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Part II: Bubble Entrainment by Drop-Formed Vortex Rings

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A bubble bursting on the surface of superheated water causes nucleation of clusters of bubbles a few mm beneath the surface after a few milleseconds, Bergman and Mesler (1981). The cause of the nucleation is not clear but one plausible mechanism is the entrainment of tiny vapor bubbles into the liquid. When a bubble bursts through the interface the liquid film ruptures. Liquid accumulates along the torn edge of the film as the edge rapidly recedes. Drops are formed along the edge of the film and are pulled into the miniscus at appreciable velocities. Do these drops entrain tiny vapor bubbles which become the nuclei for later growth of clusters of bubbles a few mm beneath the surface? This investigation was begun to attempt an answer to this question.

Before addressing the question of entrainment it is first necessary to understand that the impact of a drop onto a surface of the same liquid is a much more complicated phenomenon than might be supposed. A number of studies are found in the literature. These studies fall into two general categories based upon drop velocity. One group of investigators studied the impact of low velocity drops and the other high velocity drops. The drop and surface interactions in each case differ considerably. Curiously, a unified study consisting of both high velocity and low velocity drops was not found.

Two classic studies of low velocity drops falling into a liquid pool are Rogers (1858) and Thomson and Newall (1885). Both studies report that a vortex ring forms when a low velocity drop strikes the liquid surface. Coloring the drop permits the flow of its contents to be seen. This makes the vortex ring visible. The rotation of the vortex ring on its circular axis is directed upwards on the outer periphery, and downwards on the inner. Rogers describes the vortex ring as a coil of colored fluid enfolding a parallel uncolored coil. Bands are visible due to the two fold structure of the vortex ring. The vortex ring formed by a falling low velocity drop appears quite similar to the vortex ring formed by a burst of gas or liquid issuing from an orifice, with a smoke ring being a familiar example. Chapman and Critchlow (1967) photographed the falling drops and report that a spherical drop changing to a prolate spheroid just as it arrives at the surface produces vortex rings with greater penetrating power.

The classic study of high velocity drops was that of Worthington (1908). Using spark photography, Worthington examined drops falling from 40 to 137 cm. Water was the principal fluid investigated but milk was sometimes substituted to illuminate certain aspects of the drop and surface interactions with little change in the properties of the fluids.

Worthington's photographs indicate that the high velocity water drop flattens as it strikes the pool surface. A crater is formed, with the liquid from the drop lining the inside surface of the crater. Jayaratine and Mason (1964) suggest that a thin film of air separates the liquid of the drop from the pool liquid. A film of liquid rises from the periphery of the crater. Milliseconds later, the walls of the crater begin to converge upon the center. Simultaneously, most of the lining of the cavity flows to the bottom of the crater and forms the top of an ascending jet. The jet often pinches off due to surface tension and forms drops. The jet and drops reach a maximum height and then fall back to the pool surface. A series of ripples radiate outward from the point of impact. When a pinched off drop falls back it will often form a vortex ring as was reported by Thomson and Newall. Mitzutani (1977) has published results of a cine-photographic study made at 72 frames/s which shows this for a 3-mm diameter water drop falling 99 cm.

Blanchard and Woodcock (1957) studied entrainment of bubbles by raindrops falling at terminal velocity onto water and report that entrainment depends upon raindrop size. They report small drops about 0.4 mm in diameter produce 2 or 3 bubbles of about 50 μm diameter that are carried only 1-3 mm beneath the surface. The number increases rapidly with drop size as a 2.2 mm diameter drop was observed to produce 50-100 bubbles that were often carried down in a vortex ring to depths of 2-4 cm. The vast majority of these bubbles appeared to be under 50 μm in diameter. On occasions it appeared to them that the vortex ring of bubbles formed not at the moment of impact of the drop with the water but at the collapse of the water column that rises from the bottom of the impact cavity. This, Blanchard and Woodcock observe, is consistent with the photographic study of Worthington and Cole (1897) which shows the water column which was said to form the vortex ring upon collapse. Blanchard and Woodcock remark that Worthington and Cole make no mention of bubbles in the vortex ring but that the bubbles probably passed undetected as only the closest scrutiny will discover them.

There are two subtle puzzling elements in Blanchard and Woodcock's results. One is they attribute the formation of the vortex ring to the collapse of the water column without considering that it could be the return of a pinched off drop that causes the vortex ring. Perhaps this is implied. The other element is the report that only on occasions did it appear that the vortex ring of bubbles was not formed at the moment of impact. Perhaps the "on occasions" simply indicates that they could not be certain of it all the time. A drop of this size impacting at terminal velocity should always form a crater on impact followed by the rising water column. High speed photography which could resolve both these points was not used by Blanchard and Woodcock.

Two other brief references were found which mention bubble entrainment by drops. Rogers (1858) remarks on the tendency for drops to entrain such large bubbles that they spoil the appearance of the vortex ring. Macklin (1976) mentions an un-

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published observation of Hobbs and Osheroff that air bubbles form during splashing of high velocity drops.

Entrainment in a vortex ring is not limited to entrainment of bubbles in drop-formed vortex rings. Rogers shows that a smoke filled bubble forms a smoke ring upon bursting. Day (1964) studied bubbles bursting from a water surface into a cloud chamber. He reports that tiny drops from the bubble wall are entrained in the vortex ring formed by the bursting bubble.

MacIntyre studied the bursting of both large and small bubbles at an interface. A difference arises because they sit quite differently on the surface. As Princen (1963) has shown a 1-cm diameter bubble sits on top of the water while a 2-mm diameter bubble is virtually submerged.

MacIntyre (1972) observed that, under some conditions, the rupture of a large bubble will generate numerous small bubbles with diameters less than 100 μm at the meniscus apparently when droplets or irregularities in the film splash into the meniscus. The bubbles are carried 1-2 cm beneath the surface and MacIntyre claimed they were swept down by a downward jet which must exist to balance the momentum of the upward jet. These results correspond to a bubble bursting on the surface of a superheated liquid except that without the superheat the small bubbles do not act as nuclei for the rapid growth of a vapor bubble.

There are similarities between the rupture of a small bubble at an interface and the collapse of the cavity initially formed with the impact of a high velocity drop on a liquid surface. Both Newitt et al. (1954) and Kientzler et al. (1954) have shown that after bubble rupture a jet rises up from the center of the cavity to form a drop as happens in the collapse of the impact cavity. MacIntyre (1968) devised a simple experiment to study the rupture of a small 2-3 mm diameter bursting bubble. A small bubble was blown with diluted India ink. It was carefully placed on the surface of a clear pool of water. A half second after being punctured a picture was taken which showed a vortex ring had been ejected downward containing a portion of the India ink. MacIntyre explained the vortex ring as being formed by a downward jet which must balance the momentum of the upward jet. MacIntyre did not consider that the vortex ring might simply be formed by a drop at the top of the upward jet falling back onto the surface. A drop formed from the tip of the jet would contain ink and would likely form a vortex ring.

EXPERIMENTAL PROGRAM

Two experiments were made. The first was to investigate the bubble entrainment capabilities of drops, and drop-formed vortex rings in particular, and the second was to test whether drops formed in the film of a burst bubble would cause vortex rings when they strike the meniscus.

Waterdrops 1.5 to 2 mm in diameter were formed on the needle of a microsyringe and allowed to fall variable distances into demineralized water. In some experiments the impact was photographed with a Fastax WF 17 high speed camera. In other experiments a beam of light from a high intensity microscope lamp illuminated the impact to aid in examining for entrained bubbles. The drop was usually colored with ordinary food dye to make the vortex ring visible.

Initially fall heights of 130 cm were investigated in the belief that higher fall heights would cause more entrainment. High speed motion pictures of the drop impact were taken and these supported Worthington's description of the high velocity impact of a water drop falling into a pool of water. Numerous bubbles were observed entrained in the liquid. The bubble entrainment did not occur with the initial impact of the drop just as Blanchard and Woodcock reported. Instead, entrainment occurred following the collapse of the jet with the impact of the drop which had pinched off from the jet.

It was suspected that it was simply a drop with less velocity formed as a result of the surface contortions that was responsible for most of the entrainment. A test of this hypothesis was in order. Would drops with an initial low velocity exhibit entrainment without the jet? Experiments were made with fall heights of 10 cm or less where vortex rings form nearly every time and not after first forming a jet. Careful examination of the vortex rings in the intense beam of light from the microscope lamp revealed that many tiny bubbles were captured in the eye of the vortex ring. The photographs in Figure 1 show a variety of typical vortex rings

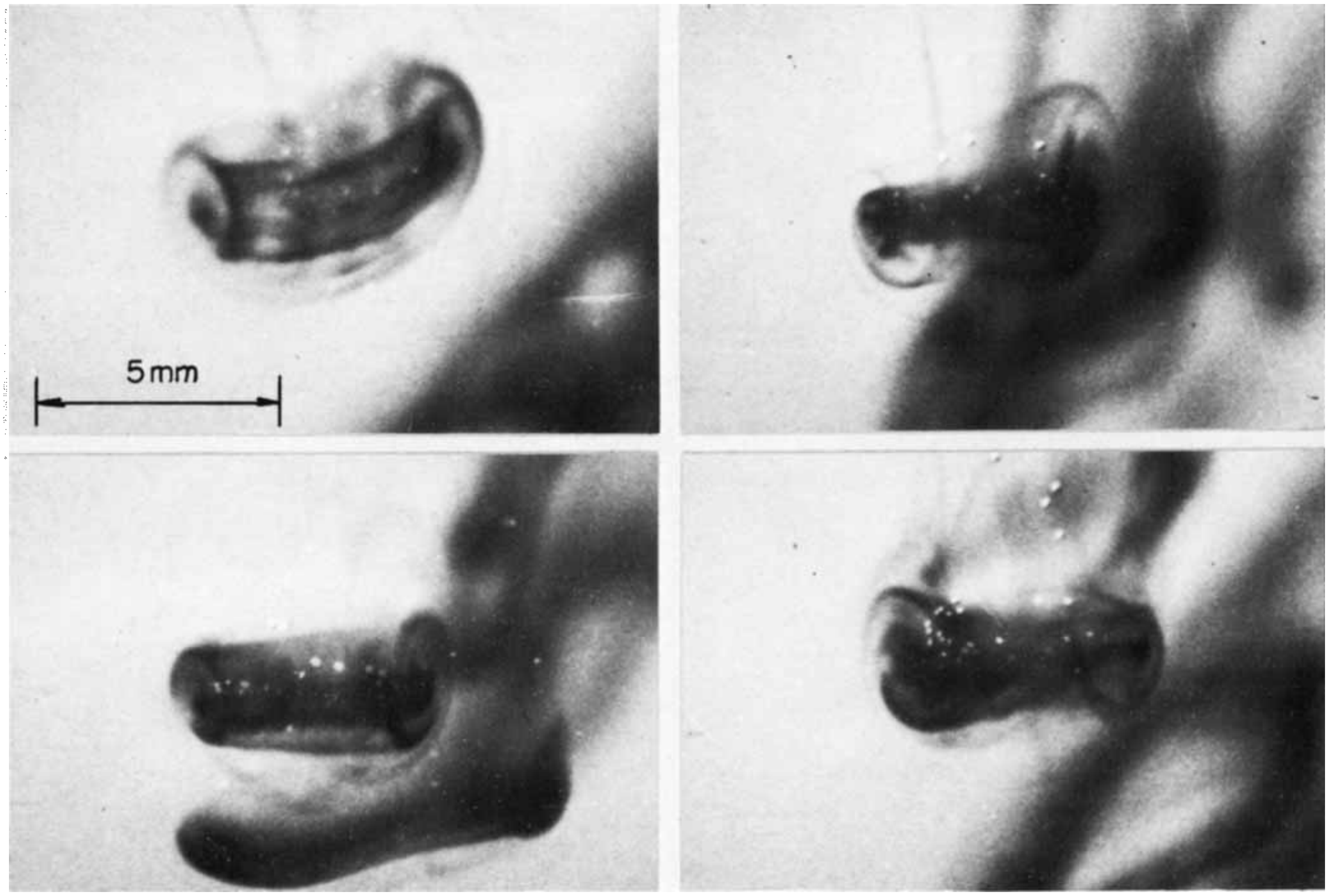

Figure 1. Examples of a drop formed vortex ring entraining air bubbles.

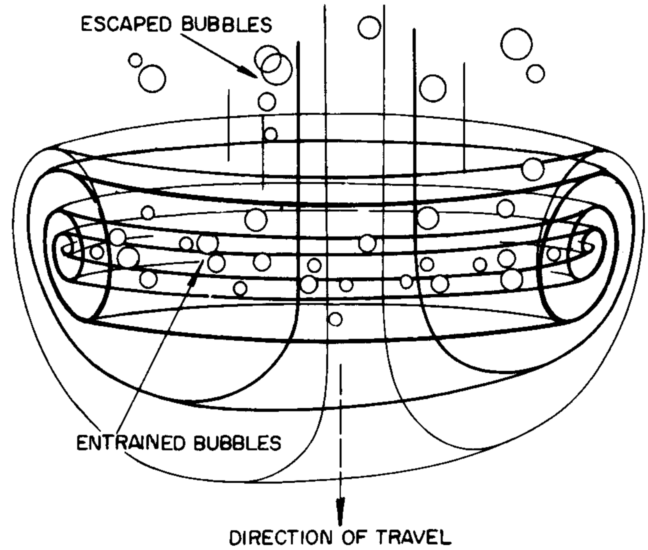

Figure 2. Sketch of a drop-formed vortex ring showing entrained and escaped bubbles.

as they travel downward. The layered structure of the ring is apparent. Tiny bubbles are seen within the ring mostly near the circular axis of the ring. A few tiny bubbles that have already escaped are seen above the ring. Figure 2 is a composite sketch showing the important characteristics. The bubbles are estimated to be a few hundred μm in diameter but may be even smaller. Most are so small that they are only seen under the special lighting employed.

The vortex rings propel themselves downward enlarging the ring and slowing their vortex motion. Often bubbles in the vortex ring can be seen rapidly spinning around with the vortex motion. As the vortex motion slows smaller bubbles escape and begin to rise.

Once the bubble entrainment capabilities of drop-formed vortex rings are recognized a question that arises is do impacting drops form the receding liquid film of a bubble bursting through an interface cause vortex rings? To seek an answer to this question MacIntyre's experiment was repeated but with larger bubbles. Food coloring was used instead of India ink, and some sodium lauryl sulfate was added as a surfactant to increase the stability of the large bubbles. Large colored bubbles were blown and carefully placed on a clear water surface. The bubbles were burst by piercing them with a needle as quickly as possible so the coloring had little time to drain from the bubble. The results were photographed from above approximately one second after the bubble burst. One such photograph is shown in Figure 3. Dye markings and bubbles upon or near the surface make a circle in the photograph. The circle marks the former meniscus which had a 2-cm diameter. Amongst the dye markings are small circles which indicate small vortex rings. Thin streamers of dye connect some of the bubbles and the vortex rings. These streamers provide a definite association between the bubbles and the vortex rings. It appears that the film drops plunged into the meniscus and formed vortex rings which entrained the bubbles. The bubbles are considerably larger than those entrained by the low velocity drops studied possibly due to the action of the surfactant. Such large bubbles would not remain long in a vortex ring. The lighting here was not the beam of light necessary to detect the tiny bubbles seen in Figure 1 so tiny bubbles may also be present.

CONCLUSIONS

Drops impacting a liquid surface do cause entrainment of tiny bubbles. Thus, such entrainment is a possible cause of subsequent nucleation when a bubble bursts on the surface of superheated water.

Entrainment of tiny bubbles is often associated with vortex rings. Vortex rings formed simply by the impact of a low velocity water drop upon a water surface have been shown capable of entraining tiny bubbles beneath the surface. The vortex rings retain bubbles on their axes where they remain separated from the ambient liquid for appreciable periods. Drops impacting at higher velocities also form vortex rings after first interacting with the surface. The vortex rings are self propelling and can quickly carry entrained bubbles to significant depths.

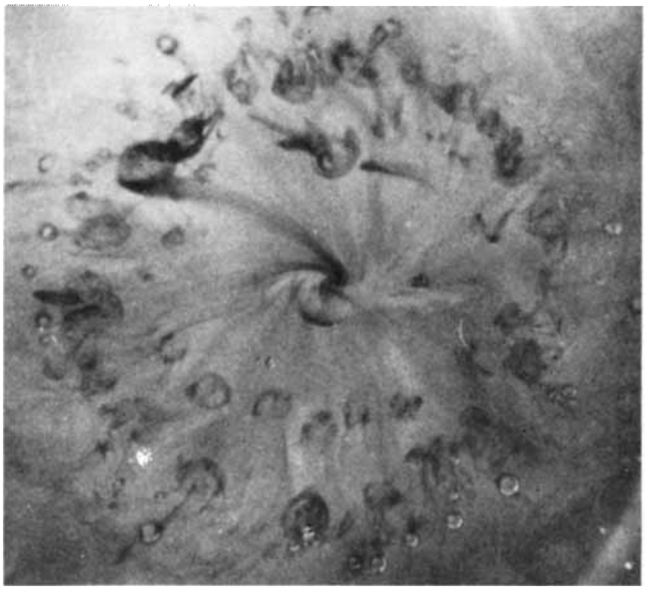

Figure 3. A photograph from above following the bursting of a 2 cm colored bubble placed on a clear water surface. Vortex rings and entrained bubbles are shown near the periphery of the bubble.

It is important to know whether the film drops in the receding film of a bubble bursting through an interface form vortex rings when they impact the surface in order to understand the entrainment by these drops. That film drops can form vortex rings was demonstrated for a 2-cm diameter bubble bursting on a water surface.

When a bubble bursts on the surface of superheated water and causes subsequent nucleation two characteristics of the nucleation are unique and need explanation. The nuclei appear a few mm beneath the surface and a few milliseconds later. Together these characteristics imply the action of vortex rings. The ability of vortex rings to carry tiny bubbles beneath the surface has been demonstrated. Tiny bubbles are carried in the eye of the vortex where they are protected from the ambient fluid. After a while they escape and in a superheated liquid would start rapid growth. This would account for the delayed nucleation.

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Solubility and Rate of Hydrolysis of Chlorine in Aqueous Sodium Hydroxide at 273 K

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Absorption of chlorine into aqueous media has been of interest because of its reaction to form hypochlorite which is used in industrial processes as a bleach or disinfectant. More recently, Cl_2 has been found to react in aqueous alkaline hydrogen peroxide to generate oxygen chemically in its lowest excited state, O_2 $(a^1\Delta_g)$, along with some in the ground state O_2 $(X^3\Sigma_g^-)$ (Held et al., 1978; McDermott et al., 1978). A possible mechanism for this reaction is given by Eqs. 1 to 3 (Held et al., 1978).

$$Cl_2 + OH^- \xrightarrow{k_1} Cl^- + HOCl \qquad (1)$$

$$HOCl + OH^- \xrightarrow{\text{fast}} H_2O + ClO^- \qquad (2)$$

$$ClO^- + H_2O_2 \xrightarrow{k_3} H_2O + Cl^- + O_2(^3\Sigma_g \text{ or } ^1\Delta_g) \qquad (3)$$

The first step of the reaction involves the absorption of Cl_2 followed by hydrolysis by OH^- to give hypochlorous acid. In alkaline media, the HOCl is dissociated into hypochlorite, which then reacts with H_2O_2 to form oxygen. In concentrated peroxide, a similar mechanism may be postulated with HO_2^-, HOOCl, and $ClOO^-$ substituted for OH^-, HOCl, and ClO^-, respectively. Under usual operating conditions of low pressures and relatively long contact times the rate limiting step in this sequence appears to be the absorption of chlorine.

To model the rate of absorption of chlorine it is necessary to be able to predict both the solubility of chlorine in the liquid phase and the kinetic rate constant for the reaction described by Eq. 1. This note presents the results of a study carried out to measure these two parameters at 273°K.

EXPERIMENTAL APPARATUS AND PROCEDURE

The gas-liquid contacting device utilized in these studies was a roller-drum reactor shown schematically in Figure 1.

Aqueous sodium hydroxide solution entered the vacuum reactor through a Teflon nozzle and wetted roller 2 which was directly geared to the large roller 1 such that their surface speeds were matched. The wetted surfaces of both rollers were high density aluminum oxide. The gap between the rollers was variable and kept at approximately 5.1×10^{-4} m (0.020 in.). By controlling the aqueous hydroxide flowrate, roller speed, and the roller gap, a layer of base of even thickness and width could be applied to the large roller. Roller 1 had a diameter of 0.101 m and was actively cooled to 273°K with a methanol/water mixture which was circulated beneath the aluminum oxide sleeve. Thermocouples at the inlet and outlet of the roller indicated the temperature of the coolant. Typically they were not more than 1/4 to 1/2 °K apart during an experiment. Additionally, a thermocouple was located in the reaction zone to monitor the reacting liquid temperature. The roller speed was variable from 0 to 10 rpm, however, most data were accumulated at a roller speed of 5 rpm. The width of the wetted reaction zone (axial distance across the alumina surface) was variable but was maintained at 0.0254 m for these experiments. The unwetted portion of roller 1 was sleeved in Teflon and the reaction zone was an annular channel having rectangular cross section 0.0254 by 0.0066 m. The 0.0254 m wide surfaces were the wetted alumina surface and a coaxial Teflon baffle spaced 0.0066 m from roller 1. This baffle was held in place in grooves machined in annular Teflon baffles which were stationary and extended radially from the wetted surface to the reactor housing, which was 6 inch (0.1524 m) ID commercial Pyrex pipe.

An alumina scraper was located above a cold trap for removing the reaction by-products and unused base-solution from the roller. This waste slurry fell from the scraper into the cold trap below. The external casing of the roller drum reactor and trap were constructed of Pyrex thus allowing visual observation of the base application, reaction zone and scraping process throughout each run.

Flowrates of the reactants were carefully monitored. The aqueous base solution was delivered to the roller drum at ambient temperature from a burette and liquid volume versus time elapsed was recorded.

Chlorine was delivered into the reactor through an all Teflon slit nozzle. The slit width was 0.025 m and thus provided a homogeneous flux of Cl_2 gas across the reaction zone width. The slit height could be varied to control the exit gas velocity and the nozzle was designed to provide gas flow tangential to the surface of roller 1. The height of the nozzle above the alumina drum was adjustable such that the wetted surface of the drum could be made to pass beneath the nozzle with minimal clearance.

The chlorine gas flowrate was monitored with a rotameter and the pressure upstream of the rotameter was controlled to 101,000 Pa (14.7 psia). Figure 2 shows the vacuum system employed. Traps 1, 2 and 3 were maintained at 195°K using dry ice-trichlorethylene slurry and trap 4 was maintained at 77°K using liquid nitrogen.

A calibration of P_1 vs. chlorine flow was obtained with all traps cooled and with the reactor dry. This calibration was then used to determine the Cl_2 absorbed during a run. Typically, a fixed liquid concentration, liquid flowrate and roller speed, the Cl_2 flow was varied over the range from 0 to 0.7×10^{-6} kg · mol/s. Additional runs were made at different liquid flowrates and roller speeds. In the series of runs the concentration of base was increased sequentially. Figure 3 shows some typical data in the form of a plot of molar flow of Cl_2 out vs. Cl_2 in.

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