The Sonophysics and Sonochemistry of Liquid Waste

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Basic Bubble Dynamics

Acoustic Cavitation

If an intense acoustic field is applied to a liquid, the liquid can fail under the tensile, or negative portion of the sound field; weak sites within the liquid, probably preexisting gas pockets, called "cavitation nuclei," are caused to rapidly grow, thereby producing vapor and gas-filled cavities (i.e., bubbles). These bubbles continue to grow during the negative portion of the sound field, until the sound field turns positive. The resulting inertial implosion of the bubbles (now mostly filled with vapor and thus unable to provide stiffness) can be extremely violent, leading to an enormous concentration of energy within the small residual volume of the collapsed bubble. Consequently, the temperatures and pressures achieved by the compressed bubble contents can be respectively several thousand degrees (perhaps even higher) and several kilobars (perhaps even much higher). At the final stages of bubble collapse intense shock waves are emitted, chemical bonds are broken, and even light is emitted — called "sonoluminescence."

Figure 1 illustrates the nonlinear radial response of a single bubble to an applied sound field. When the pressure within the bubble falls below the vapor pressure of the liquid, the bubble begins to grow while the bubble fills with vapor. When the pressure turns positive, the vapor condenses and the bubble accelerates rapidly inward. Consider that even for the modest applied pressure amplitude used in Figure 1 (we used 0.13 MPa — most industrial systems use at least an order of magnitude higher pressures), the temperature (assuming adiabatic compression) within the bubble can exceed 5,000 K.

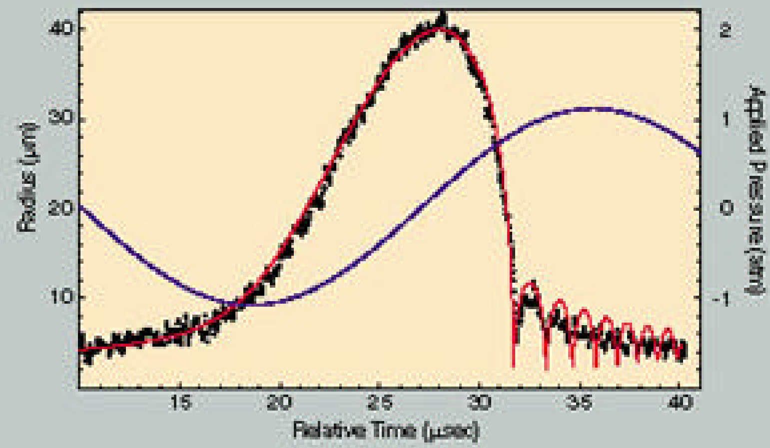


Figure 1. *The radial response of a cavitation bubble. During the tensile portion of the sound field the bubble grows. The normalized drive pressure amplitude is shown in blue. The data points are overlayed with a fit from our bubble dynamics code.*

Bubble Response in Standing Wave

In an acoustic standing wave, bubbles can be levitated against the gravitational force of buoyancy by the well-known Bjerknes force, $F_{bj}=-V(t)\ \nabla P$, where ∇P is the gradient of the applied acoustic pressure [Eller, 1968; Crum, 1975]. Physically, the Bjerknes force arises from a pressure difference (gradient) across the bubble. Figure 2 illustrates this force for the case of small driving pressures (and for drive frequencies below the bubble's natural resonance frequency). During the negative portion of the sound field, the bubble grows. There is a net force on the bubble due to a slight difference in pressure exerted on either side of the bubble's surface. This net force directs the bubble towards the pressure antinode. During the compressive phase of the sound field, the bubble is small, and the net force is directed away from the pressure antinode. However, since the corresponding volume is smaller, this force is smaller, and hence, over an acoustic cycle the net force directs the bubble towards the antinode. This argument on the direction of the force applies only to a bubble that is driven below its natural resonance frequency. For bubbles driven above their natural resonance frequency, a different phase response requires them to be forced away from the pressure antinode and toward a node. Thus, in a cavitation field, one expects a size distribution that includes bubbles in both regimes; large bubbles migrating to pressure nodes, small bubbles migrating to pressure antinodes. Large bubbles scatter and absorb acoustic energy, and we believe these large bubbles may cause inefficient sonochemistry.

Another influence that occurs is termed rectified diffusion [Crum, 1980]. When the bubble grows during the negative portion of the sound field, the gas concentration inside the bubble is less than in the surrounding bulk fluid. Gas will therefore diffuse into the bubble. Conversely, when the bubble is compressed, the gas concentration within the bubble is greater than in the bulk, and gas will dissolve out of the bubble. Since the bubble has more surface area when it is large, there will be a net increase of gas within the bubble during a given acoustic cycle. Over time, the bubble will grow, until it becomes unstable and fragments, subsequently repeating the rectification cycle.

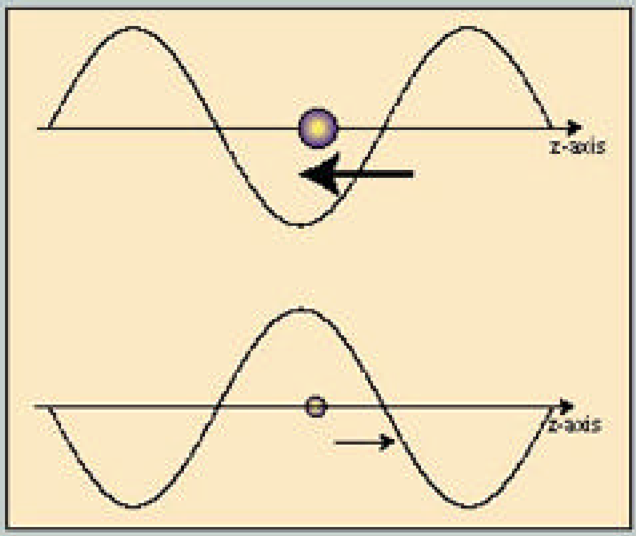


Figure 2. *The response of bubbles to an applied acoustic pressure depends on their size. Small bubbles (smaller than resonance size) are driven towards pressure antinodes, where they pulsate in phase with the driving pressure, as shown in this figure. Large bubbles are driven toward pressure nodes.*

Experimental Setup

Studies are being conducted in both cavitation-field and single-bubble systems. The single-bubble system can be controlled to a high level, allowing us to make direct correlations with changes in physical or chemical properties to changes in a particular parameter being modified.

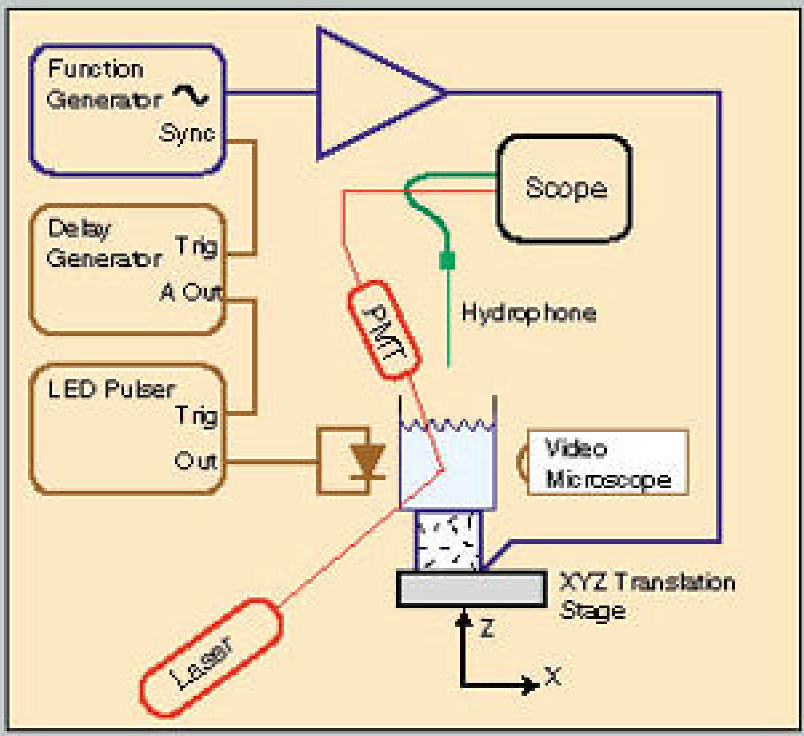
Single-Bubble System

Figure 3(a) illustrates our single-bubble apparatus. A small bubble is levitated in an acoustic standing wave. A hydrophone measures the driving pressure amplitude directly at the location of the bubble. A light-scattering system measures the radial pulsations of the cavitation bubble (see Figure 1). An imaging system is used to calibrate the light-scattering system. The parameters that can be controlled (and measured) in this system include the gas content and concentration, the ambient pressure and driving acoustic pressure amplitude, the driving frequency, and the temperature. Note that if the bubble is driven above the incipient luminescence threshold, light emission (sonoluminescence, or SBSL) occurs when the bubble collapses. This emission can be analyzed with a photomultiplier tube and spectrometer.

Cavitation-Field System

Figure 3(b) illustrates our experimental system for cavitation field studies. Controllable parameters in this system include the driving pressure amplitude, frequency, ambient pressure, gas content and concentration, and temperature. As in the single-bubble system, when driven with sufficient power, sonoluminescence occurs. The light emission for this system can also be analyzed with a photomultiplier tube and spectrometer.

(a)



(b)

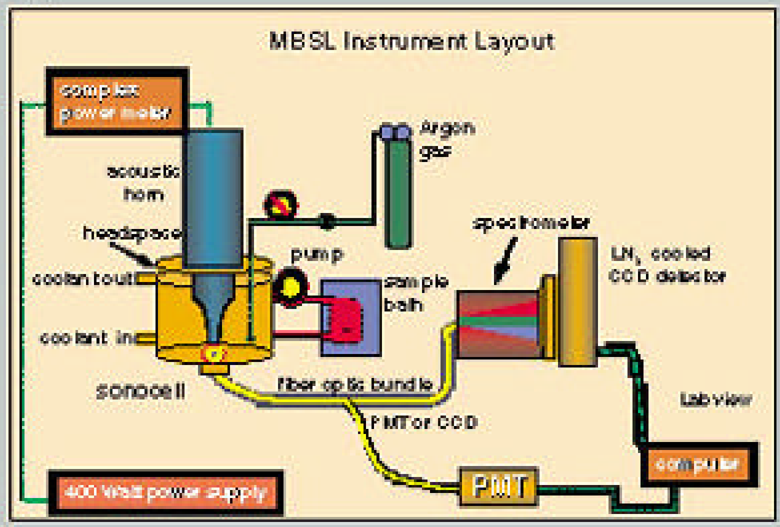
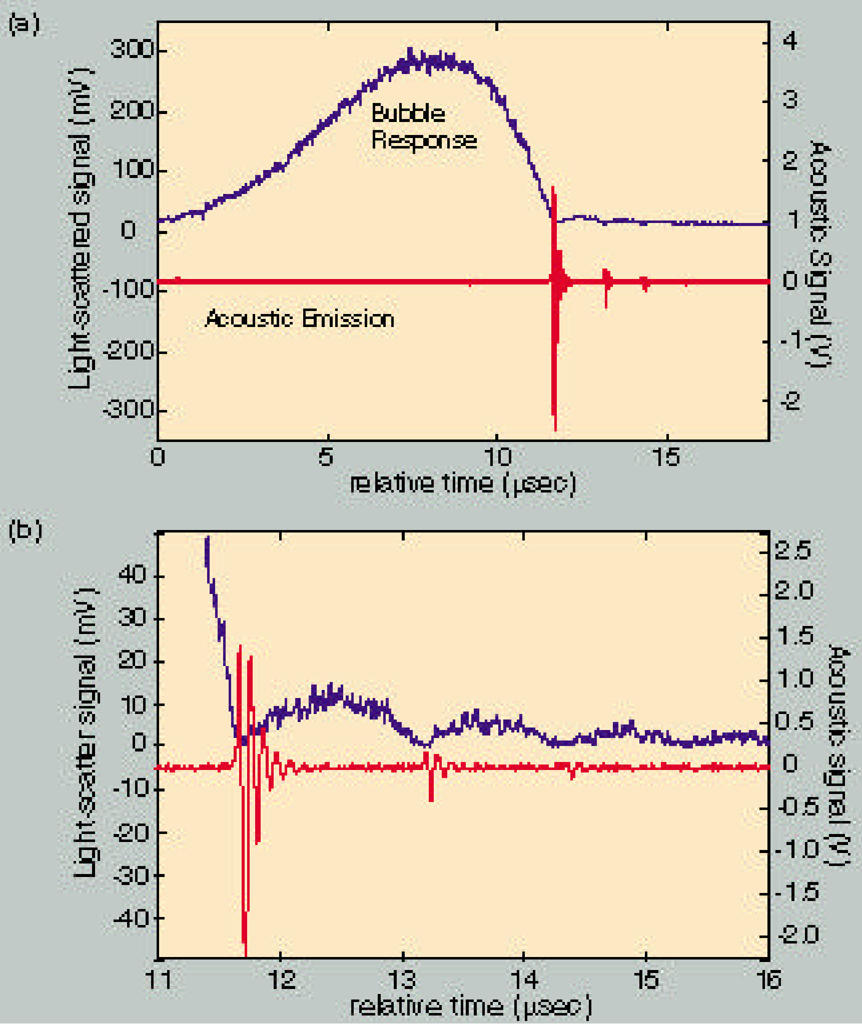


Figure 3. *(a) Our single-bubble cavitation system includes a cell for levitating a bubble, a light-scattering system for measuring the dynamical response of a single bubble, and imaging system that allows calibration of the light-scattering apparatus, and a calibrated hydrophone to measure the acoustic pressure amplitude. (b) The corresponding multi-bubble sonoluminescence (or MBSL) experimental setup.*

Emission Characteristics

Acoustic emissions from cavitating bubbles

The highly energetic collapse of cavitation bubbles can generate intense shock waves. Figure 4 shows the acoustic emission from the main collapse, as well as from several afterbounces [Matula, 1998]. Although not shown here, there is experimental evidence that the emitted shock wave from the main collapse can exceed several thousand atmospheres.



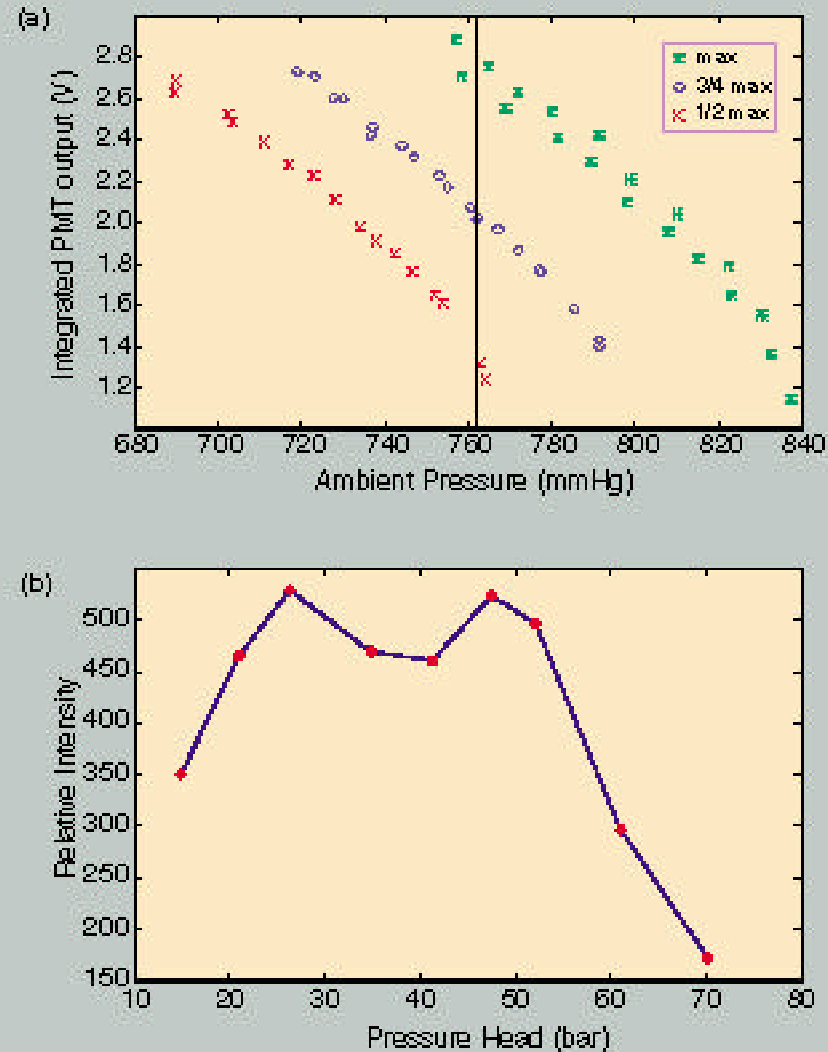


Figure 5. *(a) The static, or ambient pressure has a great effect on the light intensity in SBSL. Increasing the static pressure results in a decreases in light intensity. This added pressure keeps the bubble from expanding, and thus serves to limit the collapse energy. (b) In MBSL, increasing the static pressure causes the light intensity to increase to a maximum, before decreasing again. This effect is opposite to what is observed in SBSL.*

Figure 4. *(a) The violent collapse of bubbles leads to the emission of an intense shock wave which can exceed thousands of bars very near the bubble. (b) Enlargement of area inside dashed line.*

Static pressure effects in SBSL and MBSL

Changes in the driving pressure amplitude have great effects on cavitation and sonoluminescence properties. Typically, increasing the driving pressure amplitude results in more cavitation, and more light emission. In the single-bubble system, the extinction threshold limits the amplitude that can be used to drive a bubble; above this threshold, the bubble only exists in a transient fashion. In a cavitation-field, increasing the driving pressure amplitude too much may result in large bubbles that deflect and absorb the acoustic energy, and thus serves to limit the effectiveness of increasing the driving pressure amplitude.

In a series of experiments, we have attempted to control the static pressure of our systems. Figure 5 (a) illustrates the effect of changing the static pressure in our single-bubble system. The sonoluminescence intensity was monitored as the static pressure was changed. Note that the overall intensity decreases as the static pressure increases. Figure 5(b) illustrates the corresponding effect in a cavitation field. Here, note that the opposite effect is observed. In a cavitation field, the overall intensity increases as the static pressure increases. The effect may be partly explained by Figure 6. Here, the near IR spectrum of the cavitation field sonoluminescence is compared with and without the static pressure change. Although the overall light emission increases with an increase in the static pressure, the spectra have similar slopes. In fact, a ratio of the two spectra indicates that the "temperature" of the sonoluminescence does not change. We conclude that with an increase in the static pressure, more cavitation bubbles are sonoluminescing, but they are not "hotter."

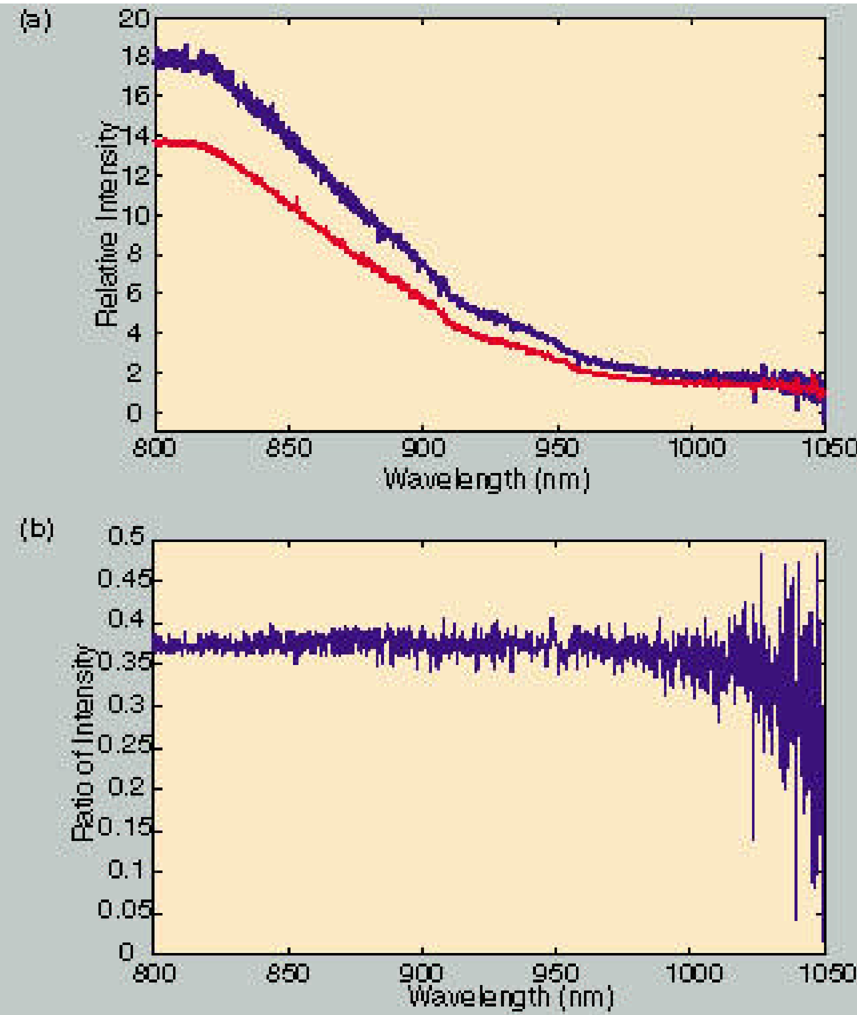


Figure 6. *Introducing a static pressure head of approximately 3 atmospheres results in a large increase in MBSL intensity. (a) Near-IR spectra shows that the intensity is increased over the entire wavelength region. (b) The ratio of the spectra is flat, indicating that the increase in intensity is not due to "hotter" bubbles, but more likely, more emitting bubbles.*

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Figure 10. *(a) and (b) The addition of the second harmonic to the fundamental drive frequency results in a modified radial response from cavitation bubbles. P_1 and P_2 are the measured fundamental and 2nd harmonic pressure amplitudes. The measured phase difference is $\Delta\theta$. (c) The third harmonic can also be used to generate stable, but modified cavitation cycles.*

Conclusions

The fundamental relationship between cavitation and the sonochemistry of aqueous waste is being explored in a systematic fashion. Comparisons to a single bubble system have allowed us to examine fundamental relationships between parameters and sonochemical and sonoluminescence effects. Current observations indicate that a static pressure head of approximately 3 atmospheres should increase the efficiency of sonochemical yields. Similarly, we find a correlation between the addition of a harmonic frequency to the fundamental frequency that might be exploited in future studies. Some preliminary evidence for the benefits of the addition of multi-frequencies has already been published [Kawabata, 1995]. Our studies on the static pressure effect in MBSL and multi-frequency insonification in SBSL indicate that the addition of harmonics may result in additional bubbles available for sonochemical activity. Finally, we find that small additions of alcohols have a dramatic influence on the sonoluminescence emission. This may have some applications for detecting contaminants.

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Spectra

Another comparison that shows interesting differences and similarities is in the spectra of the emitted light. Figure 6 shows how the spectra compare with a 0.1 molar solution of sodium chloride. In Figure 6(a) the MBSL spectrum shows the sodium doublet near 589 nm, while the SBSL spectrum shows no sodium emission [Matula, 1996]. One possible explanation is that the spherical symmetry of SBSL prevents any nonvolatile alkali metal from entering the bubble, and subsequently, no sodium emission can occur. Also, the lack of sodium emission may show that the temperature of the fluid immediately surrounding the bubble does not get hot. Also note the observed hydroxyl radical emission near 310 nm in MBSL. Again, no such emission is observed in SBSL.

Figure 6(b) shows a similar comparison in the near-IR. Again, one can observe the sodium peak near 819 nm in the MBSL system, but not in the SBSL system. As the concentration of sodium is increased, the MBSL line increases in strength. As the concentration increases in the SBSL system, the bubble becomes unstable, and thus we are prevented from looking for sodium emission at much higher concentrations.

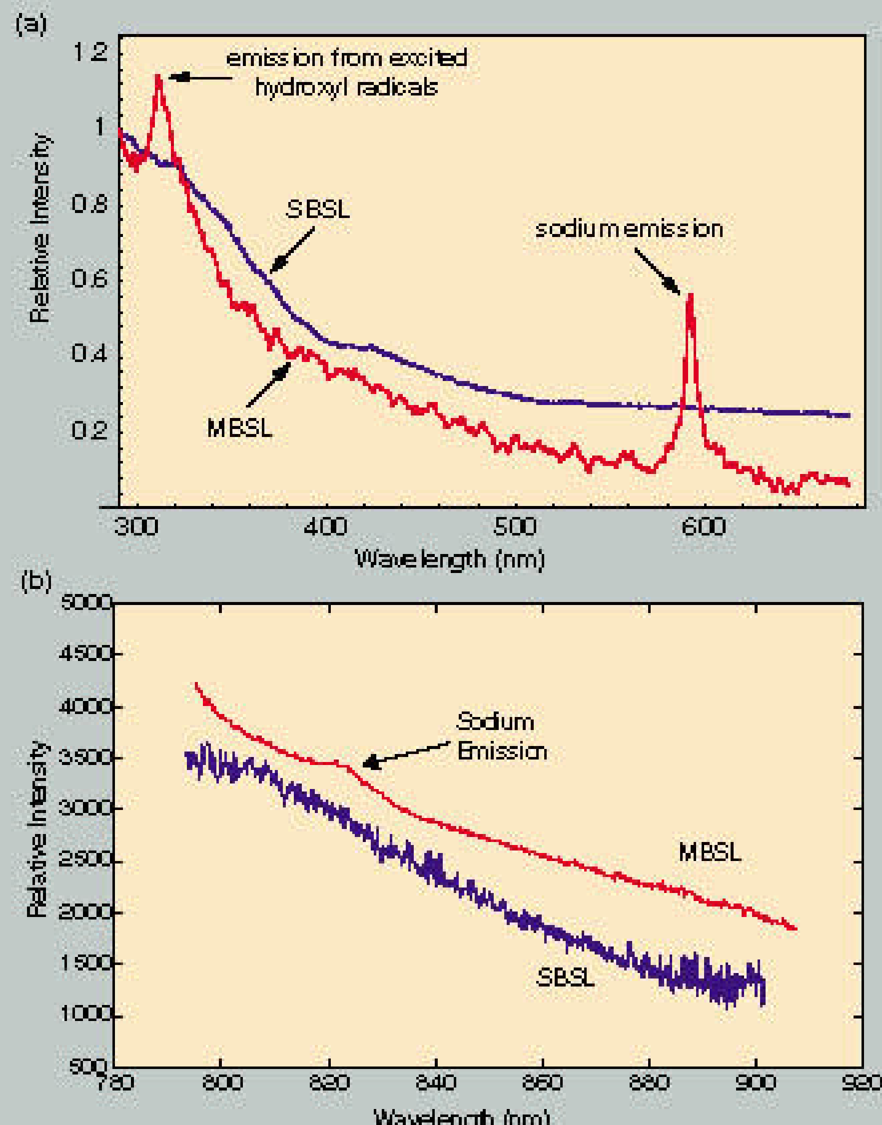


Figure 6. *Some similarities and differences between single bubbles and cavitation fields are clearly seen in this spectral comparison in this 0.1 molar sodium chloride aqueous solution. In SBSL, the spectrum is void of features, and appears as a tail of a blackbody radiator. (a) The MBSL spectrum shows evidence of sodium emission at (a) 589 nm, and (b) 819 nm, as well as band emission from excited state hydroxyl radicals.*

Organic Doping

In a series of experiments, we compared the overall sonoluminescence intensity between MBSL and SBSL with the addition of small quantities of alcohol. In our initial experiments, we chose to study methanol, ethanol, propanol, butanol, and pentanol, for the relative simplicity of the contaminants. Figure 9(a) shows the effects of the addition of minute quantities of some of these alcohols for SBSL. A similar trend is observed in MBSL [Ashokkumar, et al., 1997]. Note that in each case, as the chain length of the alcohol increases, the overall light intensity decreases.

An interesting effect occurs when the intensity of the light is plotted against the 2-D surface excess concentration. The surface excess is defined as the change in the surface tension with alcohol concentration, or

$$\Gamma = \frac{-1}{k_b T}\frac{\partial \sigma}{\partial(\ln[ROH])},$$

where, k_b is the Boltzmann constant, s is the surface tension, and [ROH] is the concentration of alcohol. Figure 9(b) shows that all the data line up when plotted in this fashion [Ashokkumar, et al., 1998]. Similar observations are observed with MBSL data. Current experiments are underway to more precisely measure the spectral properties of the light emission, and radial dynamics of the bubble, in order to understand the mechanism for the light "quenching."

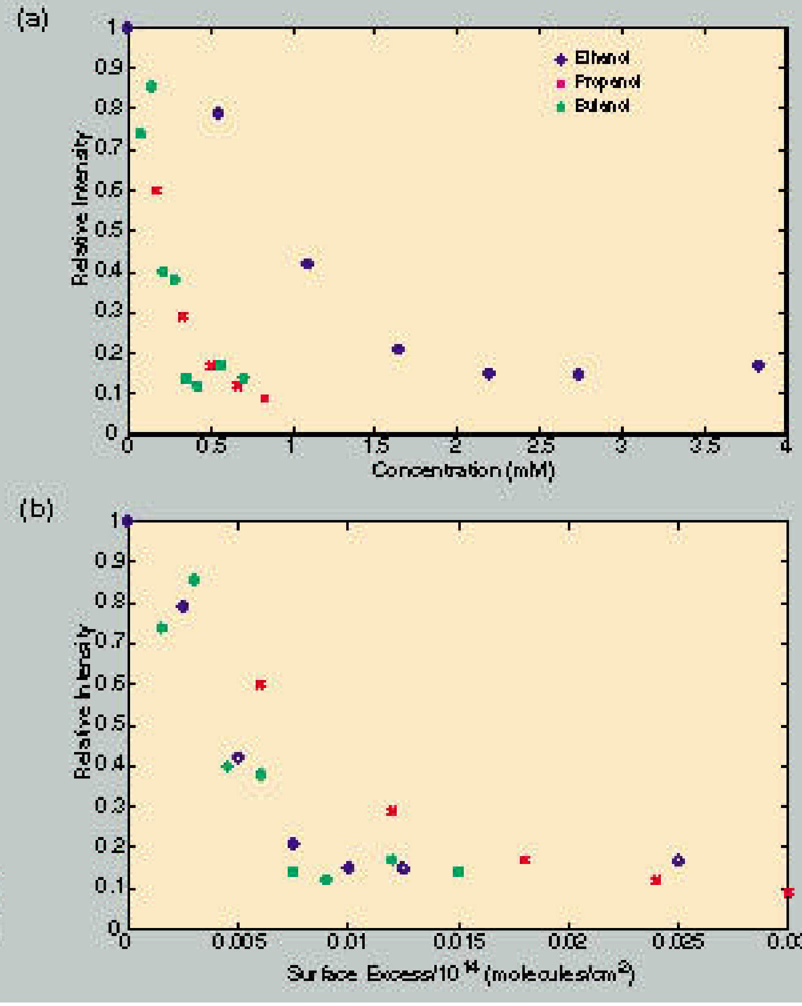
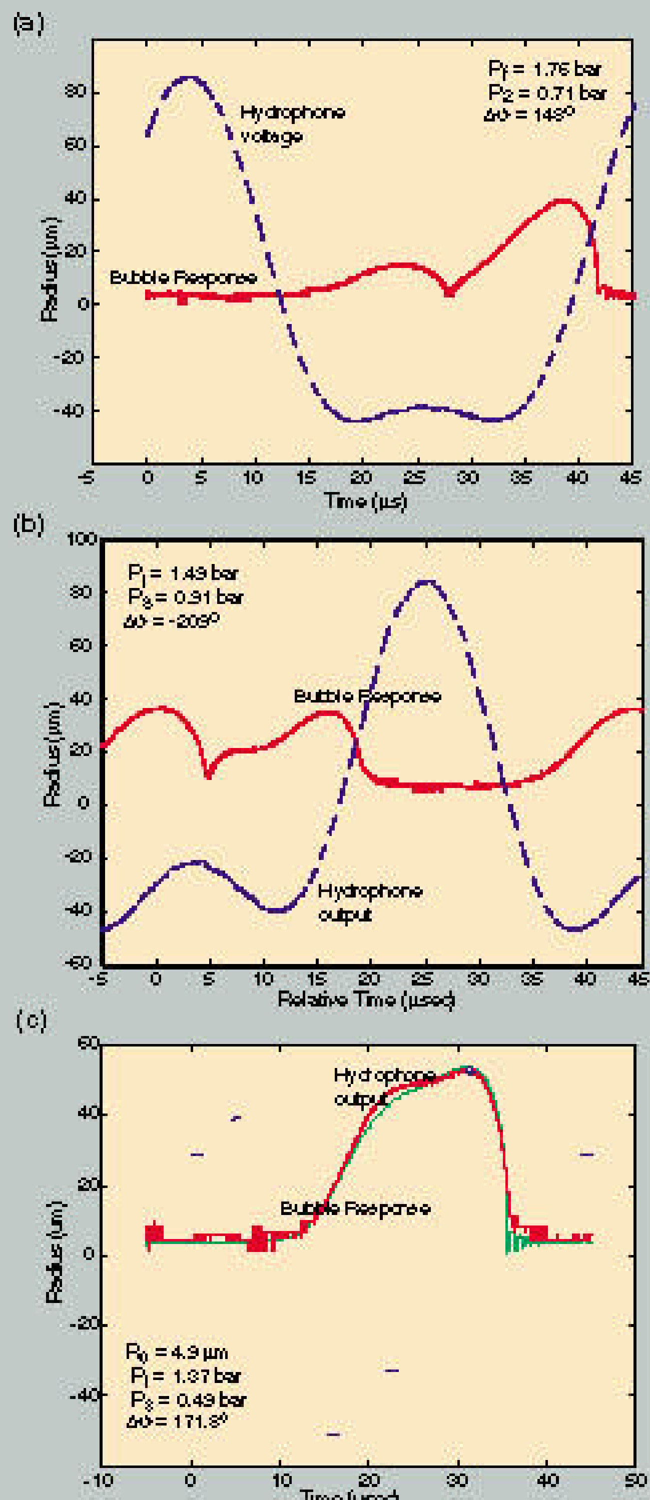


Figure 9. *(a) The effects of adding minute quantities of alcohol to our single-bubble system. For a given concentration, the intensity decreases with increasing chain length. (b) When the intensity is plotted as a function of the surface excess concentration, the data appear to group together.*

Multi-frequency Studies

Previous research has shown the potential of increasing the sonochemical yield by applying non-sinusoidal waveforms to certain systems. A typical application might involve the application of a 20 kHz sinusoid with a much higher sinusoid, around 500–1,000 kHz. We have examined in a fundamental way the non-sinusoidal application of ultrasound, and the corresponding effect on a single cavitation bubble. Due to system constraints, we chose to examine the addition of the second and third harmonic frequencies to the fundamental frequency. The results are shown in Figure 10, and should be compared with figure 1. Note how the expansion and collapse sequence can be modified. Also note that the modified radial motion agrees well with bubble dynamics codes.



SBSL/MBSL Comparisons

Argon Rectification

The highly controllable system of a single bubble may be extremely useful for predicting cavitation-field effects. One question that arises is how closely a single bubble corresponds to bubbles in a cavitation field. It turns out that single bubbles are in a steady-state, and the contents of these bubbles may be different from bubbles in a cavitation field, which only exist for a few acoustic cycles. Figure 7 shows that a single air bubble may undergo rectification of argon, which results in the bubble contents being mostly argon. The mechanism is rather straightforward [Lohse, 1997]. During the bubble collapse, the contents heat up. Nitrogen and oxygen undergo molecular dissociation into excited state species, and form products such as NO, NO_2, H_2O_2, etc. These products irreversibly leave the bubble, leaving mostly argon inside. This hypothesis was tested by looking at the temporal history of sonoluminescence from a single bubble [Matula and Crum, 1998].

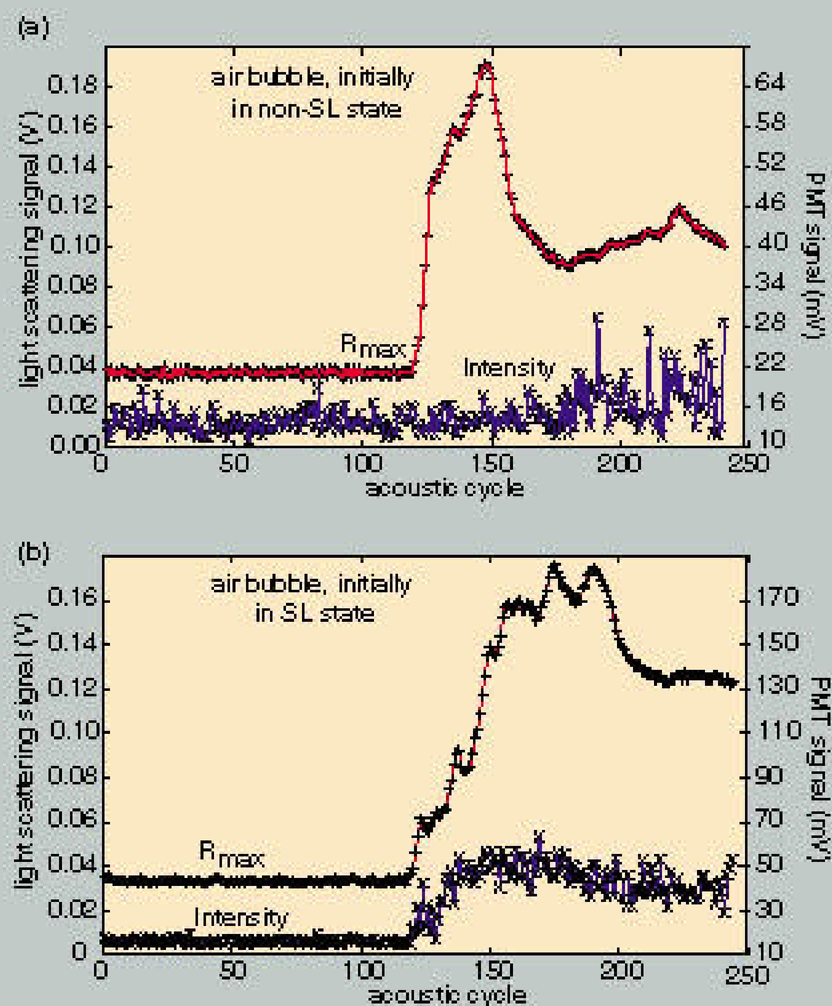


Figure 7. *With a single bubble, the steady-state response may involve gas diffusion, or even preferred rectification of particular gases. (a) Here, we show that an air bubble in water responds differently, depending on the past history of the bubble. In (b), the temporal history of SBSL is similar to an argon bubble.*