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# ON BUBBLE CAVITATION AND DISSOLUTION

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**Abstract**—The equilibrium equations of a bubble–droplet system are derived under more general conditions than previously reported. The stability of such a bubble–droplet system is examined via a diffusion argument. It is shown that the bubble-droplet system possesses not only a dissolution limit, known previously, but also a cavitation limit. Results of diffusion consideration supports that of thermodynamic analysis which demonstrated that both limits exist for a system without a droplet. Thus, the results of this paper further confirms the earlier conclusion that a bubble can remain in a state of stable equilibrium in a finite system under certain circumstances. Applications of the results require that a system boundary be identified such that little or no net mass transfer occurs across the boundary.

## NOMENCLATURE

| | |
|---|---|
| $H$, | Henry's law constant; |
| $F$, | Helmholtz free energy; |
| $n$, | number of moles; |
| $N$, | total number of moles; |
| $p$, | partial pressure of gases; |
| $P$, | liquid pressure or total pressure of mixture of gases; |
| $r$, | radius of a bubble; |
| $R$, | universal gas constant; |
| $T$, | absolute temperature; |
| $v$, | molar specific volume; |
| $V$, | volume; |
| $x$, | mole fraction. |

Greek symbols

| | |
|---|---|
| $\mu$, | chemical potential; |
| $\sigma$, | surface tension or surface tension at the bubble–liquid interface. |

Subscripts

| | |
|---|---|
| 1, | solvent component; |
| 2, | solute component; |
| gL, | interface between the droplet and the surrounding liquid; |
| s, | bubble–liquid interface. |

Superscripts

| | |
|---|---|
| $'$, | gas or vapor (bubble); |
| $''$, | liquid immediately adjacent to the bubble (droplet); |
| $'''$, | liquid surrounding the droplet. |

## INTRODUCTION

GAS AND/OR vapor bubbles are found in many scientific and engineering systems. These bubble-related phenomena received wide attention in the past 30 years and were the subjects of many theoretical and experimental studies. This is particularly true in the areas of boiling and cavitation where bubbles play the most important role. Many aspects of these bubbles become clear as a result of intense investigations in the past. However, one particular aspect, i.e. the origin of bubbles in a liquid, is still not well understood. It is well known in cavitation [1] that the growth of a bubble begins with a nucleus in the liquid and many experimental results can only be explained by postulating the existence of either free or hydrophobic nuclei in the liquid [2]. In boiling, nucleation sites on the solid boundary are observed to be the places for the initiation of bubble growth. Certain nucleation sites attached to a solid surface can be demonstrated theoretically to be stable [1]. Therefore, there is little disagreement between experimental observation and theoretical consideration regarding the existence and persistence of nucleation sites attached to a solid surface. This is not the case when free nuclei are considered to be of the source for bubble growth. It is well known that a vapor bubble cannot remain in equilibrium when the pressure is greater than the vapor pressure and that a vapor bubble is in a state of unstable equilibrium when the pressure is less than the vapor pressure. A gas bubble will grow in a supersaturated solution and collapse in an undersaturated solution. Even in a saturated solution, a gas bubble is considered to be unstable since surface tension will force the bubble into solution, according to Epstein and Plesset [3] who analyzed the growth and collapse of a gas bubble in an infinite system. Therefore, gas and vapor bubbles are considered to be unstable and cannot persist in a liquid from a theoretical viewpoint which contradicts experimental observations.

In 1977, Mori *et al.* [4] reported the results of experimental and theoretical investigations of bubble dissolution in a finite system. Their system, shown in Fig. 1, consisted of a spherical gas/vapor bubble in a spherical droplet which was surrounded by a second liquid. The inert gas is assumed to be insoluble in the surrounding (second) liquid which is immiscible with the droplet and forms a distinct interface between the two liquids. There is no mass transfer across the interface between the two liquids. Thus, the surrounding liquid serves primarily for transmitting the pressure to the bubble–droplet system. Mori *et al.* performed a thermodynamic analysis of the system and

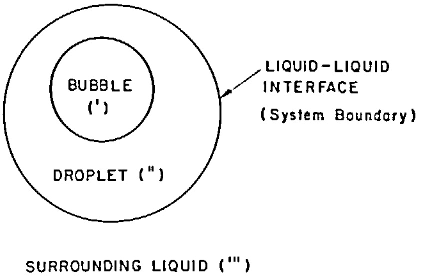


FIG. 1. Schematic of a bubble–droplet system.

the results show that, for a given system, when the pressure is below a critical value, a bubble can have two equilibrium radii; the smaller one is unstable and the larger one is stable. When the pressure exceeds the critical pressure of the given system, there is no equilibrium radius for a bubble. Thus, the critical pressure corresponds to the lowest pressure that such a bubble can remain in a state of stable equilibrium for a finite system.

This important result was confirmed by their experiments. However, Mori *et al.* did not investigate the stability of the bubble–droplet system at reduced and negative pressures. Based on an equilibrium analysis of a bubble containing insoluble gases, Blake has shown that there are two equilibrium radii for a bubble when the pressure is less than the vapor pressure of the liquid and greater than some critical pressure; the smaller one is stable and the larger one is unstable [1]. When the pressure is less than the critical pressure, a bubble can no longer remain in a state of equilibrium. This critical pressure is often referred to as the cavitation limit of a bubble containing some insoluble gases [1]. When the pressure is greater than the vapor pressure of the liquid, this theory predicts that a bubble can always remain in stable equilibrium regardless of how large the system pressure is. This is, of course, the consequence of the assumption that the gas in the bubble is insoluble. Thus, it appears that a gap exists between the result of Mori *et al.* [4] and that of equilibrium analysis of an insoluble bubble [1]. The former has been successfully applied to the prediction of dissolution of a bubble in a finite system while the latter has some success in predicting cavitation inception.

In 1981, Cha [5] reported a thermodynamic analysis of a gas/vapor bubble in a finite system similar to that of Mori *et al.* [4]. The major contribution from Cha's analysis was the result that a bubble can remain in a state of stable equilibrium provided that the ratio of the total number of moles of the solute to the total number of moles of the solvent in the system is not too small and that the system pressure falls between an upper bound and a lower bound. Cha termed the upper bound "dissolution limit" and the lower bound "cavitation limit" of a bubble in a state of stable equilibrium. Figure 2 shows the results of system pressure vs bubble radius at equilibrium condition from Cha's analysis reproduced here for convenience of discussion since we shall refer to this figure quite frequently. Figure 2 contains the essential feature of the result of Mori *et al.* for bubble dissolution and that of bubble cavitation. It appears that Cha's result bridged the gap described previously and helped in resolving the dilemma between theoretical and experimental observations regarding the persistence of free nuclei in a liquid.

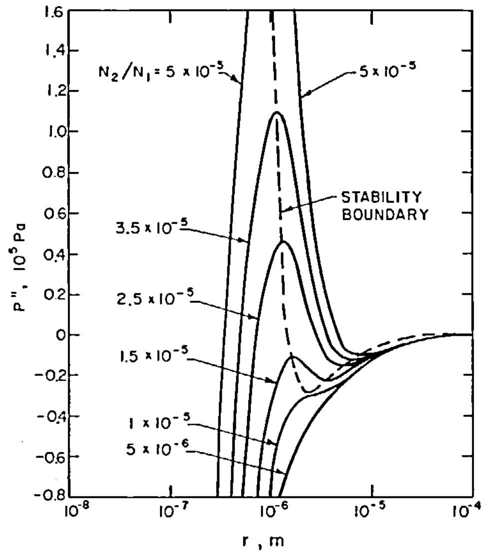


FIG. 2. System pressure vs equilibrium bubble radius for a nitrogen bubble in water with $N_1 = 10^{-10}$ mol for various values of $N_2/N_1$. (From ref. [5].)

Since Cha's analysis is similar to that of Mori *et al.*, the result of Cha's analysis should also apply to the bubble–droplet system. However, as Cha [6] pointed out, there is an important difference between the two analyses. Cha employed the constraint that the total volume is constant while Mori *et al.* assumed that the volume of the liquid droplet is constant. It is the objective of this paper to clarify this difference and to derive the equilibrium equations under more general conditions. Furthermore, we shall examine the stability of bubbles in a state of equilibrium by employing the diffusion argument of Plesset and Sadhal [7], who recently reaffirmed the findings of Mori *et al.* but did not address the problem of the stability of a bubble under reduced or negative pressures.

## CONDITIONS OF EQUILIBRIUM

To derive the general equilibrium equations, let us employ the bubble–droplet system of Mori *et al.* as shown in Fig. 1. As described previously, the droplet and the surrounding liquid are assumed to be immiscible and the inert gas is assumed to be insoluble in the surrounding liquid. Thus, no mass transfer occurs across the interface between the two liquids. Our system contains the bubble and the droplet. The pressure of the system is not excessively high so the solution can be assumed to be dilute and the liquids incompressible.

The free energy variations during an infinitesimal transformation in the bubble and the droplet are:

for the bubble,

$$\mathrm{d}F' = -P'\,\mathrm{d}V' + \mu_1'\,\mathrm{d}n_1' + \mu_2'\,\mathrm{d}n_2' \tag{1}$$

for the droplet,

$$\mathrm{d}F'' = -P''\,\mathrm{d}V'' + \mu_1''\,\mathrm{d}n_1'' + \mu_2''\,\mathrm{d}n_2''. \tag{2}$$

The total free energy variation for the bubble–droplet system is then

$$\mathrm{d}F = \mathrm{d}F' + \mathrm{d}F'' + \frac{2\sigma}{r}\,\mathrm{d}V' + \frac{2\sigma_{\mathrm{gL}}}{r_{\mathrm{gL}}}\,\mathrm{d}V_{\mathrm{gL}}. \tag{3}$$

It should be noted that in equation (2), we have retained the term $-P''\,\mathrm{d}V''$ in the free energy expression for the droplet. Thus, equation (2) is more general than the equation employed by Mori *et al.* [4]. The change in free energy of the droplet–bubble system must equal the external work,

$$\mathrm{d}F = -P'''\,\mathrm{d}V_{\mathrm{gL}}. \tag{4}$$

We now introduce the following constraints:

$$V_{\mathrm{gL}} = V' + V'', \qquad \mathrm{d}V_{\mathrm{gL}} = \mathrm{d}V' + \mathrm{d}V'', \tag{5}$$

$$n_1' + n_1'' = N_1 = \text{constant}, \qquad \mathrm{d}n_1' = -\mathrm{d}n_1'', \tag{6}$$

$$n_2' + n_2'' = N_2 = \text{constant}, \qquad \mathrm{d}n_2' = -\mathrm{d}n_2''. \tag{7}$$

In equation (5), we did not assume that $\mathrm{d}V'' = 0$; thus equation (5) is less restrictive than the equation employed by Mori *et al.* Also, we did not assume that the total volume of the system is constant ($\mathrm{d}V_{\mathrm{gL}} \neq 0$), therefore the result is more general than that reported by Cha [5].

Substituting equations (1)–(3) and equations (5)–(7) into equation (4) resulted in the following condition for equilibrium:

$$\left(-P' + P''' + \frac{2\sigma}{r} + \frac{2\sigma_{\mathrm{gL}}}{r_{\mathrm{gL}}}\right)\mathrm{d}V' + \left(-P'' + P''' + \frac{2\sigma_{\mathrm{gL}}}{r_{\mathrm{gL}}}\right)\mathrm{d}V'' + (\mu_1' - \mu_1'')\,\mathrm{d}n_1' + (\mu_2' - \mu_2'')\,\mathrm{d}n_2' = 0. \tag{8}$$

If $\mathrm{d}V'' = 0$, equation (8) reduces to the equation derived by Mori *et al.* The equilibrium equations follow immediately from equation (8),

$$-P' + P''' + \frac{2\sigma}{r} + \frac{2\sigma_{\mathrm{gL}}}{r_{\mathrm{gL}}} = 0, \tag{9}$$

$$-P'' + P''' + \frac{2\sigma_{\mathrm{gL}}}{r_{\mathrm{gL}}} = 0, \tag{10}$$

$$\mu_1' = \mu_1'', \tag{11}$$

$$\mu_2' = \mu_2''. \tag{12}$$

Subtracting equation (10) from equation (9), we obtain

$$-P' + P'' + \frac{2\sigma}{r} = 0. \tag{13}$$

Equations (10)–(13) are the primitive equilibrium equations since they can be written down directly. Equation (10) describes the mechanical equilibrium between the droplet and surrounding liquid and equation (13) describes the mechanical equilibrium between the bubble and the droplet. Equations (11) and (12) dictate diffusion equilibrium of the individual component between the bubble and the droplet. Equations (9), (11), and (12) were employed by Mori *et al.*, while equations (11)–(13) were employed by Cha in his analysis. Now with the help of equation (10), the difference between the analysis of Cha [5] and that of Mori *et al.* [4] becomes clear. Since equation (10) describes the mechanical equilibrium (force balance) between the droplet and the surrounding liquid, its only function is to transmit the external pressure ($P'''$) to the droplet through the spherical interface between the two liquids. Cha's system does not have such a spherical interface between the two liquids. Thus, the droplet pressure ($P''$) must be specified. Under such a circumstance, the equilibrium and stability conditions of Cha [5] and Mori *et al.* [4] must be the same. In other words, if the droplet pressure, instead of the external pressure of the surrounding liquid, is specified, the result of Cha's analysis should apply to the bubble–droplet system of Mori *et al.* This is, indeed, the consequence of the assumption of no mass transfer across the interface between the droplet and the surrounding liquid. This important result implies that the bubble–droplet system must have not only a dissolution limit but also a cavitation limit as shown in Fig. 2. We shall further demonstrate this result through stability considerations in the next section.

It should be emphasized that we have derived the equilibrium equations (11)–(13) without employing the constraint of either constant total volume or constant liquid (droplet) volume. Since equations (11)–(13) are identical to those derived by Cha, the results and conclusions reached in that paper are, therefore, not limited to the case of constant total volume. This should clarify some of the concern expressed in refs. [6, 7]. It is also interesting to note that equation (9) is identical to that derived by Mori *et al.*, who assumed that the volume of the droplet is constant.

Following the procedures outlined in ref. [5], an equilibrium equation can be obtained by combining equations (10)–(13) and the expressions for the chemical potentials,

$$P''' = p_1' + \frac{N_2}{N_1/H + 4\pi r^3(1 - p_1'/H)/3RT} - \frac{2\sigma}{r} - \frac{2\sigma_{\mathrm{gL}}}{r_{\mathrm{gL}}}. \tag{14}$$

As pointed out by Cha, equation (14) is slightly different from the equilibrium equation reported by Mori *et al.* [4]. They employed $n_1'$ and $n_2'$ (which are variables) in their equation while equation (14) employs $N_1$ and $N_2$, which are constants for a given system. If a distinct spherical interface does not exist between the droplet and the surrounding liquid, $r_{\mathrm{gL}} \to \infty$ while $N_1$ remains finite (or $\sigma_{\mathrm{gL}} = 0$), equation (14) becomes identical to that of Cha. We shall discuss the implication of this particular case later and proceed to examine the stability of equilibrium given by equation (14).

## STABILITY AND DIFFUSION CONSIDERATION

The stability of a bubble in a state of equilibrium can be determined by examining the free energy of the system; the equilibrium is stable if the free energy is a local minimum and unstable if the free energy is a local maximum. This approach has been employed by both Mori *et al.* [4] and Cha [5]. An alternate approach was recently reported by Plesset and Sadhal [7], who examined the stability of a bubble through some kind of diffusion argument. The results of Plesset and Sadhal agree with those of Mori *et al.*, who found that a bubble can remain in a state of stable equilibrium if the pressure is below some critical pressure (greater than the vapor pressure of the liquid). However, both Mori *et al.* and Plesset and Sadhal did not examine the stability of a bubble when the pressure is below the vapor pressure of the liquid. Cha [5] has demonstrated, through thermodynamic analysis, that there is also a lower limit of pressure below which a bubble can no longer remain in a state of stable equilibrium. In this paper we shall confirm the results of Cha by using the diffusion argument proposed by Plesset and Sadhal [7]. Furthermore, we shall use this diffusion approach to examine the difference between the stability of a bubble in a liquid with or without the second interface described previously.

Assuming that mechanical equilibrium exists between the bubble and the surrounding liquids, Plesset and Sadhal [7] obtained the following expression for the average mole fraction of the gas in the liquid droplet:

$$x_2'' = \frac{N_2RT-(P'''-p_1'+2\sigma/r+2\sigma_{gL}/r_{gL})4\pi r^3/3}{(N_1+N_2)RT-(P'''+2\sigma/r+2\sigma_{gL}/r_{gL})4\pi r^3/3}. \tag{15}$$

If diffusion equilibrium exists at the interface between the bubble and the liquid, the mole fraction on the liquid side of this interface is given by

$$x_{2,s}'' = p_2'/H = (P'''-p_1'+2\sigma/r+2\sigma_{gL}/r_{gL})/H. \tag{16}$$

Complete thermodynamic equilibrium exists only if diffusion equilibrium between the bulk of the liquid and the interface is assured,

$$x_2'' = x_{2,s}''. \tag{17}$$

It should be noted that we are only interested in the states of complete thermodynamic equilibrium, given by equation (17), and in infinitesimal deviations from these states. These can be accomplished by plotting $x_2''$ and $x_{2,s}''$ vs bubble radius, and the equilibrium positions are determined by the intersections of these two curves. The stability can then be determined by examining the behaviors of $x_2''$ and $x_{2,s}''$ right next to these points of intersections as demonstrated by Plesset and Sadhal [7].

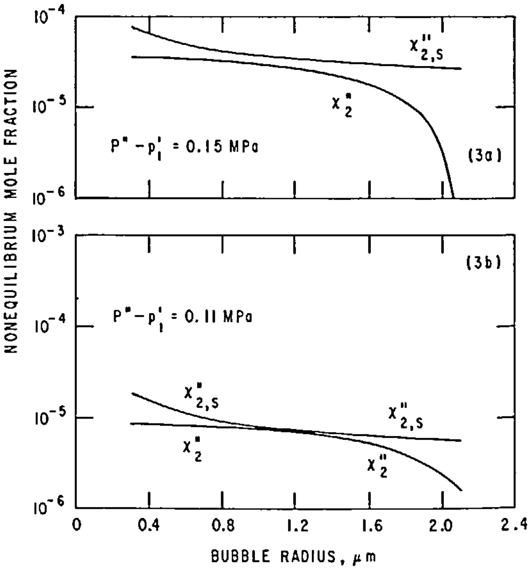
## RESULTS AND DISCUSSIONS

To confirm the results of the stability analysis of Cha [5], we shall attempt to reproduce some of the results shown in Fig. 2 by using the diffusion argument. Figure 2 is the plot of system pressure $P''$ vs equilibrium radius for various values of $N_2/N_1$ of a nitrogen bubble in water. Cha [5] has found that the equilibrium is stable if the slope is negative and unstable if the slope is positive in Fig. 2. The stability boundary (dashed curve in Fig. 2) separates the region of stable equilibrium from that of unstable equilibrium. We shall select one typical equilibrium curve ($N_2/N_1 = 3.5 \times 10^{-5}$ and $N_1 = 10^{-10}$ mol) and examine the stability of these equilibrium positions. The values of constants used in calculations are the same as Cha [5]: $T = 293$ K, $p_1' = 2.337 \times 10^3$ Pa, $R = 8.313$ J mol$^{-1}$ K$^{-1}$, $\sigma = 7.32 \times 10^2$ N m$^{-1}$, and $H = 8.13 \times 10^9$ Pa.

Figures 3(a)–3(f) show the results of diffusion analysis using equations (15) and (16). We have set $\sigma_{gL} = 0$ just to demonstrate the equivalence of Figs. 2 and 3. Later on we shall show the results with $\sigma_{gL} \neq 0$ and examine the difference between the two cases.

In Fig. 3(a), the system pressure (0.15 MPa) is relatively high, no bubble can remain in equilibrium and $x_2''$ does not intersect $x_{2,s}''$. As shown in Fig. 2, there is indeed no equilibrium position at this pressure with $N_2/N_1 = 3.5 \times 10^{-5}$.

When the system pressure equals 0.11 MPa, Fig. 3(b) shows that $x_{2,s}''$ intersect tangentially $x_2''$ at one position. This is the only equilibrium position of the given system at this pressure. Figure 3(b) also shows that $x_{2,s}''$ is always greater than $x_2''$ except at the tangential point where they are equal. If there is an infinitesimal disturbance from this equilibrium position that causes



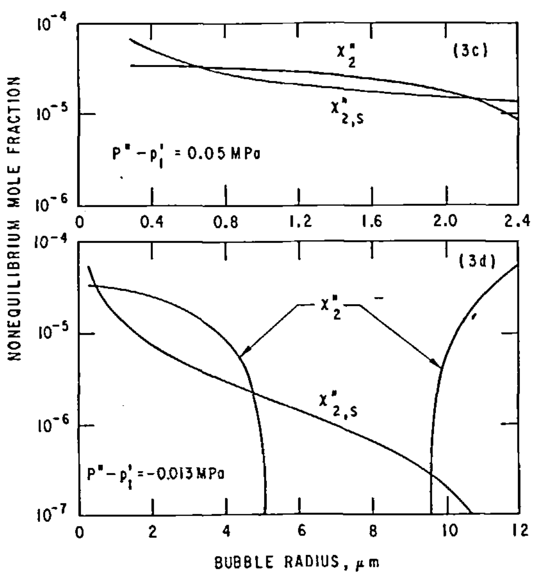
FIGS. 3(a) and 3(b). Nonequilibrium mole fraction vs bubble radius for a nitrogen bubble in water with $N_1 = 10^{-10}$ mol, $N_2 = 3.5 \times 10^{-15}$ mol, and $\sigma_{gL} = 0$. Equilibrium positions are at the intersections of $x_2''$ and $x_{2,s}''$.

the size of the bubble to increase by a small amount, the concentration at the interface ($x''_{2,s}$) becomes greater than the concentration of the bulk liquid ($x''_2$). This would cause mass diffusion from the interface to the bulk liquid and the bubble will return to its equilibrium position. Thus, the equilibrium is stable against growth. On the other hand, if the disturbance is in the direction of reducing the size of the bubble from its equilibrium position, then Fig. 3(b) shows that the concentration at the interface is greater than that of the bulk liquid. This would cause diffusion from the bubble to the bulk liquid and the bubble would continue to shrink until it collapses completely since there is no equilibrium position smaller than the original one. Thus, the results in Fig. 3(b) indicate that the equilibrium is stable against growth but unstable against collapse. The equilibrium position in Fig. 3(b) corresponds to the relative maximum in Fig. 2 with $P'' = 0.11$ MPa and $N_2/N_1 = 3.5 \times 10^{-5}$. Cha [5] has named this maximum pressure the "dissolution limit" of the bubble. Stability considerations from the diffusion argument indicates that this name is indeed proper since the bubble is unstable against collapse and will completely dissolve into solution.

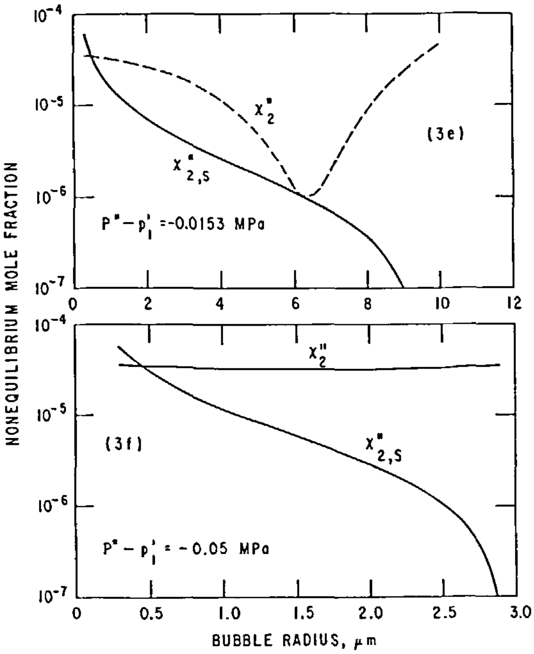
Figure 3(c) shows the results of diffusion analysis when the system pressure equals 0.05 MPa. There are two equilibrium positions. It can be shown using the diffusion argument that the smaller one is unstable against either growth or collapse while the larger one is stable against both growth and collapse. This result again corresponds to the result shown in Fig. 2. At a pressure of 0.05 MPa, there are indeed two equilibrium positions with $N_2/N_1 = 3.5 \times 10^{-5}$. The smaller one stays on the LHS of the stability boundary and has a positive slope, therefore, it is unstable. The larger one stays on the RHS of the stability boundary and has a negative slope, and therefore is stable.

When the pressure is slightly below the vapor pressure of the liquid, it is possible to have three equilibrium radii as shown in Fig. 2. Figure 2 also indicates that the medium equilibrium position is stable and that the smallest one, as well as the largest one, is unstable. This is indeed also the result of the diffusion analysis as shown in Fig. 3(d). It is interesting to note that even when the pressure is below the vapor pressure, a bubble can still remain in a state of stable equilibrium under certain circumstances.

Figure 3(e) shows the result of the diffusion analysis when the system pressure equals $-0.0153$ MPa. There are two equilibrium radii at this negative pressure. The smaller one is obviously unstable from the diffusion argument. The larger one is the point of tangential intersection between $x''_2$ and $x''_{2,s}$. If there is an infinitesimal disturbance which causes the bubble to grow a little from this equilibrium position, the concentration in the bulk of the liquid becomes greater than that at the bubble–liquid interface. This would cause diffusion from the bulk liquid to the bubble and, therefore, the bubble would continue to grow indefinitely since there is no stable equilibrium radius greater than this radius. On the other hand, if the disturbance is in the direction of reducing the radius by an infinitesimal amount, $x''_2$ is again greater than $x''_{2,s}$, which causes diffusion from the liquid towards the bubble and the bubble would return to its original



FIGS. 3(c) and 3(d). Nonequilibrium mole fraction vs bubble radius for a nitrogen bubble in water with $N_1 = 10^{-10}$ mol, $N_2 = 3.5 \times 10^{-15}$ mol, and $\sigma_{gL} = 0$. Equilibrium positions are at the intersections of $x''_2$ and $x''_{2,s}$.



FIGS. 3(e) and 3(f). Nonequilibrium mole fraction vs bubble radius for a nitrogen bubble in water with $N_1 = 10^{-10}$ mol, $N_2 = 3.5 \times 10^{-15}$ mol, and $\sigma_{gL} = 0$. Equilibrium positions are at the intersections of $x''_2$ and $x''_{2,s}$.

equilibrium position. Thus, the larger equilibrium radius in Fig. 3(e) is stable against collapse but unstable against growth. These results again correspond exactly to the results shown in Fig. 2 with $N_2/N_1 = 3.5 \times 10^{-5}$. If one starts with a pressure of $-0.0153$ MPa and draw a horizontal line across Fig. 2, this horizontal line will intersect the equilibrium curve at two points. The first intersection (with a smaller radius) has a positive slope and therefore is unstable. The second intersection occurs tangentially at the local minimum and sits right on the stability boundary. Cha [5] has named this point the "cavitation limit" of the bubble. Diffusion consideration again supports this term since this particular equilibrium radius is stable against collapse and unstable against growth and will grow indefinitely. This is just the opposite of the result shown in Fig. 3(b) where the bubble will dissolve completely.

Figure 3(f) shows the plot of nonequilibrium mole fraction vs bubble radius at a pressure of $-0.05$ MPa. There is only one equilibrium radius and it is unstable. Thus, the cavitation limit shown in Fig. 3(e) is indeed the pressure below which no stable equilibrium radius exists. This is clearly shown in Fig. 2.

Figure 2 also indicates that when the gas inventory is small compared to the water inventory (for example, $N_2/N_1 = 10^{-5}$), there is no equilibrium position when the pressure is above the vapor pressure and there is an unstable equilibrium radius when the pressure is below the vapor pressure of the liquid. This result is expected since when the gas inventory becomes small compared to the liquid (water) inventory, the equilibrium characteristics of the bubble should approach that of a vapor bubble. This result is again confirmed by the diffusion analysis shown in Figs. 4(a) and 4(b).

We shall now proceed to examine the effect of a second interface ($\sigma_{gL} \neq 0$) on the stability of a bubble-droplet system employed by Mori *et al.* [4]. As we pointed out previously, if the pressure in the droplet ($P''$), instead of the pressure in the surrounding liquid ($P'''$), is specified, then the results of Cha's analysis can be applied directly to the bubble–droplet system of Mori *et al.* The only difference lies in equation (10), which states that there is a difference in $P''$ and $P'''$ due to the presence of a liquid–liquid interface. If one specifies $P'''$ instead of $P''$, the equilibrium positions shown in Figs. 2–4 will be shifted, but the basic characteristics should remain the same. This is demonstrated by the results shown in Figs. 5(a) and 5(b). The difference between Figs. 2–4 and Fig. 5 is due to the term $2\sigma_{gL}/r_{gL}$. We have employed $\sigma_{gL} = 6.34 \times 10^{-2}\,\mathrm{N\,m^{-1}}$. It should be noted that $r_{gL}$ is not independent of the other variables and can be calculated approximately as follows.

For dilute solutions, the volume of the liquid droplet, excluding the bubble, is approximately

$$V'' \doteq n_1''v_1'' = (N_1 - p_1'V'/RT)v_1'' \tag{18}$$

where $V' = 4\pi r^3/3$ is the volume of the bubble. The radius of the droplet is given by the following equation:

$$\tfrac{4}{3}\pi r_{gL}^3 = V' + V''. \tag{19}$$

Eliminating $V''$ from equations (18) and (19) gives the following expression for $r_{gL}$:

$$r_{gL}^3 \doteq 3[V' + (N_1 - p_1'V'/RT)v_1'']/4\pi. \tag{20}$$

In Figs. 5(a) and 5(b), we have specified the system pressure using $P'''$, instead of $P''$ as in Figs. 2–4. If one

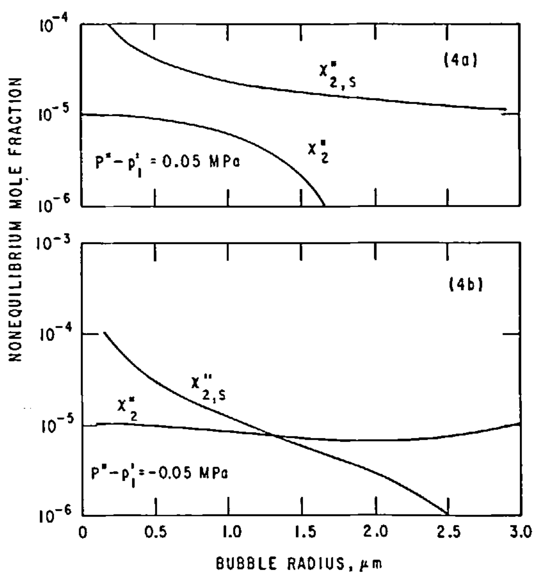


Fig. 4. Nonequilibrium mole fraction vs bubble radius for a nitrogen bubble in water with $N_1 = 10^{-10}$ mol, $N_2 = 10^{-15}$ mol, and $\sigma_{gL} = 0$. Equilibrium positions are at the intersections of $x_2''$ and $x_{2,s}''$.

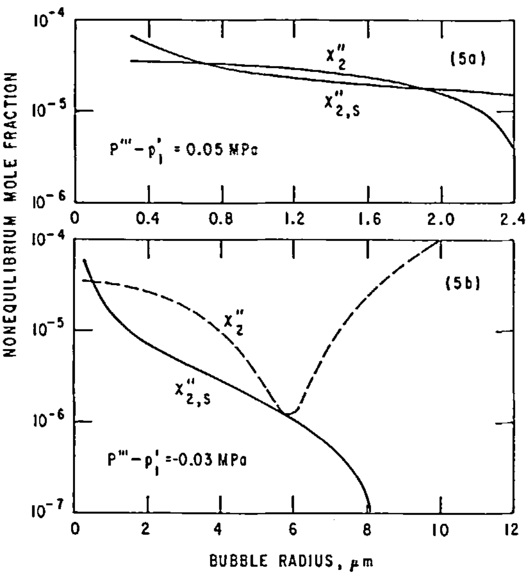


Fig. 5. Nonequilibrium mole fraction vs bubble radius for a nitrogen bubble in water with $N_1 = 10^{-10}$ mol, $N_2 = 3.5 \times 10^{-15}$ mol, and $\sigma_{gL} \neq 0$. Equilibrium positions are at the intersections of $x_2''$ and $x_{2,s}''$.

compares Fig. 5(a) with Fig. 3(c), the difference caused by the presence of a second interface is seen to shift the equilibrium positions slightly, but the basic characteristics remain unchanged as we stated previously. The interesting question to be answered is whether the bubble–droplet system of Mori *et al.*, does have a "cavitation limit" or not. Figure 5(b) shows that such a "cavitation limit" indeed exists for the bubble–droplet system. Comparison between Figs. 5(b) and 3(e) again shows that the basic characteristics of the two systems (with and without a second liquid–liquid interface) are similar.

Before summarizing the results obtained so far, it is helpful to point out some further implications and possible applications of the results of Cha [5]. As mentioned previously, the external pressure is transmitted to the bubble–droplet system through the spherical interface between the droplet and the surrounding liquid. However, in many practical systems, such a spherical interface between two immiscible liquids may not exist. Transmitting pressure to the liquid surrounding a bubble does not always have to go through a spherical liquid–liquid interface. For example, consider a closed container containing liquid and gas. Equilibrium between the gas and the liquid in the absence of gravity is a perfect application of the analysis of Cha since a second spherical interface between two immiscible liquids does not exist. Keller [8] was the first to demonstrate that a bubble can remain in a state of stable equilibrium under such circumstances. Keller also remarked that the Russian astronaut, Colonel Nikolayev, reported an observation of a closed bottle containing liquid and gas, which he made while orbiting around the earth in a satellite. The gas formed a single spherical bubble near the center of the bottle. Since gravitational acceleration in an orbiting satellite is counter balanced by the centrifugal acceleration, the equilibrium analysis of Cha [5] is directly applicable. The major assumption made in the thermodynamic analysis is that there is no net mass transfer across the system boundary, be it large or small. In any system, if such a boundary can be identified, or if the practical condition closely approximates the ideal situation, the the results of Cha [5] are expected to apply.

## SUMMARY AND CONCLUSIONS

We have derived the equilibrium equations for a bubble–droplet system without assuming either that the total volume or that the liquid volume is constant. We have demonstrated that the difference between the results of Mori *et al.* [4], for a bubble–droplet system and those of Cha [5] is due to the presence of a second liquid–liquid interface. However, the presence of this interface does not change the basic characteristics of the equilibrium and stability of a bubble. This is further demonstrated by the result that the bubble–droplet system of Mori *et al.* also have, in addition to a dissolution limit, a cavitation limit, similar to that shown by Cha. The reason that the results of the two systems are similar is due primarily to the assumption of no mass transfer between the system boundary and the surrounding liquid.

It has been demonstrated that the diffusion analysis of Plesset and Sadhal [7] supports the results of thermodynamic analysis of Cha [5]. The names "cavitation limit" and "dissolution limit" of a bubble introduced by Cha are shown to be reasonable from diffusion considerations.

It has been shown that the equilibrium equations reported previously by Cha [5] are not restricted to the case of constant total volume. This, and all the other results described in this paper, implies that the results and conclusions reached by Cha [5] are correct and have wider applications. It is not necessary to repeat all the results of that paper here and the readers are referred to the original paper. It is also pointed out that a bubble–droplet system may not always exist in a practical situation. In order to apply the equilibrium theory of Cha, one needs to define a system boundary where little or no net mass transfer occurs across this boundary.

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## SUR LA CAVITATION DE BULLE ET LA DISSOLUTION

**Résumé**—Les équations d'équilibre du système bulle-goutte sont écrites pour des conditions plus générales que celles reportées jusqu'ici. La stabilité d'un tel système est examinée à travers un argument de diffusion. On montre que le système bulle-goutte possède non seulement une limite de dissolution, déjà connue, mais aussi une limite de cavitation. Les résultats de la considération de la diffusion confortent ceux de l'analyse thermodynamique qui démontrent que les deux limites existent pour un système sans goutte. Ainsi, cette étude confirme une conclusion antérieure selon laquelle une bulle peut rester dans un état d'équilibre stable, dans un système fini, sous certaines circonstances. Des applications de ces résultats demandent qu'une frontière du système soit identifiée de telle sorte qu'un transfert massique faible ou nul existe à travers cette frontière.

## ÜBER BLASENBILDUNG UND -AUFLÖSUNG

**Zusammenfassung**—Die Gleichungen für den Gleichgewichtszustand eines Blasen-Tröpfchen-Systems werden unter allgemeineren Voraussetzungen abgeleitet als in einer bereits früher veröffentlichten Arbeit. Die Stabilität eines solchen Blasen-Tröpfchen-Systems wird mit Hilfe eines Diffusionsterms untersucht. Es wird gezeigt, daß das Blasen-Tröpfchen-System nicht nur—wie bereits bekannt—eine Grenze für die Auflösung besitzt, sondern auch eine Grenze für die Blasenentstehung. Die Ergebnisse der Diffusionsbetrachtung stützen die der thermodynamischen Untersuchung, die gezeigt hat, daß beide Grenzen für ein System ohne Tröpfchen existieren. So bestätigen die Ergebnisse dieser Arbeit den bereits früher gezogenen Schluß, daß eine Blase in einem begrenzten System unter bestimmten Umständen in einem stabilen Zustand verharren kann. Die Anwendung der Ergebnisse fordert, daß eine Systemgrenze so festgelegt wird, daß insgesamt wenig oder gar kein Stofftransport über diese Grenze stattfindet.

## О КАВИТАЦИИ И РАСТВОРЕНИИ ПУЗЫРЬКОВ

**Аннотация**—Выведены уравнения равновесия системы пузырек-капля при более общих, чем ранее условиях. Устойчивость такой системы пузырек-капля исследовалась с помощью диффузионного подхода. Показано, что система пузырек-капля обладает не только пределом растворения, известным ранее, но и пределом кавитации. Данные диффузионного анализа согласуются с результатами термодинамического анализа, из которого следует наличие обоих пределов в случае отсутствия в системе капли. Таким образом, результаты данной работы еще раз подтверждают ранее сделанный вывод, что при определенных условиях пузырек может находиться в состоянии устойчивого равновесия в конечной системе. С точки зрения приложения результатов необходимо определять систему на границе таким образом, чтобы через границу перенос массы был незначительным или вообще отсутствовал.