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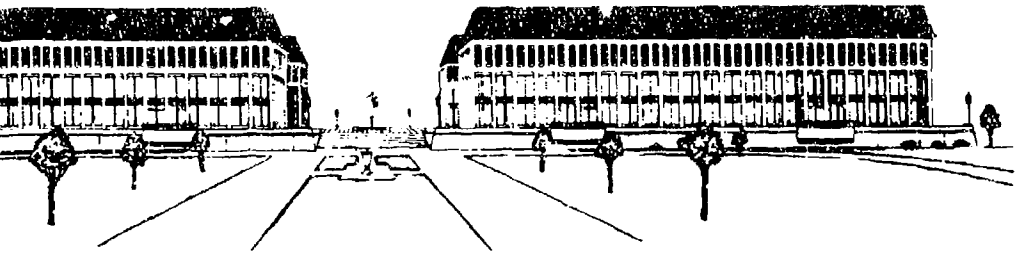

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Technical Report No. 377

August 1977

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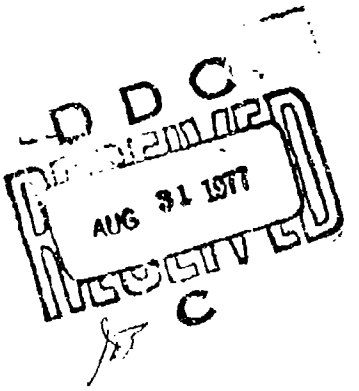
Measurements of the Growth of Air Bubbles by Rectified Diffusion



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Measurements are reported of the growth of air bubbles by rectified diffusion at 21.6 kHz. Values of the threshold acoustic pressure amplitude were obtained as a function of bubble radius and liquid surface tension and show good agreement with theory. Measurements of the rate of growth of bubbles by rectified diffusion as a function of acoustic pressure amplitude for varying surface tension show agreement only for high surface tension. When the surface tension is lowered by the addition of a surfactant,

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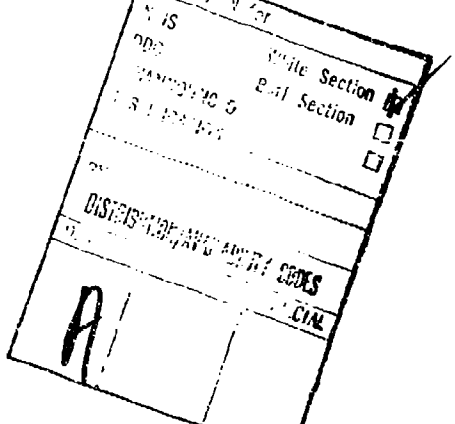
the observed growth rates become much larger than predicted. Surface wave activity that could increase the growth rate by acoustic streaming was not observed at low radii and was discounted as the responsible mechanism. A possible explanation for the large growth rates is given in terms of a retardation of outward gas diffusion by an organic monolayer present on the surface of the air bubble.



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ABSTRACT

Measurements are reported of the growth of air bubbles by rectified diffusion at 21.6 kHz. Values of the threshold acoustic pressure amplitude were obtained as a function of bubble radius and liquid surface tension and show good agreement with theory. Measurements of the rate of growth of bubbles by rectified diffusion as a function of acoustic pressure amplitude for varying surface tension show agreement only for high surface tension. When the surface tension is lowered by the addition of a surfactant, the observed growth rates become much larger than predicted. Surface wave activity that could increase the growth rate by acoustic streaming was not observed at low radii and was discounted as the responsible mechanism. A possible explanation for the large growth rates is given in terms of a retardation of outward gas diffusion by an organic monolayer present on the surface of the air bubble.

INTRODUCTION

This paper concerns the phenomenon of rectified diffusion of gas into air bubbles that are caused to pulsate in a liquid by the action of an acoustic field. Free bubbles present in water that would normally dissolve may be caused to grow due to the unequal mass transfer across the air-water interface during bubble oscillation.

Theoretical predictions of the threshold for rectified diffusion have been shown to agree with experiment[1,2] and rates of growth that seemed excessive were shown to be due to increased acoustic streaming introduced by surface waves present on the bubble.[3] In this paper, measurements will be presented of the growth of air bubbles by rectified diffusion, both at and above the threshold, for various values of the liquid surface tension, the acoustic pressure amplitude and bubble radius. Comparisons with theoretical predictions indicate a substantial disagreement with theory for the rate of bubble growth at low surface tensions.

In a historical sense, it is desirable to briefly review the progress of research concerning rectified diffusion. The phenomenon seems to have originated with Harvey,[4] and was first discussed in some detail by Blake,[5] who formulated an inadequate theory for predicting the threshold. Attempts by Pode[6] and Rosenberg[7] were also found inadequate to explain some of the early measurements by Strasberg.[8] Hsieh and Plesset,[9] by adding a convection term in the diffusion equation, considerably improved upon Blake's approximate results. Their theory was shown by Strasberg[10] to be in good agreement with his measured values. Eller and Flynn[11] extended the

theory to include nonlinear or large amplitude effects and Safar[12] showed that the Hsieh-Plesset and Eller-Flynn treatments were essentially equivalent when inertial effects were not neglected in the Hsieh-Plesset approach. Eller[1,2] made several measurements of both the threshold and the growth rate and found that his theory was adequate in predicting thresholds but was unable to account for some very large growth rates that he observed. He suggested that the rapid rates of growth may be accounted for by acoustic microstreaming. Gould[3] has observed bubbles growing by rectified diffusion and has found agreement with Eller's theory in the absence of streaming. By observing the bubble directly in a microscope he was able to detect the onset of surface oscillations of the bubble that in turn introduced significant acoustic microstreaming. This streaming greatly enhanced bubble growth and was likely the explanation for the large growth rates seen by Eller. Attempts by Davidson[13] and by Kapustina and Statnikov[14] to account for enhanced growth rates by microstreaming appear to be inadequate.[3]

I. EQUATIONS FOR BUBBLE GROWTH

Eller[2] has simplified the more general theory[11] and obtained an approximation for the growth rate that is easy to apply to the data of this experiment. The rate of change of the equilibrium bubble radius with time is

$$\frac{dR}{dt} = \frac{Dd}{R}\left[\frac{2(1 - \beta^2/8)}{3\delta(1 - \beta^2)^2}\left(\frac{P_a}{P_0}\right)^2 - \frac{2\sigma}{RP_0}\right] , \qquad (1)$$

where D is the diffusion constant, P_a is the acoustic pressure amplitude, P_0 is the ambient pressure, σ is the surface tension of the liquid, d is the ratio of the concentration, in mass per unit volume, of dissolved gas to the density of gas in equilibrium with the solution, and β^2 is given by

$$\beta^2 = \rho\omega^2R^2/3\delta P_0 . \qquad (2)$$

In Eq. 2, ρ is the density of the liquid and ω the angular frequency. In these equations, δ is a constant that has the value 1.0 for isothermal pulsations and the value 1.4 for the adiabatic case. Since the gas in the interior of the bubble behaves isothermally in some cases and adiabatically in others, Eller found it simpler to solve the diffusion problem for the two limits rather than the general case. Unfortunately, for the range of values in this experiment, the gas behaves neither isothermally nor adiabatically, but in an intermediate region. It is possible to approximate the effect of heat conduction on the diffusion problem by using the value of the heat conduction parameter η calculated for a pulsating bubble without diffusion and obtained by Crum and Eller[15] based on the work of Devin[16].

it is thus assumed that the gradual diffusion will not affect the heat conduction properties of the gas within the bubble. The heat conduction parameter is given by

$$\eta = \gamma\,(1 + d_{th}^2)^{-1}\left[1 + \frac{3(\gamma - 1)}{X}\left(\frac{\sinh(X) - \sin(X)}{\cosh(X) - \cos(X)}\right)\right]^{-1}, \qquad (3)$$

where

$$d_{th} = 3(\gamma - 1)\left[\frac{X(\sinh(X) + \sin(X)) - 2(\cosh(X) - \cos(X))}{X^2(\cosh(X) - \cos(X)) + 3(\gamma - 1)\,X(\sinh(X) - \sin(X))}\right],$$

and $X = R\,(2\omega/D_1)^{1/2}$.

γ is the ratio of specific heats of the gas within the bubble. The constant $D_1 = K_1/\rho_1 c_{p1}$, where K_1 is the thermal conductivity of the gas in the bubble, ρ_1 is the density of the gas, and c_{p1} is the specific heat at constant pressure for the gas.

The growth rate equation used for calculations in this experiment was thus Eq. 1 with δ replaced by η as given in Eq. 3. The equation for the threshold for rectified diffusion is obtained by setting the growth rate equal to zero in Eq. 1 and solving for the acoustic pressure amplitude. The threshold acoustic pressure amplitude required for growth is then

$$P_a = P_0\,(1 - \beta^2)\left[\frac{3\eta\sigma/RP_0}{1 - \beta^2/8}\right]^{1/2}. \qquad (4)$$

Note that δ has been replaced by η.

The constants that were used in the above equations and applicable to this experiment are $f = \omega/2 = 21.6$ kHz, $\gamma = 1.4$, $D_1 = 0.20$ cm^2/sec, $P_0 = 1.01 \times 10^6$ dyn/cm^2, and $\rho = 1.0$ gm/cm^3. The constants D and d were corrected for temperature variations by the following equations: $D = (6.15 \times 10^{-7}\,T - 15.6 \times 10^{-5})$ cm^2/sec and $d = 1.02 \times 10^{-1} - 2.80 \times 10^{-4}\,T$

(unitless), where T is the absolute temperature. Distilled water used for the experiment was tested with an oxygen analyzer and found to be near saturation.

II. EXPERIMENTAL PROCEDURE AND SOME RESULTS

The various data concerning the growth of bubbles by rectified diffusion was obtained by acoustically levitating the air bubbles near the antinode of an acoustic stationary wave. This technique[1,2,3,17,18] has become quite common for many applications and will not be described here. The stationary wave system was constructed by cementing a hollow glass cylinder between two matched hollow cylindrical transducers, fitted with a flexible pressure release diaphragm on one end and open at the other. The composite system was approximately 7.5 cm in diameter by 10 cm in height; the width of the glass in the middle about 2.5 cm. This system was driven at its $(r,\theta,z) = (1,0,1)$ mode at a frequency of 21.6 kHz. The bubble was clearly visible through the glass cylinder under dark field illumination and measurements of its terminal rise velocity were made through the glass wall with a precision cathetometer. The bubble's size was measured by iterating the rise velocity equation of Langmuir and Blodgett[18,19]

$$R^2 = \left(\frac{9\nu}{2g}\right) u \left[1 + 0.20\, R_e^{0.63} + 2.6 \times 10^{-4}\, R_e^{1.4}\right], \quad (5)$$

where ν is the kinematic viscosity of the liquid, u is the terminal rise velocity, g is the gravitational acceleration and $R_e = 2Ru/\nu$ the Reynolds number.

The variation of the acoustic pressure amplitude along the vertical axis of the system was measured with a small calibrated probe hydrophone, and by positioning the hydrophone accordingly, was used to monitor the acoustic pressure at the bubble position during measurements. Because the position of the bubble in the stationary wave system is a function of the acoustic pressure amplitude and its gradient, but independent of bubble size, measurements of the growth rate of the bubble for a particular acoustic pressure amplitude could be obtained simply by measuring the rise velocity as a function of time. This investigation of rectified diffusion was also made as a function of the surface tension of the liquid. A commercially available surfactant, ethoxylated octaphenol, marketed under the brand name Photoflo, and common in photographic applications, was used. The addition of 25 ppm by weight was sufficient to lower the surface tension from 72.4 dyn/cm to 50 dyn/cm. Addition of large amounts of surfactant lowered the surface tension to a minimum of approximately 30 dyn/cm. The surface tension of the bulk liquid was measured while in the transducer system with a Du Nouy ring tensiometer.

The various rectified diffusion measurements will now be described.

A. Threshold for Rectified Diffusion

The threshold for rectified diffusion was determined by observing the bubble's growth rate as a function of time and acoustic pressure amplitude. A bubble was levitated in the system and observed through the cathetometer. Its rise velocity was measured for equal time intervals, and if the rise velocity decreased or increased the pressure amplitude was below or above threshold respectively.

Figure 1 shows a graph of the acoustic pressure amplitude as a function of bubble radius for a surface tension of 55 dyn/cm. Plotted on the graph are points where the bubble was observed to be growing, dissolving or stable. Also shown are theoretical curves calculated using Eq. 4 with $\eta = 1.0$ (isothermal case), $\eta = 1.4$ (adiabatic case) and η given by Eq. 3.

It is seen first of all that reasonably good agreement is obtained between theory and experiment in confirmation of the earlier results of Eller[1,2]. Further, the addition of the heat conduction parameter does not significantly improve the agreement; it merely solves the dilema of the choice between the two heat conduction limits. Actually, the data are probably not good enough to resolve the difference in this particular case.

Similar data to these were taken for other liquid surface tensions and a graph of the threshold acoustic pressure amplitude as a function of surface tension for a radius of 5.0×10^{-3} cm is shown in Fig. 2. Again good agreement is found and it is reasonable to assert that the threshold for rectified diffusion of gas into air bubbles for a wide range of bubble radii and surface tension can be adequately predicted by theory.

B. Bubble Growth Rates

In this experiment, it was possible also to obtain the absolute radius of the air bubble as a function of time. Data for the bubble radius as a function of time for a surface tension of [illegible] cm and acoustic pressure amplitudes of 0.20 bar and 0.36 bar are shown in Figs. 3 and 4 respectively. Also shown in these figures is the theoretical radius as a function of time obtained by numerically integrating Eq. 1 (with δ replaced by η) and the

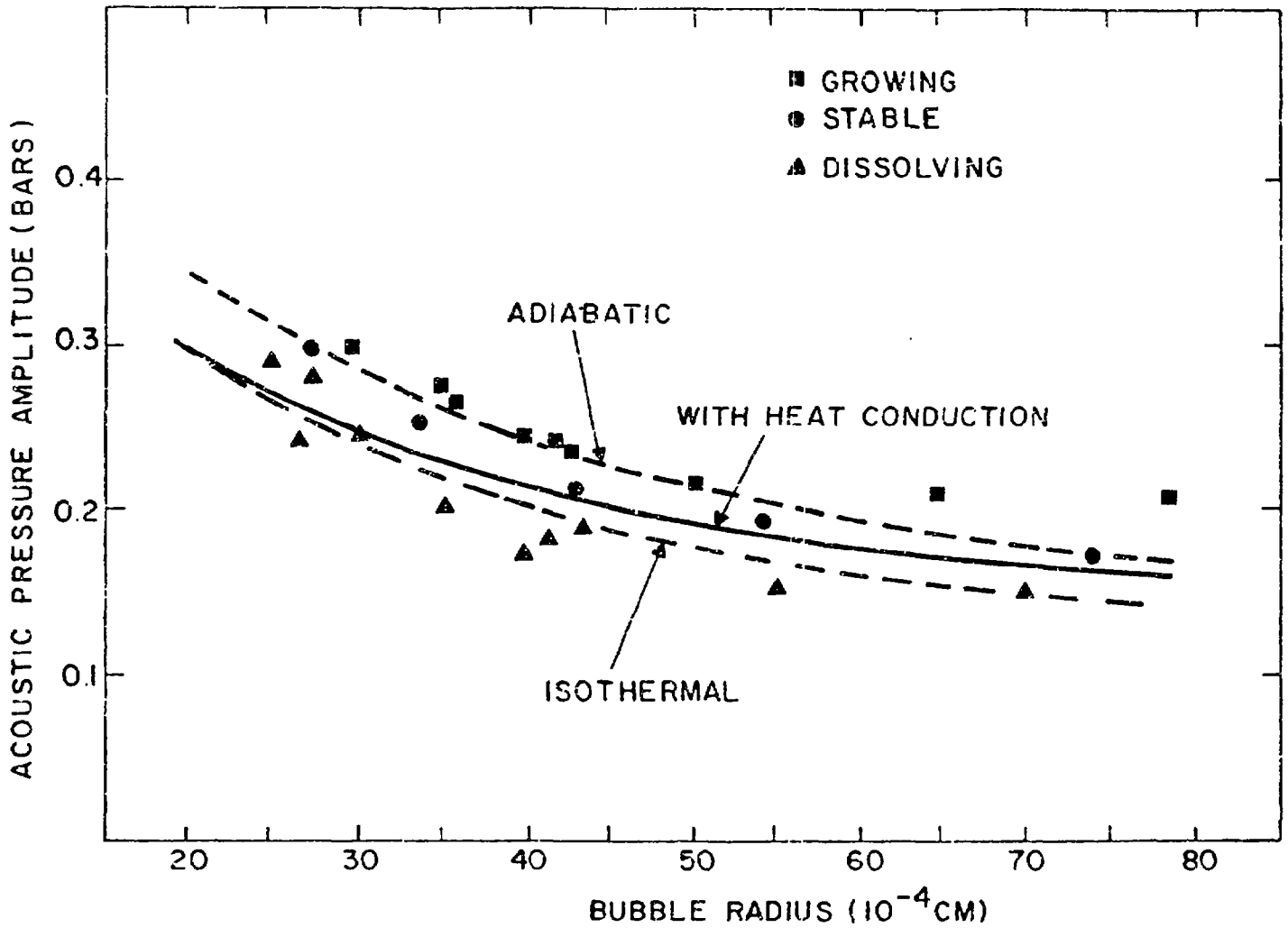

Figure 1. Values of the threshold for rectified diffusion as a function of radius for a surface tension of 55 dyn/cm and a frequency of 21.6 kHz. The curves indicate the calculated thresholds using Eq. 4 for the limiting cases of isothermal and adiabatic pulsations and when the approximate heat conduction parameter in Eq. 3 is used.

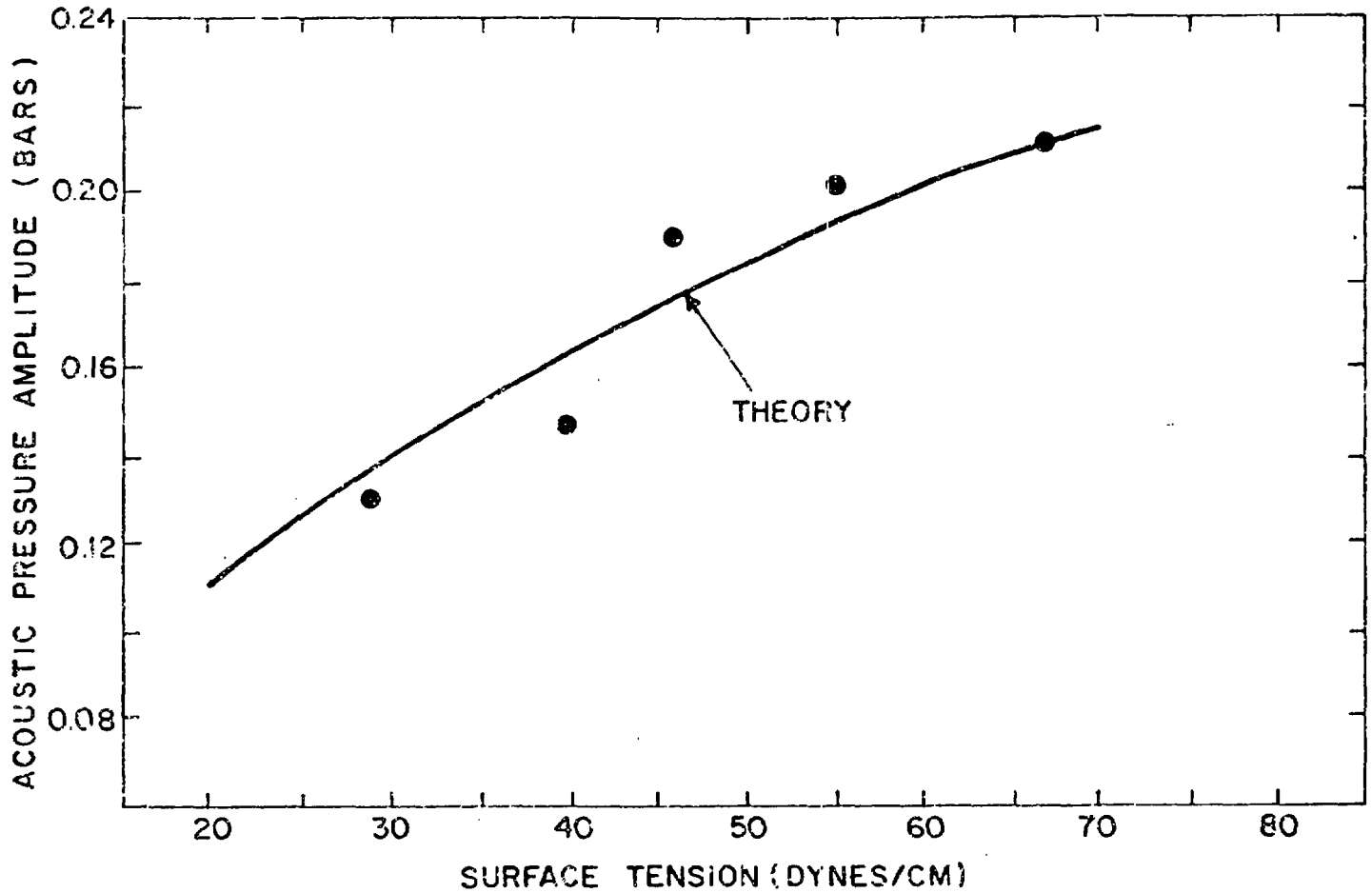

Figure 2. Variation of the threshold for rectified diffusion as a function of surface tension for a radius of 5.0×10^{-3}cm. The circles are the experimental points and the curve is calculated from Eq. 4.

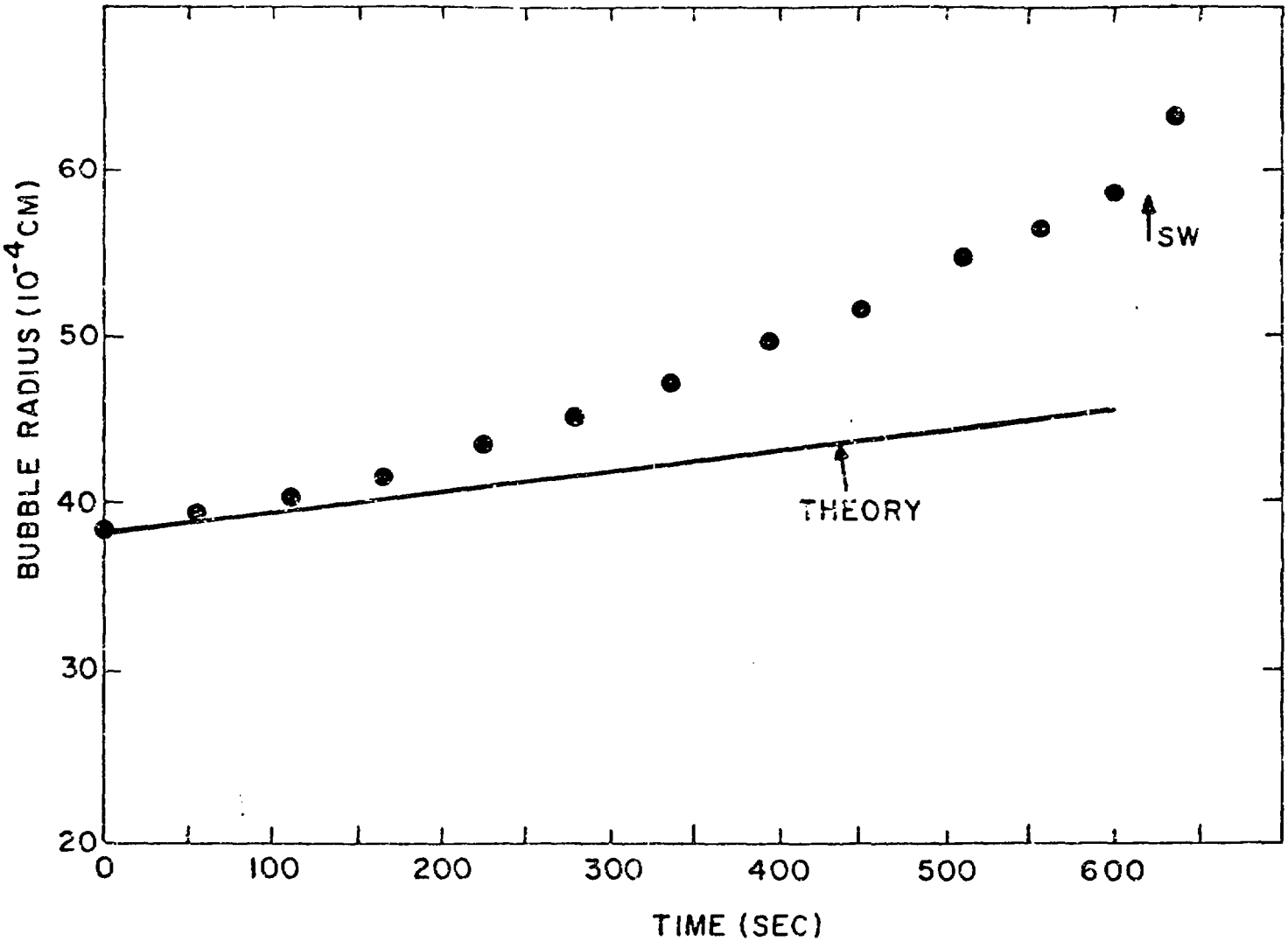

Figure 3. Variation of the bubble radius with time for a liquid surface tension of 32 dyn/cm and an acoustic pressure amplitude of 0.20 bar. The curve was obtained by numerically integrating Eq. 1. The arrow shows the point at which the scattered light intensity from the bubble indicated the presence of surface waves.

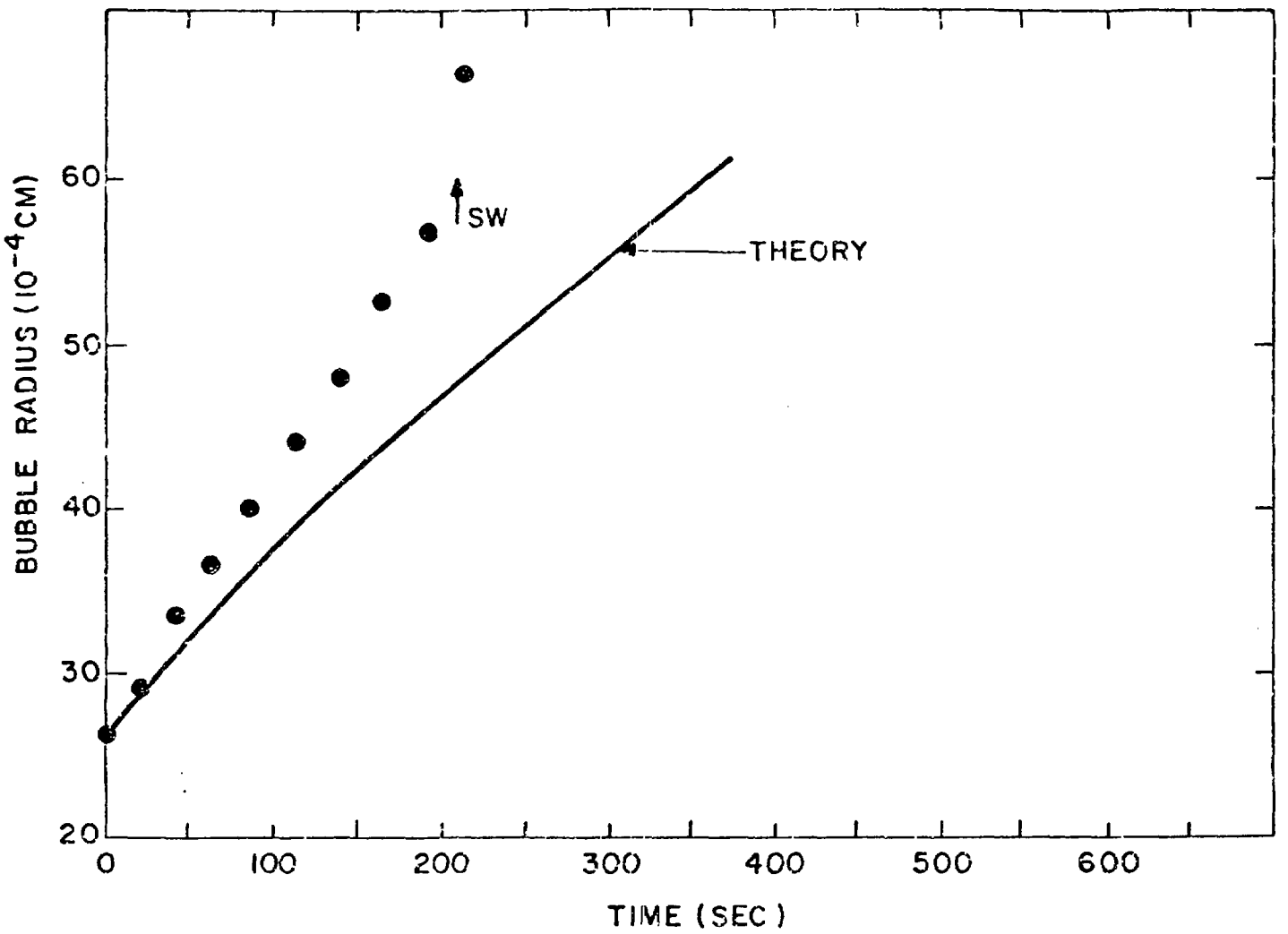

Figure 4. Variation of bubble radius with time for a liquid surface tension of 32 dyn/cm and an acoustic pressure amplitude of 0.36 bar. The curve is a numerical integration of Eq. 1 and the arrow shows the onset of detectable surface waves.

initial radius equal to the experimental one. In Fig. 3 it is seen that the experimental growth rate is not constant, but increases with time, and after a few minutes deviates markedly from the theory. Although the theoretical growth is also not exactly linear with time, it is approximately so for the range of radii covered. It should also be noted that the last data point shows a rapid increase in the growth rate. This rapid growth at radii greater than approximately 6.0×10^{-3} cm was common to most of the measurements and was accompanied by a perceptible change in the intensity and character of the scattered light from the bubble. Gould[3] has reported direct observations of surface wave activity during rectified diffusion measurements and has shown that growth rates increased rapidly after the onset of these oscillations, probably due to the induced microstreaming. In these experiments, it was not possible to observe the bubble oscillations directly but only via the scattering of light used to illuminate the bubble. Both Figs. 3 and 4 show the increased growth rates that appeared shortly after the onset of the surface waves. The fluctuating light intensity indicative of surface wave activity was not accompanied by any relative translatory motion of the bubble until the bubble had grown beyond this initial stage. The erratic dancing motion that followed has been examined previously,[20,21] and during this experiment measurements were made of the incipient threshold for dancing motion for surface tensions of 72 dyn/cm and 32 dyn/cm. It was discovered that the threshold for dancing motion for the two surface tensions was nearly identical for a range of bubble radii from 20 to 90 microns. Gould[3] observed the threshold for surface waves on bubbles with radii of 45 microns and a surface tension of 72 dyn/cm to be on the order of 0.45 bar (See Fig. 3, Ref. 3). In this experiment, values of the acoustic

pressure amplitude almost never exceeded 0.40 bar.

In Fig. 4 it is seen that the experimental growth rate is essentially constant and considerably greater than predicted. For example, at a bubble radius of 45 microns the experimental growth rate is 15.8 x 10^{-6}cm/sec while the predicted value is 8.4 x 10^{-6}cm/sec. Note also that the theory predicts an initial reduction in growth rate followed by a region in which the rate remains essentially constant.

Figure 5 is a major result of this study and shows several important features. In this graph the rectified diffusion growth rate is plotted versus the acoustic pressure amplitude for three different values of the liquid surface tension and for a fixed radius of 4.5 x 10^{-3}cm. The following features are to be noted from this graph. First, as shown earlier, the observed thresholds for rectified diffusion agree reasonably well with the predicted thresholds. Second, the observed growth rates for lower surface tensions soon deviate from the predicted values and become appreciably larger for higher pressure amplitudes. For example, for a surface tension of 32 dyn/cm and a pressure amplitude of 0.325 bar, the observed growth rate is nearly three times the predicted rate. Third, although the theory shows only a slight dependence of the growth rate on the surface tension, the observed growth rates depend markedly on it. For high surface tensions theory and experiment agree reasonably well but for low surface tensions the growth rate is appreciably larger for acoustic pressure amplitudes only slightly above threshold.

The exaggerated dependence of the growth rate on the surface tension is shown in more detail in Fig. 6. Here, the growth rate is plotted versus the surface tension for a fixed value of the radius (5 x 10^{-3}cm)

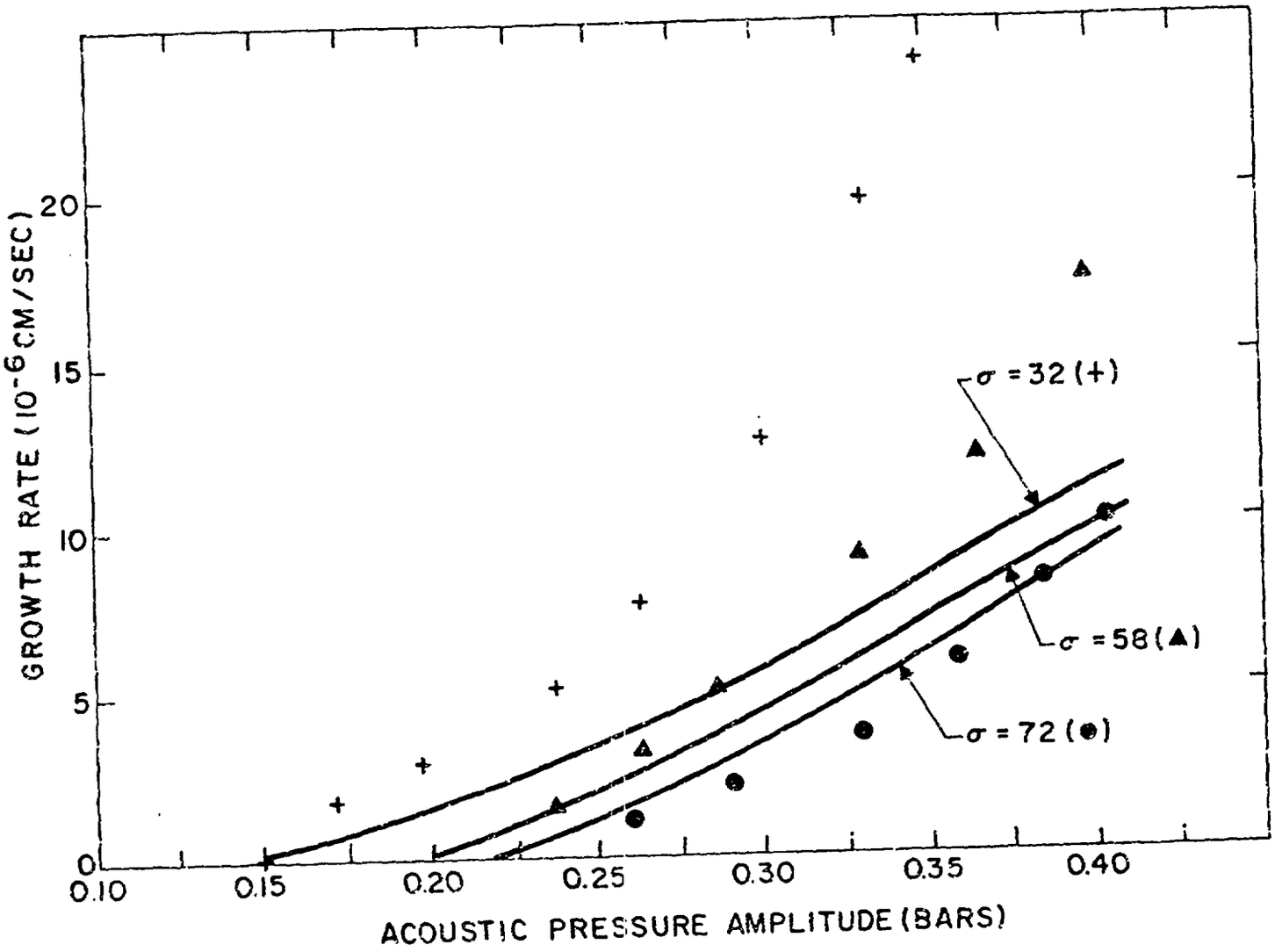

Figure 5. Variation of the rate of growth of air bubbles by rectified diffusion with acoustic pressure amplitude for a range of liquid surface tensions and a bubble radius of 4.5×10^{-3} cm. The curves were calculated from Eq. 1. Note that the threshold for rectified diffusion is correctly predicted as well as the growth rates for water at high surface tension.

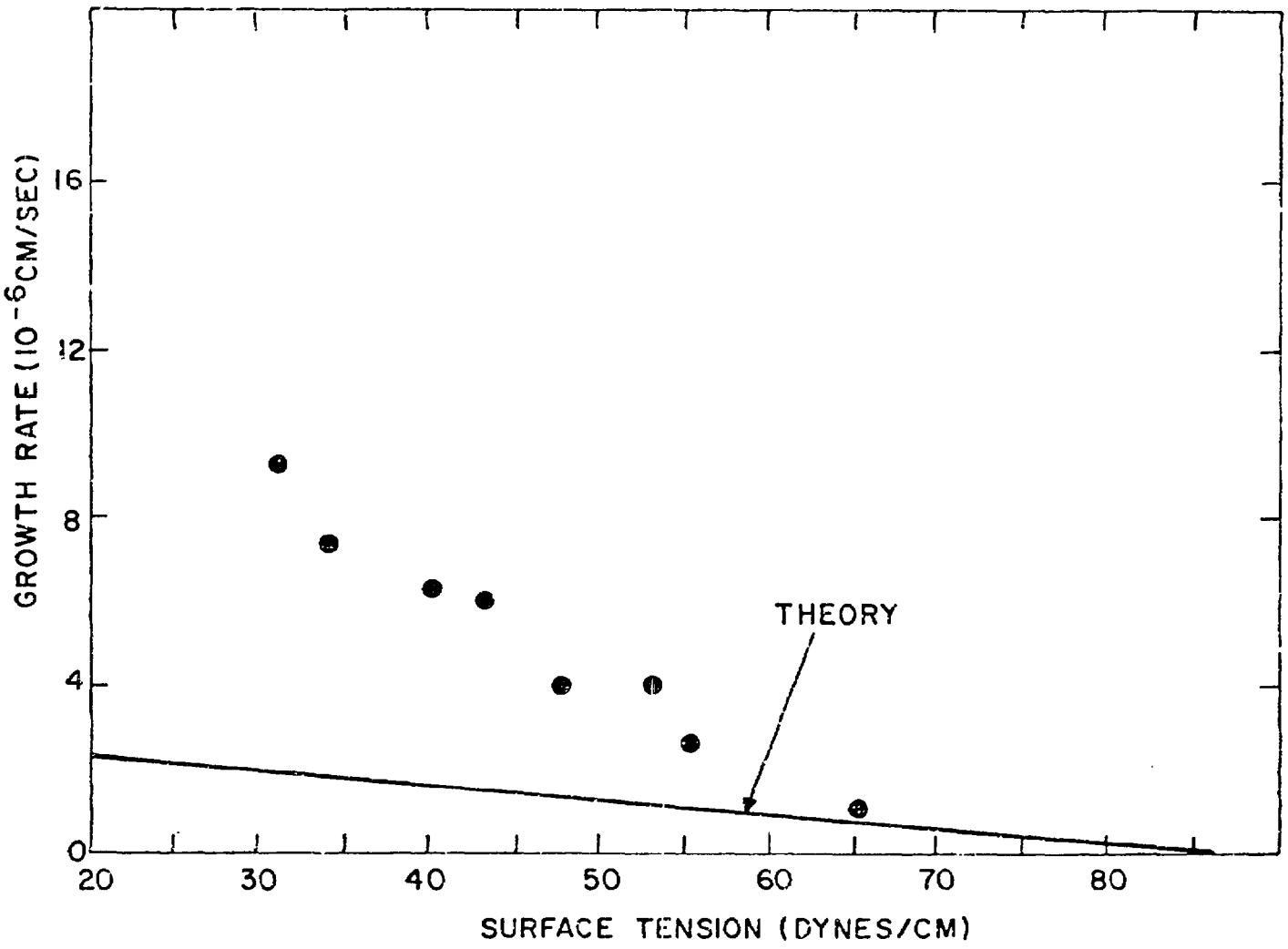

Figure 6. Variation of the rate of growth of air bubbles by rectified diffusion with surface tension for a bubble radius of 5.0×10^{-3} cm and an acoustic pressure amplitude of 0.22 bar. The curve is calculated from Eq. 1.

and a fixed pressure amplitude (0.22 bar). Note the increased deviation from theory for lower surface tensions.

When increasing amounts of surfactant are added to water, the surface tension is reduced until the monomolecular film saturates the surface. It is thought[22] that the long thin molecules are oriented with their polar ends interacting with the water and their nonpolar ends projecting away from the water. After the surfactant molecules have saturated the surface, the surface tension remains constant, and is not reduced upon the addition of more surfactant. In this experiment, it was found that 1300 ppm of Photoflo added to water was sufficient to reduce the surface tension to 32 dyn/cm; additional amounts had no further surface tension reduction.

Figure 7 shows the variation in the bubble growth rate with acoustic pressure amplitude for surfactant concentrations exceeding saturation. By saturation is meant that additional surfactant would not lower the surface tension. Growth rates are plotted for two cases: one in which the surfactant concentration is at saturation (approximately 1300 ppm) and another in which the surfactant concentration was increased to 3300 ppm. In both cases the growth rates were determined at 4.5×10^{-3}cm. It is observed that in the case of surfactant concentration above saturation, the threshold for rectified diffusion is lowered below the predicted value. The actual threshold could not be determined because of equipment limitations.

The liquid sample with surfactant concentration exceeding saturation was obtained by simply adding extra amounts of surfactant to the liquid sample at saturation. Although the growth rate curve in Fig. 7 for the second cases seems to indicate a solution oversaturated with gas, the two curves were obtained using the same sample of water. Also, measurements

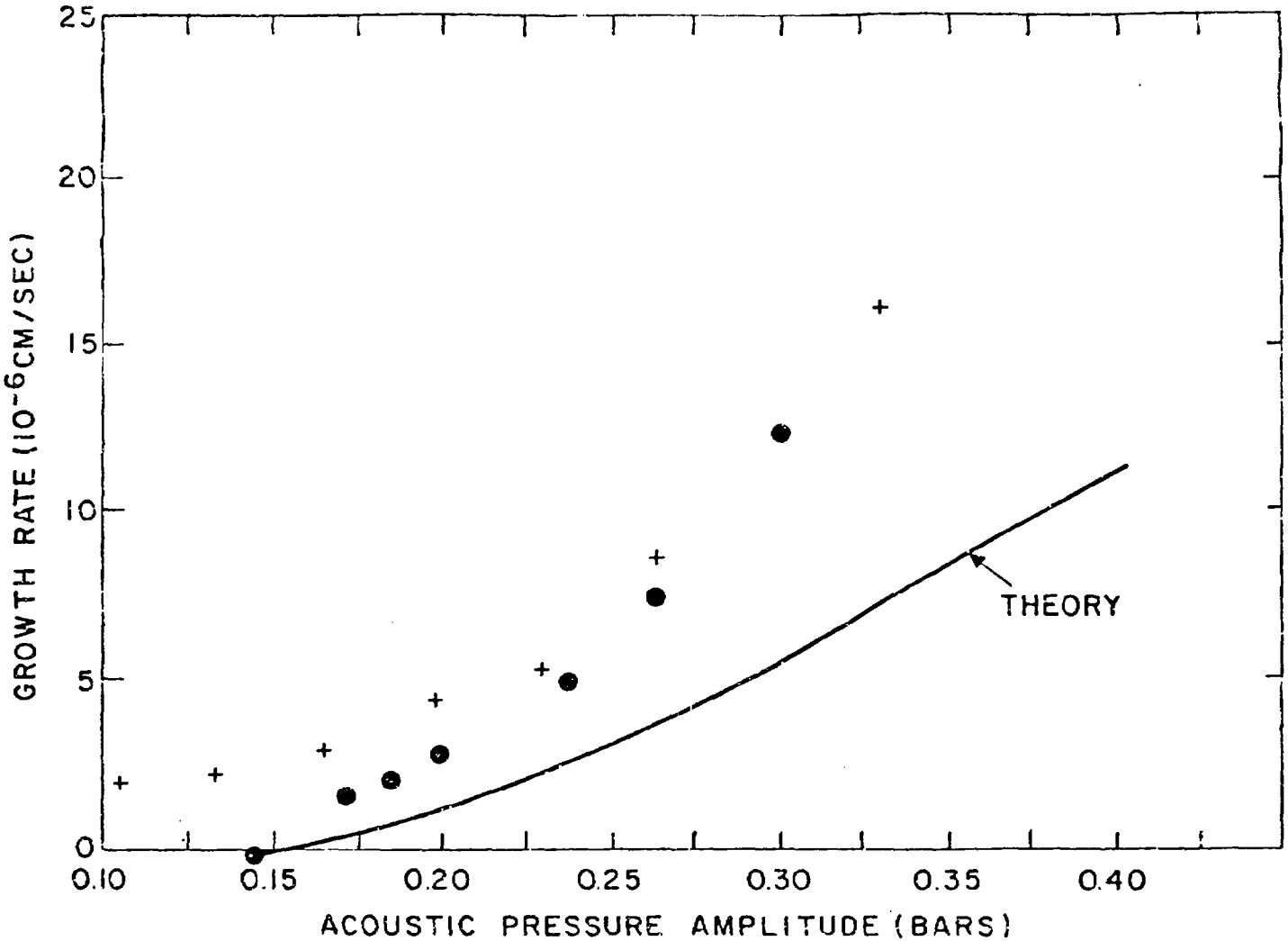

Figure 7. Variation of the rate of growth of air bubbles by rectified diffusion with acoustic pressure amplitude for a surface tension of 32 dyn/cm and at a radius of 4.5×10^{-3}cm. The closed circles (●) are for a surfactant concentration of 1300 ppm and the plus signs (+) are for a concentration of 3300 ppm. The curve is calculated from Eq. 1.

of the oxygen concentration of water with an oxygen analyzer showed no variation in the oxygen concentration of samples with varying amounts of surfactant.

Figures 5,6 and 7 give considerable support to the view that the poor agreement between observed and predicted values of the rate of bubble growth by rectified diffusion is related to surface effects on the liquid-gas interface.

III. DISCUSSION

Eller[1,2] had found that observed growth rates were larger than predicted even though observed and predicted thresholds were about the same. He suggested that a possible explanation for the increased growth rate was due to acoustic microstreaming that greatly increased the availability of gas for diffusion into the bubble. Gould[3] examined the effect of microstreaming on diffusion rates and concluded that the onset of surface wave activity did indeed induce streaming which markedly increased the diffusion rate. Further, he found essential agreement for the predicted and observed growth rates when microstreaming was absent. The results of this experiment corroborate these findings. However, it has been discovered in this experiment that at reduced surface tension, observed and predicted growth rates began to increasingly diverge as the surface tension is reduced. It was first thought that surface wave activity was responsible for the increased growth rates observed. However, in the observations by Gould[3] (see for example his Figs. 7 and 8) these surface oscillations were accompanied by such a rapid increase in the growth rate that a readily observable kink occurred in the radius-time curve. Figures 3 and 4 of this

study, which are similar to over 75 other radius-time observations made, show similar kinks in the growth curves, but only after the observed growth has deviated significantly from the theory. The possibility that surface wave activity is present in all the cases and for all the ranges observed appears highly unlikely, and thus an alternative explanation is required to explain the increased growth rates.

It has been known for some time[23,24,25] that surface active agents can reduce the evaporation rate of water. Mansfield[24] has shown that the water loss by evaporation from large lakes may be reduced by as much as 50% by addition of an appropriate monomolecular film. Archer and La Mer[26] found that the rate of evaporation may be reduced by a factor of 10^4 by the application of a fatty acid monolayer. In an attempt to account for these large reductions in the evaporation rate, Barnes[27] and co-workers calculated the evaporation resistance assuming that water molecules could only evaporate through holes in the monolayer film. With a reasonable estimate of the ratio of hole area to monolayer area they were able to calculate values of the evaporation resistance that approximated the measured values. Mansfield[24] also found that expansion of the film by as little as 10% reduced the evaporation resistance considerably, while compression of the film had little effect on the evaporation resistance.

The existence of surface active materials present on air bubble surfaces have been previously suggested as effecting the dissolution,[28,29] and the resonance frequency[30] of small air bubbles. Elder[31] visually observed the presence of a layer of surface active materials on air bubbles and its effect on acoustic microstreaming. Liebermann[32] examined the effect of surface contamination in reducing the diffusion of a stationary air bubble that was allowed to slowly dissolve in water. However, he states

that he was unable to find a significant (by a factor of two) effect on the diffusion rate by adding surface-active agents such as detergents. He did find that air bubbles left a solid particulate residue when dissolved on a glass slide.

It appears that several facts point toward the presence of a surface active monolayer as an explanation for the large growth rates observed in rectified diffusion. 1. The observation by Mansfield that expansion of a film allows more evaporation than when the film is compressed is directly applicable to the case of a pulsating air bubble. If the film allows more penetration of molecules on expansion than on compression, a rectification of diffused air would occur, in agreement with the above observations on rectified diffusion. Further, if, on expansion, the film is broken up, the time required for the film to repair itself is long compared to the period of the acoustic cycle. Lord Rayleigh,[33] in an ingenious experiment performed in 1890, showed that surface active agents needed at least 10 msec for their migration to the surface and their resultant reduction in surface tension. On the other hand, the compression may cause the repair mechanically so that no diffusion of the film from the liquid substrate is required. At any rate, it seems logical to assume that if evaporation rates can be retarded by four orders of magnitude, diffusion rates can be effected enough each cycle to cause a significant increase in the amount of gas contained within the bubble. The observations by Liebermann[32] that diffusion rates may be slightly affected by surface contaminants support this view. With the rapid pulsation, 21.6 kHz, very little rectification is required each cycle to significantly affect the growth rate. Further, although it is difficult to predict the effect

of the film on the threshold for rectified diffusion, it seems likely that the effect would be small. The retardation of outward gas diffusion by the film might lower the threshold, but since the mass transfer near threshold is small the effect would also be small. It is seen in Fig. 5 that the observed diffusion rate approaches the predicted rate at threshold, which implies that the effect of the film near threshold should be insignificant.

2. The observation that measured growth rates depend very strongly on the surface tension as shown in Fig. 6 tends to support the film hypothesis. For small amounts of surfactant (high surface tension) the difference between observed and predicted growth rates is much less than for large amounts of surfactant (low surface tension).

3. The observation in Figs. 3 and 4 of smooth radius-time curves with no kinks in the growth curves tends to rule out microstreaming due to surface wave activity as the explanation for the observed large rates of growth of an air bubble at low surface tensions. The observation in Fig. 5 that observed growth rates are larger than predicted for all values of the acoustic pressure amplitude above threshold tends to support this conclusion.

4. The curious phenomena in Fig. 7 is difficult to explain but strongly implies that the surfactant is affecting the diffusion.

Finally, as an alternative explanation, it was observed by Eller[31] in his studies of microstreaming that when surface active agents were added to water, a thin surface film would form which tended to present a no-slip boundary condition for the bubble. This boundary layer effect increased

the microstreaming until it was broken up by the bubble pulsations. It is possible that the addition of small amounts of surfactant induces microstreaming without surface waves. This streaming increases the growth rate for all values of the acoustic pressure amplitude and bubble radius, and thus shows no inception threshold.

IV. CONCLUSIONS

The principal conclusions of this report are as follows:

1. Measured values of the threshold for rectified diffusion as a function of bubble radius and liquid surface tension agree with theory.

2. Measured values of the rate of growth of air bubbles by rectified diffusion tend to be much larger than predicted for reduced values of the surface tension.

3. It is possible that surface active agents increase the rate of bubble growth during rectified diffusion by retarding outward gas diffusion through the bubble surface.

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FOOTNOTES

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