at least 10 ms after first reaching the surface, it will be motionless in an equilibrium position, and upon bursting will eject the top jet drop to the same height as it would in seawater (Blanchard, 1983).

The collision and coalescence of the 4 jet drops shown in Fig. 1 may be common when surface tension-reducing films such as oleic acid are on the surface, but it was never observed in the high-speed movies where the films were absent. Fig. 3 shows a pronounced effect of the films on the jet drops. Not only is a single drop produced when we might expect at least four, but this drop is more than twice the diameter and moving upward with a speed some 30 times less than we would expect for the first jet drop from a bubble of that size bursting in clean seawater (Blanchard, 1963).

An oleic acid monolayer on a confined surface, as in the photography here being discussed, produces a surface pressure of about 30 mN m^{-1} (Gaines, 1966). Although surface-active material is common on the open sea, the surface pressures are usually no more than about 1 mN m^{-1}. This is deduced from Garrett's (1967a) finding that the damping of capillary waves reaches a maximum when the surface pressure is only about 1 mN m^{-1}. The only place that higher film pressures, 5–20 mN m^{-1} (Barger et al., 1974), can be found are in the visible slicks associated with the convergence zones of the Langmuir circulations (Langmuir, 1938; Faller and Caponi, 1978). Since these slicks cover ony a small % of the surface area of the sea, it is unlikely that they have any significant effect on the total jet drop production. The effects shown in Figs. 1–3, therefore, should serve as an example of what can happen and not necessarily what does happen.

Although organic monolayers may not significantly affect the total jet drop production, they may influence the production of film drops. This has been observed in laboratory experiments by both Blanchard (1963) and Garrett (1968), and Paterson and Spillane (1969) found that film pressures of only a few dynes per centimeter were enough to significantly decrease film drop production.

Even if compressed organic monolayers are not present on the surface of the water, the adsorption of dissolved surface-active material onto the bubbles as they rise through the water can affect the bubbles' rise speed, the size and ejection height of the jet drops (Detwiler and Blanchard, 1978; Blanchard and Hoffman, 1978), and the amount of organic carbon carried into the atmosphere (Hoffman and Duce, 1976). It is curious that the ejection height of jet drops from larger bubbles (900 μm) is much more affected (Blanchard and Hoffman, 1978) than that from the smaller bubbles (570 μm). Since bubbles <500 μm diameter are plentiful in breaking waves (Cipriano and Blanchard, 1981; Baldy, 1988), it is tempting to conclude that the jet drops from the smaller bubbles carry proportionally less organic material than the larger drops. This conclusion, however, should await the verdict of experiment.

Finally, we wish to comment on the role of surface-active monolayers in controlling the bubble surface life in seawater, BSL, the time interval between the arrival of a bubble at the surface and bursting. In the absence of a monolayer in laboratory experiments with single bubbles, the BSL reaches a maximum of a few tens of seconds for bubbles of about 2-mm diameter, but for both larger bubbles (>5 mm) and smaller ones (<0.5 mm) it is <1 s (Gluhosky, 1983; Struthwolf and Blanchard, 1984). The windspeed and relative humidity of the air over the surface of the water also appears to influence BSL (Burger and Blanchard, 1983). However, for bubbles bursting at the natural monolayer-covered surface found in slicks at sea, Garrett (1976b) has convincingly shown that the BSL decreases with increasing monolayer pressure. In other words, the more compressed the monolayer in the slicks, the better it acts as a foam breaker. He attributes this to the more soluble of the chemical species in the monolayer being displaced by the more insoluble species as the film is compressed, leaving a relatively rigid monolayer whose properties do not promote bubble stability.

4. Acknowledgements

I am grateful to my colleagues of so many years ago, C. F. Kientzler, A. B. Arons, and A. H. Woodcock, whose curiosity about seeing the

unseen made it possible for us, after many months of working with the high speed camera, to finally photograph the manner in which jet drops are produced from bursting bubbles. The present work was supported by the National Science Foundation under grant ATM-8514211.

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