Liquid drop technique for generation of organic glass and metal shells*  

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Abstract  

We have for several years utilized the technique of capillary wave synchronization of the break-up of single and multiple component jets to produce uniform sized liquid drops and solid particles, and hollow liquid and solid shells. The technique has also been used to encapsulate a number of liquids in impermeable spherical shells.  

Highly uniform glass shells have been made by generating uniform "rops of glass forming materials in an aqueous solution, subsequently evaporating the water, and then "blowing" the remaining solids in a high temperature vertical tube furnace. Experimental results will be presented and the critical problems in further research in this field will be discussed.  

Drop generation from a liquid stream has been experimentally observed since man's beginning. In recent times more precise techniques have been developed and used in such diverse fields as electric propulsion of spacecraft, cloud physics, high speed printing, magnetic confinement, fusion reactor fueling and inertial confinement fusion target fabrication. Other uses which are perhaps more common but less well known in the physics and engineering communities are encapsulation of one fluid inside another and generation of gas filled soluble capsules for study of blood pressure in the heart and other parts of the circulatory system.  

In the time span from 1966 to 1981 our work has included liquid drop, solid particle and hollow shell generation from many different liquids from hydrogen to gold and including many organic and inorganic materials. A very brief chronology of our work is shown in Figures 1-10. Building on the work of Rayleigh, we developed techniques to produce very uniform drops with a wide range of sizes and materials.  

Figure 1 shows a "solid" jet of liquid on which a capillary wave has been launched to initiate generation of uniform drops. Figure 2 shows a jet of water into which air has been injected.  

The composite jet generated hollow shells of water around individual air bubbles. By the mid-1960's, we were interested in encapsulating fluids inside impermeable shells. Some of our first encapsulations were liquids such as silicone and organic oils in alginate shells. We were interested in multiple layers and built tri-axial systems as shown in Figure 3. However, a simple double tube concentric system was sufficient for the single shell encapsulation. An aqueous solution (Fluid #1) of sodium or potassium alginate was passed through the outer part of the system. Fluid #2 was the liquid to be encapsulated, e.g. an oil with Flame Red dye dissolved in the oil or other fluid including gases such as air. In the double concentric system, the inner tube and Fluid #3 were not present. Controlled, driven break-up of the two component jet formed highly concentric capsules. The capsules were passed through a mist or fine spray of calcium, magnesium or zinc chloride solution or into a bath of such solutions. Rapid change of the sodium or potassium alginate to calcium, magnesium or zinc occurred. The latter compounds are relatively insoluble in water and formed a "skin" on the capsule. Subsequent drying of the particles resulted in a thin walled spheroid containing the encapsulated fluid.  

Further experiments resulted in the generation of spheres of polymeric materials, water shells with air as the inner fluid, copper, and more recently gold. Epoxy resins and appropriate hardners can be dissolved in solvents such as acetone, MEK or methylchloride. If the resin and curing agent are dissolved separately in dilute solutions, mixing does not result in curing of the epoxy. However, if droplets of the mixed solution are formed, allowed to pass through a heated column and the solvents evaporated, the resin and hardner react to form a normal, cured epoxy shell or solid bead (depending on temperature, rate of transport, etc.).  

An apparatus (Figures 4 and 5) to produce copper shells from molten copper was constructed and operated and produced the spheres shown in Figure 6. The high temperature parts of the apparatus (copper reservoir, gas injection tube, orifices, etc.) were quartz. The apparatus was filled with hydrogen gas to reduce the formation of oxides. All the copper was run through the quartz system before cooling was allowed because of differences in expansion coefficients of copper and quartz. Copper will wet clean high temperature quartz and will shrink enough to pull pieces out of the quartz as it cools.
Hollow hydrogen shells were produced in the early 1970's by initiating bubbles in jets of liquid hydrogen. The shells were frozen and had diameters of over a hundred micrometers and wall thicknesses of about ten micrometers. Solid spheres of hydrogen were also produced using some of the same techniques to launch capillary waves on a liquid hydrogen jet for control of jet break-up to generate uniform drops. The hydrogen spheres (hollow and solid) have both immediate and potential use in the magnetic confinement and inertial fusion programs. Figure 7 shows hollow hydrogen shells produced from jets of liquid hydrogen.

As the laser fusion program developed during the early 1970's it became necessary to produce glass shells with exceptionally smooth surfaces and uniform walls. A solution of glass forming chemicals in water was used to form a cylindrical jet which was then caused to break into uniform drops. The drops passed vertically downward into a hot column. In the upper portion the solute was evaporated at about 550°C to leave dry particles. In the lower part of the column, the temperature increased to 1200-1500°C and the particle fused to form hollow glass shells. The apparatus is shown in Figure 8. Recent development of the process allows production of high quality glass shells with 90-99% having uniform walls and smooth surfaces such as those shown in an interference microscope in Figure 9.

Silver spheres have been formed by a technique similar to that used for forming glass spheres. A solution of silver nitrate was formed into drops which were allowed to fall through the low temperature-high temperature column. Figure 10 shows the spheres resulting from the process. Some are hollow and some are solid. The surfaces of the spheres are smooth to 0.1-0.5 micrometer.

We have found liquid drop techniques to be very useful in several diverse areas. For producing very uniform metallic, organic, inorganic and, in particular, glassy shells, the liquid jet method is the most reproducible and exceptionally useful of all the techniques we have studied.

References
Figure 1: A typical liquid jet on which a capillary wave has been launched to synchronize break-up of the jet into uniform drops.

Figure 2: A water-air jet from which hollow spheres of water are being generated. The inner orifice can be moved axially to optimize the shell production. Gas flow rate, liquid flow rate, orifice diameters and drive frequency are important parameters. (1974)

Figure 3: An apparatus designed to produce multilayer spheres. Encapsulation of one liquid in another can be accomplished by a double instead of a triple coaxial system. (ca 1966)

Figure 4: Schematic diagram of a system designed to produce hollow and solid spheres from high melting point materials such as copper. (1974)
Figure 5. Photograph of an experimental system used to produce copper shells and solid spheres. (1974)

Figure 6. Copper sphere produced in the apparatus shown in Figure 5. (1974)

Figure 7. Hollow spheres produced from jets of liquid hydrogen. (1972)

Figure 8. A system used to produce high quality glass shells. (1976)
Figure 9 Interference microscope fringes in glass shells produced by liquid drop techniques. Perfectly uniform (surface, wall and sphericity) shells are indicated by circular fringe patterns.

Figure 10 Silver spheres produced by liquid drop techniques. (1980)

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