

# Factors affecting the generation, detection, and removal of microbubbles in liquids

**Don Grant**

Founder, CT Associates, Inc.

10777 Hampshire Ave S, Bloomington, MN 55438

952-944-4766, don@ctassociatesinc.com

## **Abstract**

In the semiconductor manufacturing industry, microbubbles (bubbles smaller than 100  $\mu\text{m}$  in diameter) can be contaminants that reduce manufacturing yield. For example, if microbubbles in photoresist are dispensed onto a wafer, they can cause a defect in the microcircuit being produced thereby causing premature failure. This paper discusses some of the factors that influence the formation of microbubbles in liquids and how microbubbles can be differentiated from hard particles using optical particle counters. Experimental results in water and a common photoresist solvent, propylene glycol methyl ether acetate, are presented. The results are compared to theoretical predictions.

## **Introduction**

Bubbles, like particles, can cause light point defects on semiconductor wafer surfaces. During processes such as photolithography, bubbles can actually cause more severe problems than particles. They can act as a lens that diffuses the light during the light exposure step, thereby magnifying the size of the defect they cause. Little has been published about how bubbles, often referred to as microbubbles, are formed and behave in liquids. A paper summarizing the theory of bubble behavior in liquids presented last year at this conference indicated that bubbles can only be present when the liquid is supersaturated with gas and that once bubbles are formed, they rapidly grow to supermicron size (diameters  $> 1 \mu\text{m}$ ) [1].

This paper presents the results of an experimental study aimed at verifying these theoretical predictions. Testing was also performed to assess the effects of wetted materials of construction on bubble generation, the effectiveness of filters at removing bubbles, and the abilities of two classifications of particle counters to detect bubbles.

## **Results and discussion**

**The effect of saturation ratio on bubble generation:** The saturation ratio (S) is defined by the following equation:

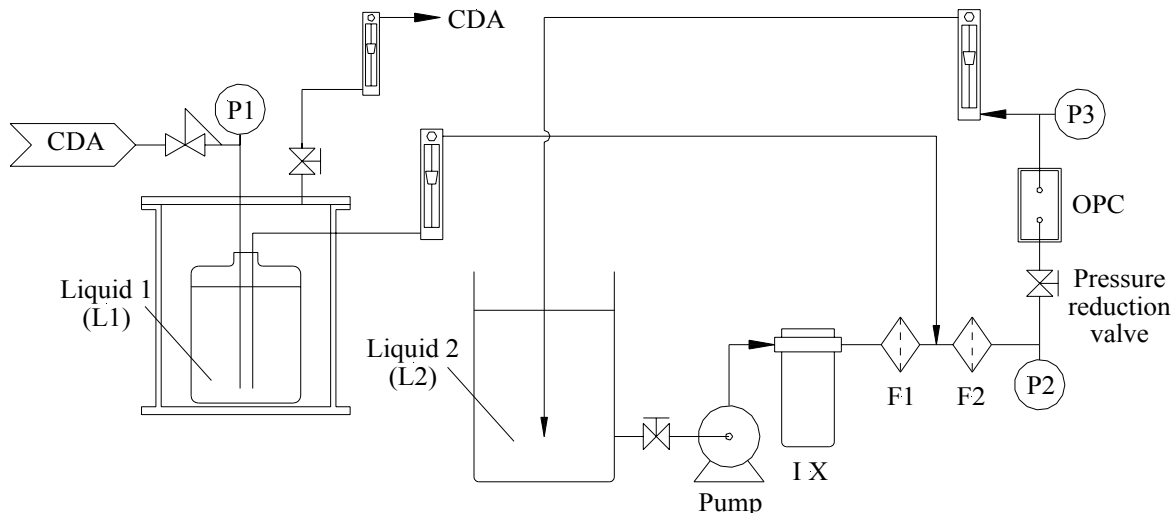
$$S = \frac{\text{Pressure in equilibrium with the gas dissolved in a liquid}}{\text{Actual pressure}}$$

When  $S > 1$  the liquid is supersaturated with the gas; when  $S < 1$  the liquid is subsaturated.

Experiments to determine the effect of S on bubble generation were performed using the system shown in Figure 1. In this system, liquids with two different dissolved air contents were mixed.

The pressure on the mixture was reduced just prior to flowing the mixture through an optical particle counter (OPC). All experiments were performed at room temperature.

**Figure 1: System to control the saturation ratio**



The dissolved air content in one of the two liquids that were mixed (L2) was simply the dissolved air in equilibrium at atmospheric pressure. The dissolved air content of the second liquid (L1) was elevated by continuously bubbling air through the liquid while maintaining the liquid and gas pressure at P1, a pressure  $> 1$  atmosphere.

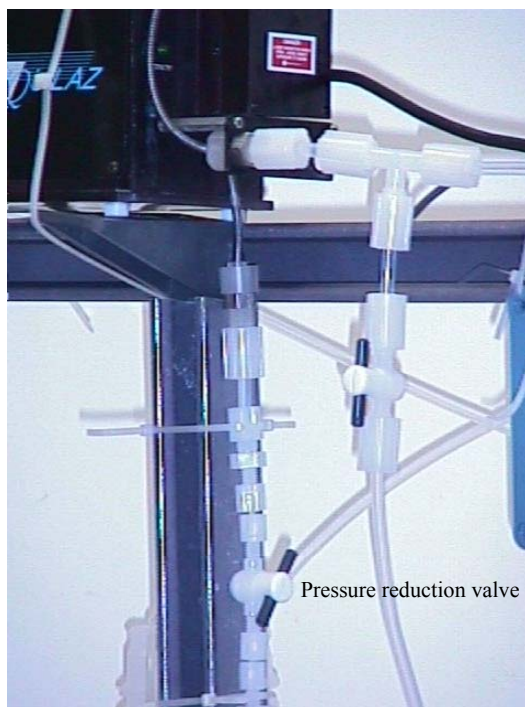
The liquids were combined in a known ratio by pumping L2 using a variable-speed positive displacement pump while pressure-dispensing L1 using pressure P1 through a rotameter with a needle valve. The pressure on the combination (P2) was then reduced to P3 using a pressure reduction valve. By controlling the flow rates of L1 and L2 and pressure P1, the saturation ratio at P3 could be varied from  $< 0.5$  (subsaturated) to  $> 2.0$  (supersaturated).

Bubble/particle concentrations were measured using optical particle counters (OPCs) located just downstream of the pressure reduction valve. OPCs actually measure “light scattering centers” which can be either particles or bubbles. They cannot differentiate between the two. The combination of the two will be referred to as bubbles/particles in this paper.

Three OPCs were used. Most measurements were made using a Liquilaz-SO2 (Particle Measuring Systems, Boulder, CO). This sensor can detect bubbles/particles as small as  $0.2 \mu\text{m}$  in diameter and has 15 size channels, the largest of which is  $> 2 \mu\text{m}$ . The Liquilaz-S05 (Particle Measuring Systems) can detect bubbles/particles as small as  $0.5 \mu\text{m}$  in diameter and has 15 size channels, the largest of which is  $> 20 \mu\text{m}$ . The third OPC was an HSLIS-M65, also from Particle Measuring Systems. This sensor can detect bubbles/particles as small as  $0.065 \mu\text{m}$  in diameter and has 4 size channels, the largest of which is  $> 0.2 \mu\text{m}$ .

The pressure reduction valve was located upstream of and directly below the OPC so that any bubbles formed downstream of the valve would rise through the OPC as shown in Figure 2. An ion exchange cartridge (IX) and filters (F1 and F2) were included in the system to reduce contamination and particle concentrations.

**Figure 2: Pressure reduction valve – OPC orientation**

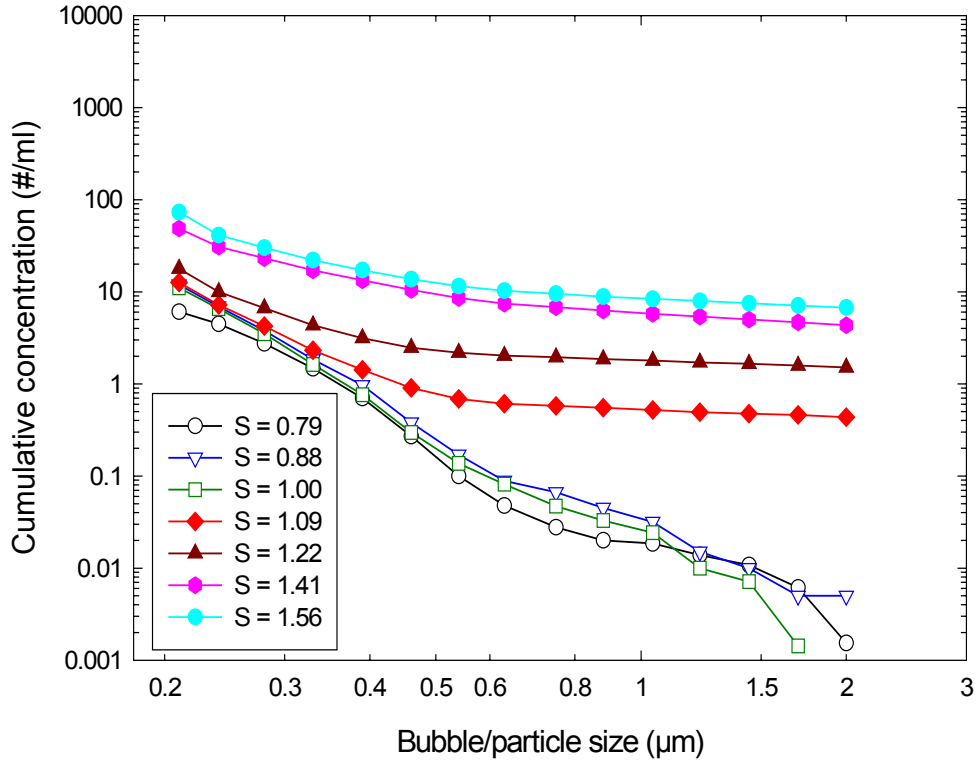


Particle/bubble concentrations measured in water when the wetted materials in the pressure reduction valve were made from stainless steel are shown in Figure 3. This figure presents log (cumulative concentration) versus log (bubble/particle size) for saturation ratios ranging from 0.79 to 1.56. Open symbols are used for saturation ratios  $\leq 1.00$  while closed symbols are used for saturation ratios  $> 1.00$ .

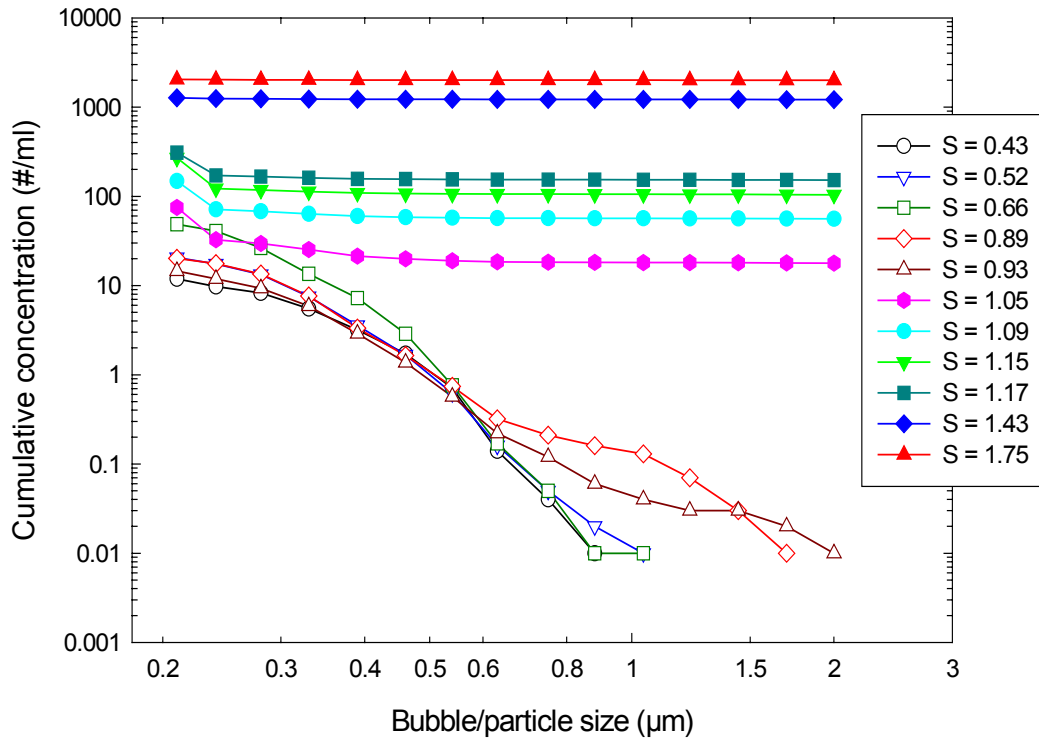
The size distributions shown in Figure 3 with the saturation ratio  $\leq 1.00$  were very similar and were approximately linear (on the log-log plot) and have a slope of approximately  $-3.5$ . Size distributions with this slope are typical of particles in high purity liquids [2]. However, when the saturation ratio was  $> 1.00$  the shape of the distribution changed substantially. The distributions became less steep – especially for the larger sizes. The distributions were almost flat for bubbles/particles  $> 1 \mu\text{m}$  in diameter.

Particle/bubble concentrations measured in water using a fluoropolymer pressure reduction valve rather than a stainless steel valve are shown in Figure 4. Once again the size distributions were fairly linear and steep for saturation ratios  $\leq 1.00$  and flat for saturation ratios  $> 1.00$ . The “flattening” of the size distribution curve was more pronounced than was observed for the stainless steel valve.

**Figure 3: Bubble generation in water using a stainless steel pressure reduction valve**



**Figure 4: Bubble generation in water using a fluoropolymer pressure reduction valve**



The time for liquid to flow from the pressure reduction valve to the OPC in these experiments was approximately 2 seconds. If bubbles begin to form when the pressure is reduced at the valve, their diameter would be expected to increase to  $> 10 \mu\text{m}$  before they reach the OPC [1]. Hence, the size distributions of bubbles would be expected to be very flat if graphed using the axes shown in Figures 3 and 4. Thus, the flattening of the distributions shown in Figures 3 and 4 can be attributed to bubble formation. Bubbles were clearly visible in both tests when  $S$  was  $\gg 1.00$ .

These data agree with the theoretical predictions that  $S$  must be  $> 1.00$  for bubbles to be present and that bubble diameters rapidly increase to  $> 1 \mu\text{m}$ .

**The effect of time on bubble size:** In order to further verify the rapid growth rate of bubbles, experiments were performed in which the travel time of liquid from the pressure reduction valve to the OPC was reduced to approximately 0.5 seconds. These experiments were performed in water with a fluoropolymer pressure reduction valve. Size distributions measured in these tests are shown in Figure 5. Once again, the distributions were very flat when  $S$  was  $> 1.00$ .

A comparison between Figures 4 and 5 reveals that similar size distributions were obtained when the liquid transit time was 2.0 or 0.5 seconds. If it is assumed that all of the bubbles/particles  $> 1 \mu\text{m}$  were bubbles and not particles, then bubble concentrations for the two liquid transit times can be compared as a function of saturation ratio. This comparison is shown in Figure 6. Essentially identical bubble concentrations were observed at equivalent saturation ratios. This is further evidence that bubble diameters rapidly grow to  $> 1 \mu\text{m}$  once the bubbles are formed.

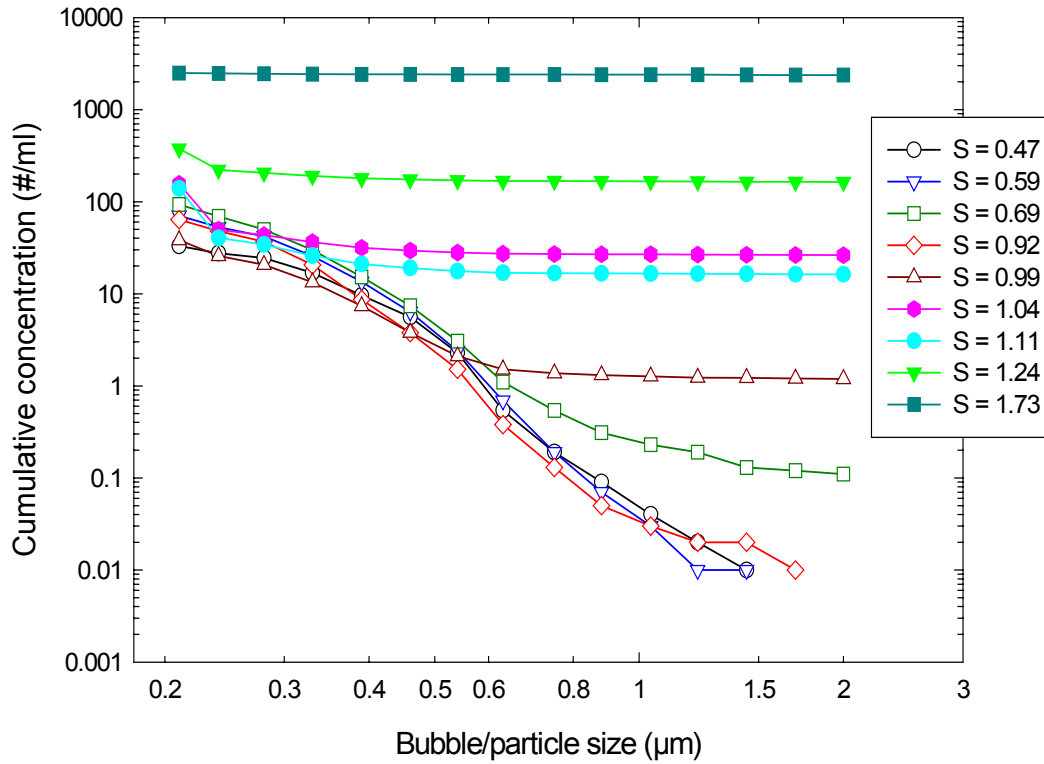
**The effect of wetted material type on bubble formation:** A comparison between Figures 3 and 4 reveals that substantially fewer bubbles were formed when the pressure reduction valve was made from stainless steel rather than fluoropolymer. This comparison is documented in Figure 7. For higher saturation ratios, the concentrations of bubbles generated using the fluoropolymer valve were more than 100 times those generated using the stainless steel valve.

Fluoropolymers are more hydrophobic than stainless steel and machined plastic surfaces are generally rougher than machined metal surfaces. Hydrophobic, rough surfaces are more likely to act as bubble nucleation sites than hydrophilic, smooth surfaces [3]. Hence, these observations are consistent with the observations of other researchers.

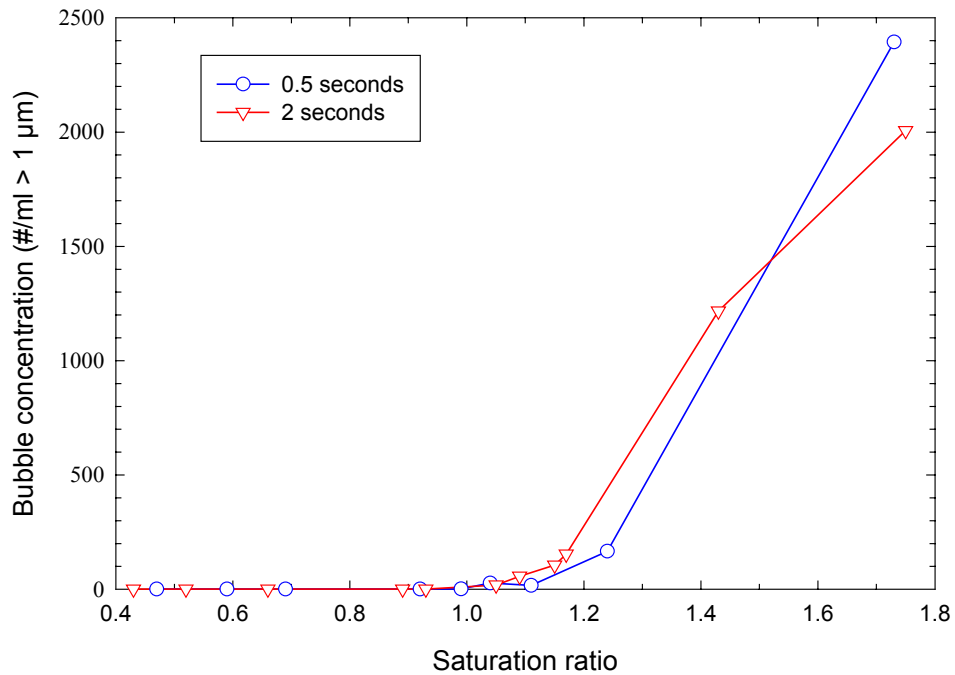
**The effect of liquid type on bubble generation:** The effect of liquid type on bubble generation was examined by measuring bubble generation in propylene glycol methyl ether acetate (PGMEA), a common photoresist solvent. The fluoropolymer pressure reduction valve was used and the liquid transit time was 0.5 seconds.

In the experiments in water, the bubble generation rate as a function of  $S$  was reversible, i.e. if the saturation ratio was changed from 1.2 to 1.4 then back to 1.2, the bubble concentration was essentially the same whenever the saturation ratio was 1.2. This was not the case in PGMEA.

**Figure 5: Bubble generation in water using a fluoropolymer pressure reduction valve (0.5 second liquid transit time from the pressure reduction valve to the OPC)**



**Figure 6: The effect of saturation ratio on bubble concentrations (fluoropolymer pressure reduction valve)**



**Figure 7: Bubble generation using stainless steel and fluoropolymer valves**

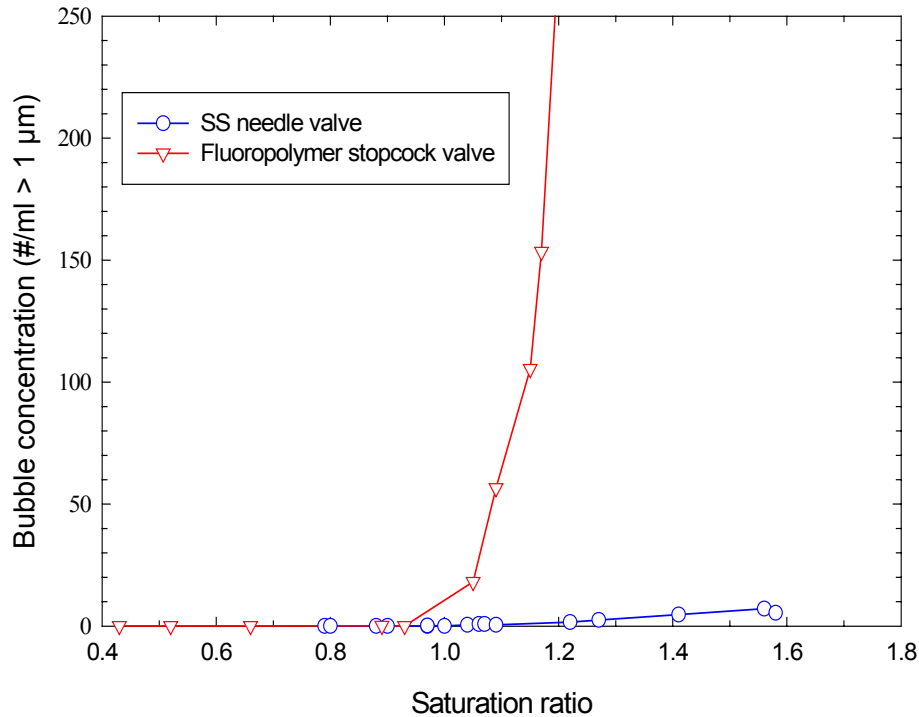
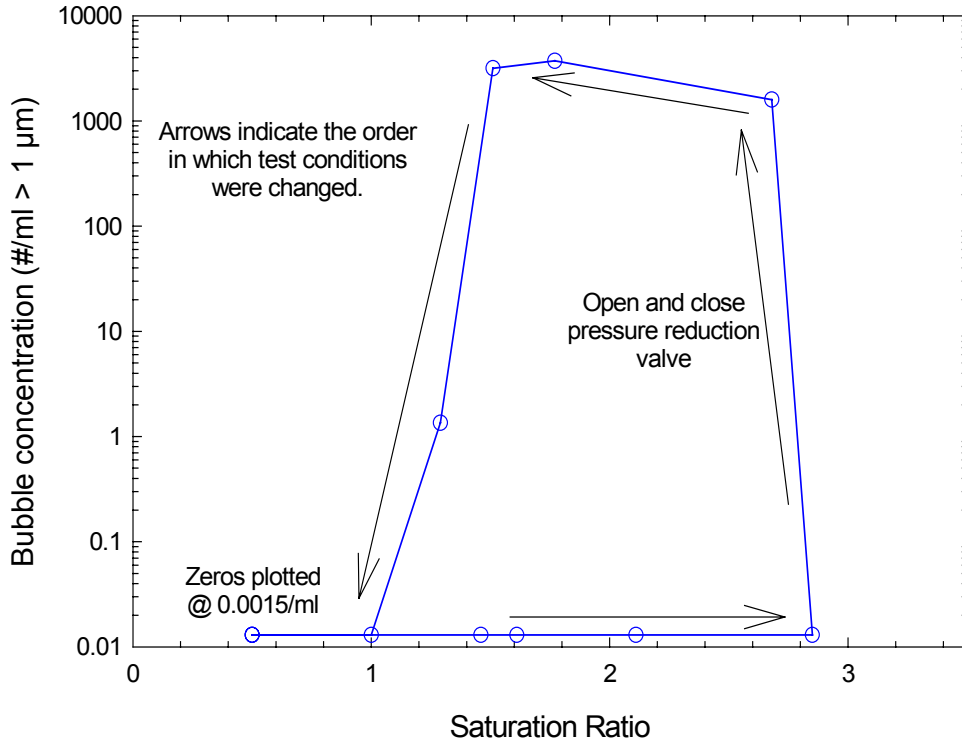


Figure 8 presents bubble concentrations in an experiment in which the saturation ratio was slowly increased from  $< 1$  to 2.9. No bubble formation was seen!!! However, when the fluoropolymer valve was closed and re-opened when the saturation ratio was 2.9, the bubble concentration increased dramatically ( $\sim 100,000$  fold). When the saturation ratio was subsequently decreased, the bubble concentration remained high until the saturation ratio approached 1.00. These observations may indicate that under certain conditions mechanical action is necessary to “activate” bubble nucleation sites. Bubble nucleation is one of the least understood processes in bubble formation and growth [4].

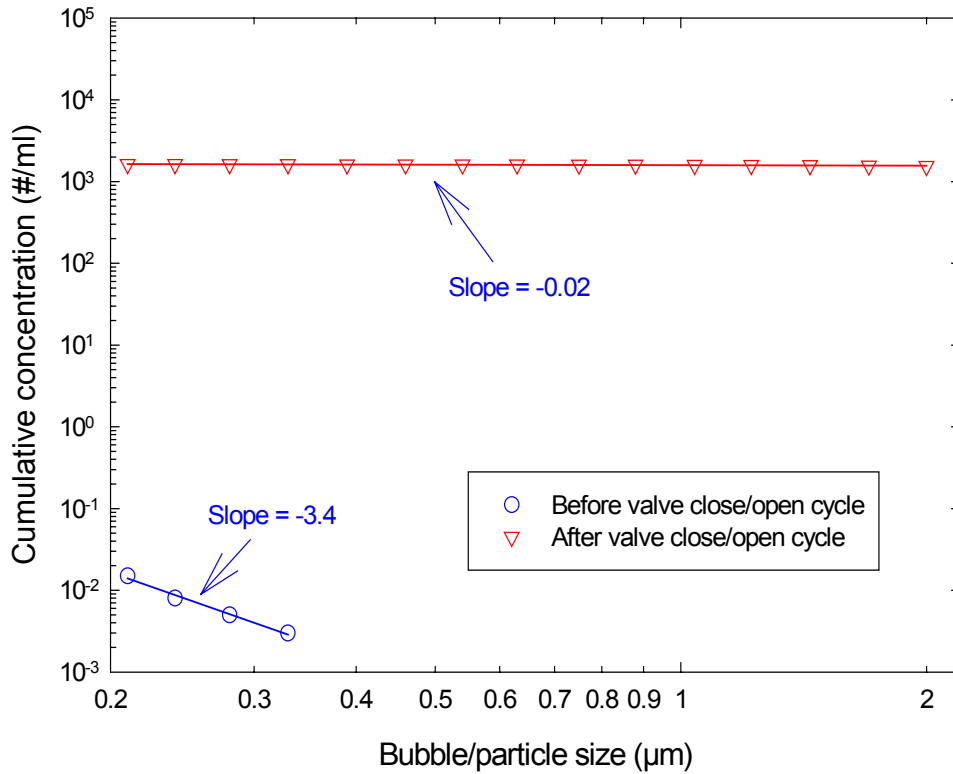
When bubbles were present the bubble/particle size distribution was similar to that observed in water as shown in Figure 9.

**Bubble removal by filters:** Testing to determine the effectiveness of filters for removal of bubbles from liquid was performed using PGMEA and microporous membrane filters. Initial testing was performed using a PTFE membrane filter. The initial intent was to generate bubbles at a fluoropolymer pressure reduction valve just upstream of the filter using PGMEA with  $S = 2.9$  and observe the filter’s ability to remove the bubbles. The testing described above indicates that it would be necessary to close and open (cycle) the pressure reduction valve to initiate bubble formation. However, before the valve was cycled, bubbles began to form on the membrane surface and be released into the PGMEA as shown in Figure 10. Hence, rather than removing bubbles, the filter acted as a nucleation site and generated them.

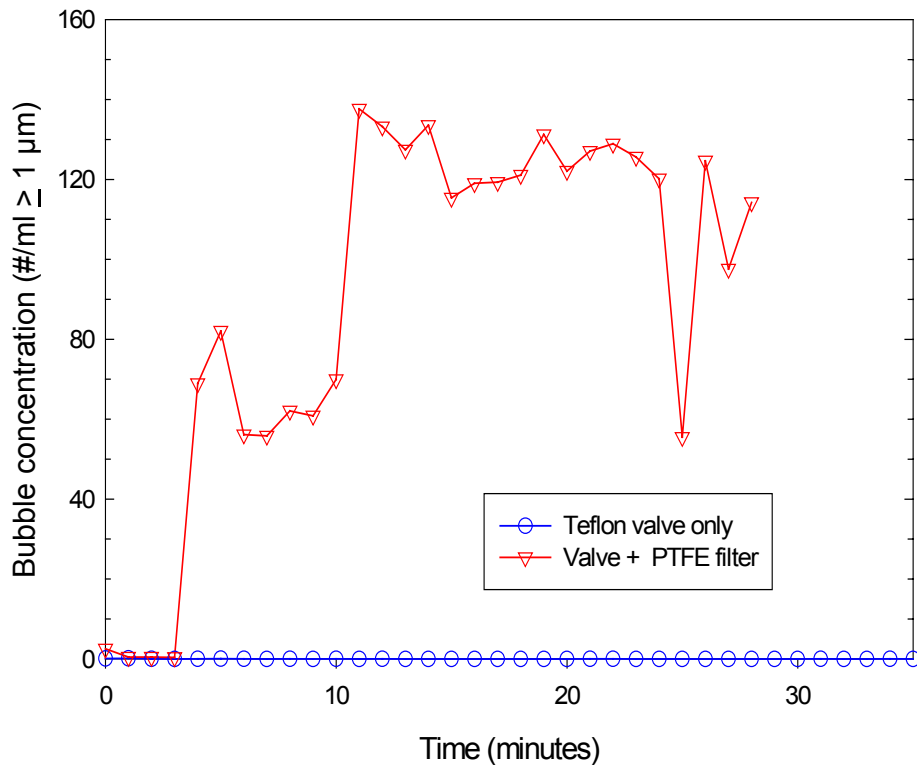
**Figure 8: Bubble generation in PGMEA**



**Figure 9: Particle/bubble size distributions in PGMEA**



**Figure 10: Bubble generation in PGMEA using a PTFE membrane filter**



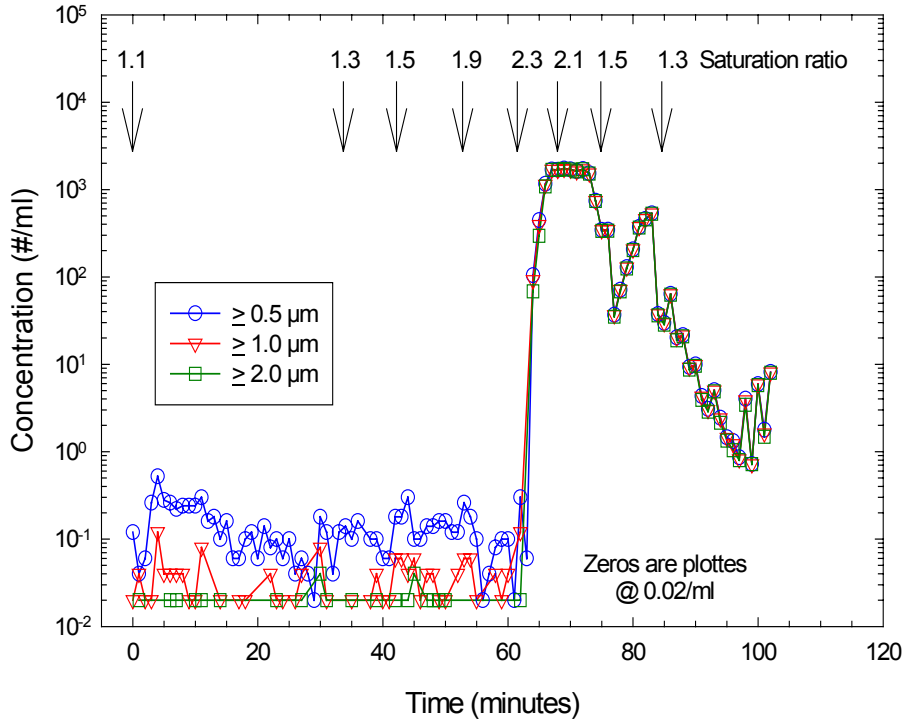
A second test was performed with the same filter in which the saturation ratio was slowly increased to determine the saturation ratio required to “activate” bubble nucleation on the filter surface. As shown in Figure 11, nucleation began when the saturation ratio was increased to approximately 2.3. Once the nucleation process was “activated”, bubbles continued to form when the saturation ratio was subsequently decreased.

These results appear to indicate that the rough, hydrophobic surface of a PTFE membrane is a very effective media for bubble generation and filters of this type are a poor choice for bubble removal.

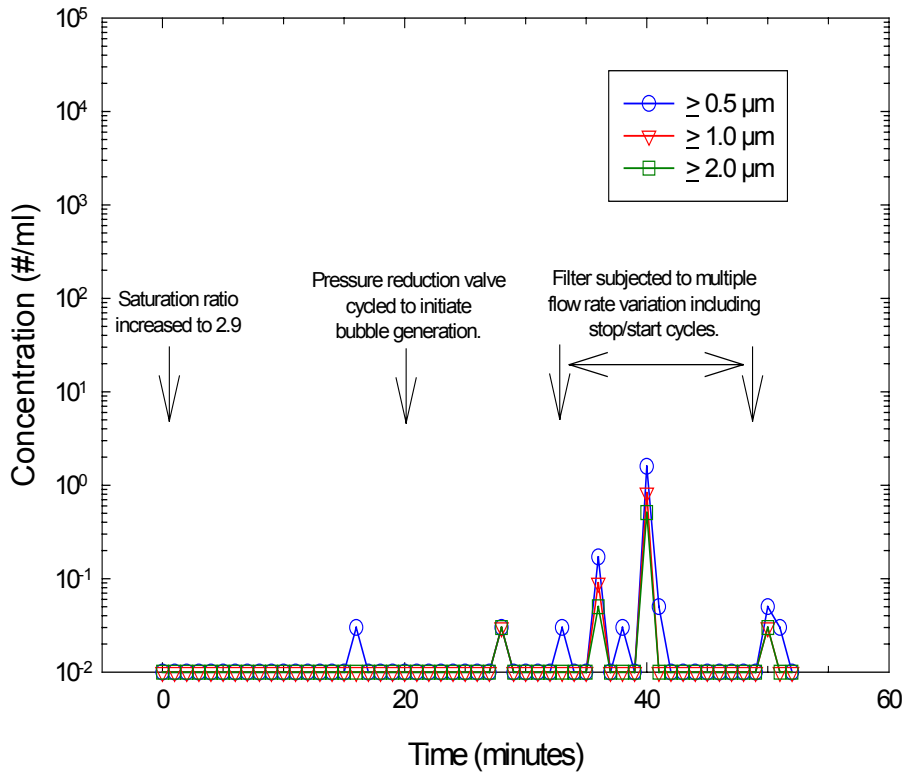
Testing was also performed using a polyethylene membrane filter (Mykrolis LHVD Catalogue number DZUV A44 01). Bubble/particle concentrations measured downstream of the filter in the test are shown in Figure 12. When PGMEA with a saturation ratio of 2.9 was passed through the filter, no bubble generation was observed. When the filter was challenged with bubbles generated by cycling the pressure reduction valve (which generated thousands of bubbles/ml in the tests described above), no bubbles were seen downstream of the filter. Few bubbles were observed even when the flow rate through the filter was subjected to large variations including stop/start cycles.

The polyethylene filter is believed to be more effective at bubble removal than the PTFE filter because of its more hydrophilic surface.

**Figure 11: The effect of saturation ratio on bubble generation in a PTFE filter**



**Figure 12: Bubble removal by a polyethylene filter**



**Particle counter comparison:** Many types of OPCs from multiple manufacturers are used to detect particles and bubbles in high purity liquids. Most of these can be divided into two general categories using terminology coined by Particle Measuring Systems [2]: spectrometers and monitors. Spectrometers are instruments in which the viewing volume is very well defined and the instrument can size particles very accurately. The viewing volume in monitors is less well defined; however, they give a reasonably accurate measurement of a particle size distribution in many fluids. They have the advantage of a higher sampling rate than spectrometers with the same sensitivity – thereby improving the measurement variability in liquids with low particle concentrations.

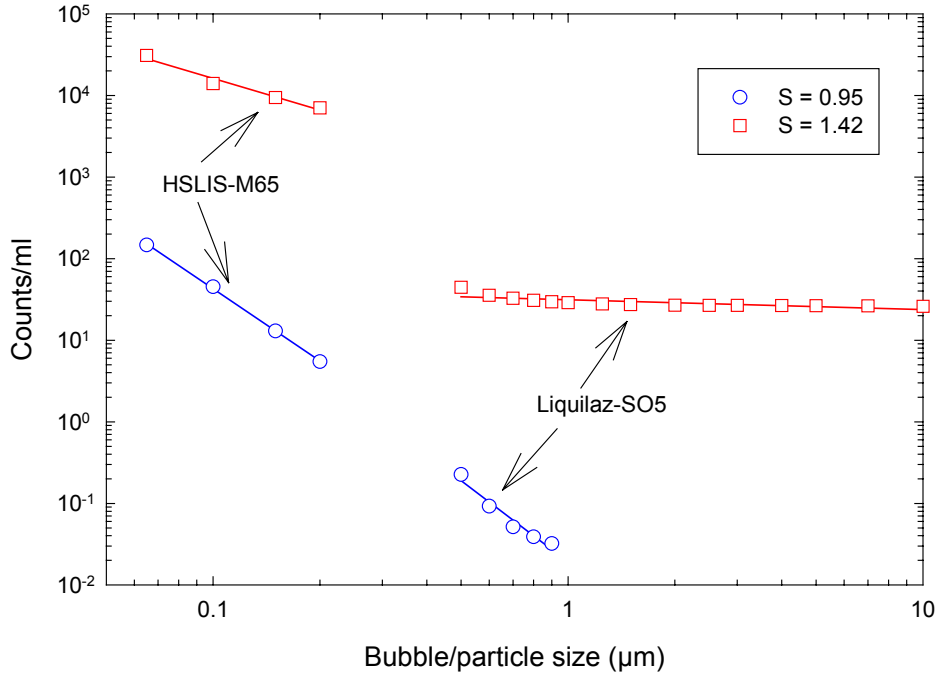
The data presented so far in this paper were all obtained using a Liquilaz-S02 – a spectrometer. Testing was also performed using a spectrometer similar to the Liquilaz-S02, a Liquilaz-S05, and a monitor - an HSLIS-M65.

Figure 13 compares concentrations measured by the Liquilaz-S05 and the HSLIS-M65 in water with and without bubbles present. At a low saturation ratio (0.95) when bubbles were not present, the size distributions measured by the two counters were similar. At a high saturation ratio (1.42) when bubbles were present, the measured concentrations increased substantially. However, while the slope of the distribution measured by the spectrometer flattened considerably, the slope of the distribution measured by the monitor showed less change.

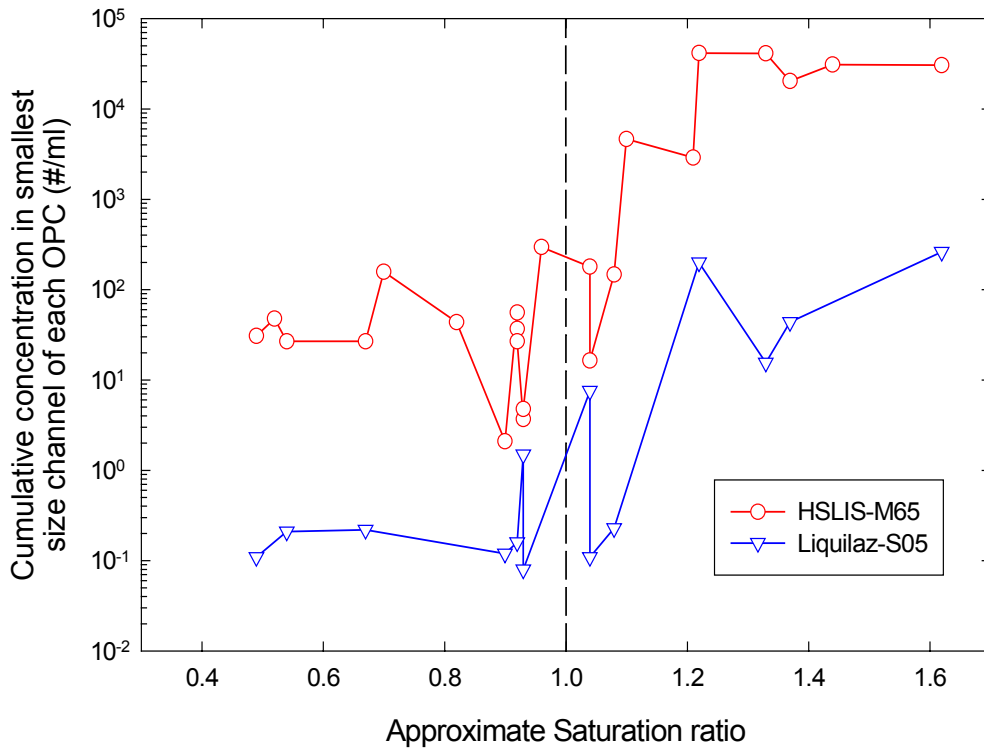
The changes in concentration and size distribution slope for the two OPCs as a function of saturation ratio are shown in Figures 14 and 15, respectively. Figure 14 indicates that when the water was subsaturated, both counters measured low concentrations that were relatively invariant with saturation ratio. Concentrations measured by both counters increased dramatically when the water became supersaturated and bubbles were present. Figure 15 indicates that the slope of the size distribution measured by the Liquilaz-S05 decreased dramatically when the water was supersaturated, while the slope of the size distribution measured by the HSLIS-M65 showed little change.

These results appear to indicate that a “flat” size distribution measured using a spectrometer is a good indicator that bubbles are present. However, the size distributions measured by monitors do not provide an indication of the presence of bubbles.

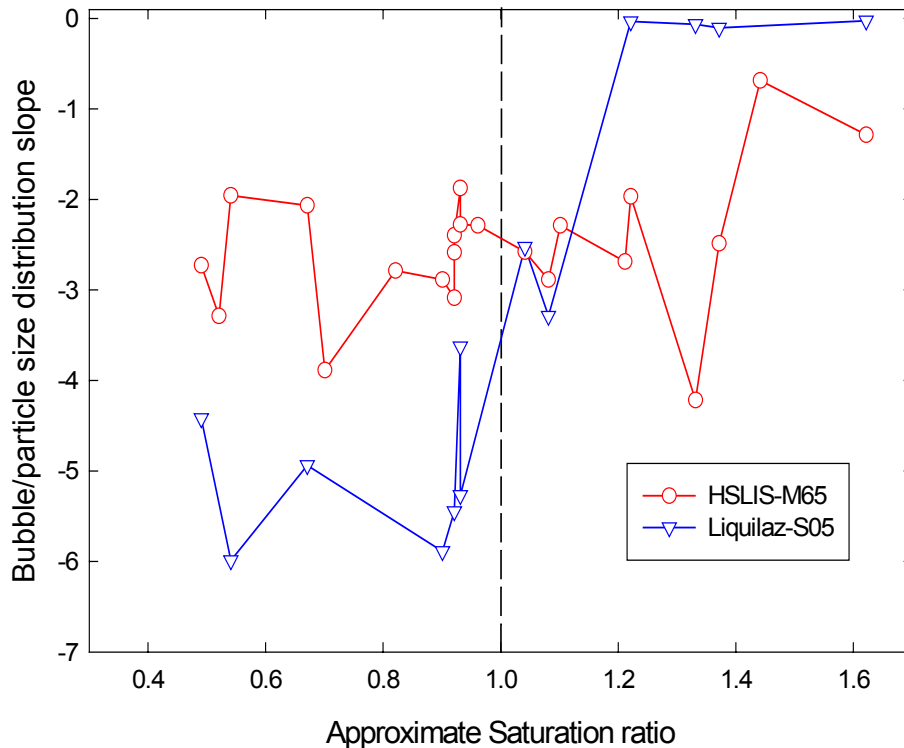
**Figure 13: Example of bubble/particle size distributions measured by a spectrometer and a monitor**



**Figure 14: Particle/bubble concentrations measured by a spectrometer and a monitor at different saturation ratios**



**Figure 15: Slopes of particle/bubble size distributions measured by a spectrometer and a monitor at different saturation ratios**



## Summary

This study was undertaken to examine some of the variables that influence the formation, growth and removal of bubbles in liquids and to characterize several optical particle counters used to detect them. Using results from experiments performed in both ultrapure water and propylene glycol methyl ether acetate (PGMEA), it showed that:

- The liquid must be supersaturated with gas for microbubbles to form
- The probability of a microbubble forming in a liquid is influenced by system wetted materials, surface state, fluid dynamics, and mechanical shock.
- Once formed, microbubbles grow to  $> 1 \mu\text{m}$  in diameter in  $\ll 0.5$  seconds.
- Optical particle counters classified as spectrometers can detect the presence of bubbles in high purity fluids by changes in the shape of the size distribution.
- The presence of bubbles probably cannot be detected by the size distribution indicated by optical particle counters classified as monitors.
- The retention of microbubbles by membrane filters is influenced by the filter's wetted materials. Filters with hydrophilic surfaces are more effective than those with hydrophobic surfaces.

## **Acknowledgments**

The author would like to thank Mykrolis Corporation for providing funding to perform this investigation.

## **Biography**

Don Grant is founder and president of CT Associates, Inc., which performs contract research and development and testing services related to contamination control, particle measurement and control, filtration, permeation and chemical engineering. He has more than 30 years of experience in analysis and purification of fluids and is the author or co-author of more than 125 technical papers and presentations. He has an M.S. in mechanical engineering from the Particle Technology Laboratory at the University of Minnesota and a B.S. in chemical engineering from Case Western Reserve University. He is a recipient of the Maurice Simpson Award from the Institute of Environmental Sciences.

## **References**

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1. Grant, DC (2003). "The anticipated behavior of bubbles in semiconductor process liquids," in *Proceedings of 22<sup>nd</sup> Annual Semiconductor Pure Water and Chemicals Conference*, Sunnyvale, CA, Feb. 2003, pp 154-168.
2. Knollenberg, RG and DL Veal (1991). "Optical particle monitors, counters and spectrometers: Performance characterization, comparison and use," in *Proceedings of the 37<sup>th</sup> Annual Meeting of the Institute of Environmental Sciences*, Mt. Prospect, IL, pp 751-771.
3. Cole, R (1974). "Boiling nucleation," *Adv. in Heat Transfer*, 10:85-166.
4. Lubetkin, SD (1994). "Bubble nucleation and growth," in Controlled Particle, Droplet and Bubble Formation, ed. DJ Wedlock, Butterworth Heinemann, pp 167-168.