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Gas diffusion from ascending gas bubbles

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General qualitative rules are derived for the behaviour of the volume of an ascending spherical bubble and of the gas pressure within it. Three modes of behaviour are discerned, corresponding to as many possible orderings of the relative influences of ascent velocity, gas leakage and surface tension on the volume and the pressure balance. These general results are nearly independent of the particular forms of the ascent velocity and gas exchange functions. Quantitative results are presented for the Stokes law régime.

1. Introduction

The dynamics of gas bubbles ascending in a liquid have been discussed in numerous papers, both from a theoretical (Levich 1962, chapter viii; Moore 1965) and from an experimental point of view (Haberman & Morton 1953). The problem of gas diffusion from such bubbles has also received considerable attention (Levich 1962; Deindoerfer & Humphrey 1961). The combined problem of the interaction between gas diffusion and the dynamics of the ascent has also been investigated (Levich 1962, §80; Calderbank 1967). This last problem is here formulated for spherical bubbles in a way which brings out remarkably clearly the relative influences of the physical processes involved. General qualitative results will be found concerning the behaviour of the volume of nearly spherical gas bubbles and of the pressure within such bubbles and these results will be seen to hold for a wide class of ascent velocities and gas exchange functions.

The volume of a gas bubble ascending in an unsaturated liquid varies through the effect of two conflicting influences. Gas continuously leaks out of the bubble to dissolve in the surrounding liquid and if the bubble were stationary the ensuing loss of mass would necessarily lead to its ultimate disappearance. On the other hand, as a bubble ascends, the ambient hydrostatic pressure decreases and so does the pressure of the gas within: the bubble tends to expand. If, as is the case for small bubbles, the outward mass flux increases with increasing bubble radius more slowly than the radius itself, the total outward leakage will be a weaker function of the radius than the volume of the bubble, and the influence of leakage on the mass balance will be more important for small than for large bubbles. The rate of ascent is also a function (generally increasing, although not monotonically) of bubble radius. One then expects that for bubbles beyond a certain size, with small enough ratio of area to volume and high enough velocity of ascent the expansion associated with the decrease in hydrostatic pressure will more than account for the loss of gas through the interface and that the bubble will grow in volume although continuously losing mass. For much smaller bubbles the outflow of gas will dominate and such bubbles will shrink as they rise. Between the two modes of behaviour, there will exist a critical radius for which a bubble will neither grow nor shrink. This critical radius should depend on the ascent velocity and on the ratio of the surface area to the volume of the bubble, all other parameters being fixed.

The pressure of the gas held within the bubble normally decreases through the ascent, as indicated above. Nevertheless, one should not forget that the gas pressure is somewhat higher than the ambient pressure, because of the effect of surface tension. The contribution of the surface tension is inversely proportional to the curvature, and will thus be most important in very small bubbles. Thus, if a bubble is so small that gas leakage controls its volume variation (the bubble shrinks), and that its internal pressure is dominated by surface tension effects, the pressure of the gas within will increase as the bubble rises, in spite of the decrease in ambient pressure. We should then expect that there exists a second critical radius for which the gas pressure does not vary as the bubble rises.

The behaviour of bubble volume and pressure is thus not *a priori* determined but depends on the relative influences of three physical processes: isothermal expansion associated with the ascent, gas leakage and the additive pressure effect of surface tension. The influence of these processes is investigated here for the particularly simple case of spherical bubbles.

2. Formulation and general results for spherical bubbles

The discussion is restricted to bubbles of very nearly spherical shape. The results will therefore hold only for Reynolds numbers, Re, such that the distortion from sphericity is less than say, 5 %. For thin liquids, such as water, this degree of distortion is reached at $Re = O(10^2)$ (Moore 1965); for thicker liquids (oils, for example) such distortion is already present for $Re = O(1)$. The liquid will be assumed isothermal, and so will the gas within the bubble. From the ideal gas law we have for the pressure inside the bubble, P,

$$P = \rho RT/M, \tag{1}$$

where ρ is the density, T the constant temperature and M the molecular weight of the gas, and R the molar gas constant. Because of surface tension, σ, the pressure P is higher than the pressure in the surrounding liquid, P_0:

$$P = P_0 + (2\sigma/r), \tag{2}$$

where r is the radius of the bubble.

Taking the z-axis vertically upwards with origin at the depth of release one has for P_0 the hydrostatic relation

$$P_0(z) = P_0(H) + \rho_0 g(H-z). \tag{3}$$

The surface of the liquid is at $z = H$ and is under atmospheric pressure $P_0(H)$; ρ_0 is the density of the liquid and g the acceleration of gravity.

The bubble ascends through the liquid at the rate

$$dz/dt = U(r,t). \tag{4}$$

The dependence on the density difference, $\rho_0 - \rho$, is neglected; ρ_0 is always much greater than ρ. Experimental curves for the terminal velocity of ascent may be found in a number of references (Datta, Napier & Hewitt 1950; Haberman & Morton 1953). As the results to be derived in this section depend neither on the shape of the velocity curve nor on the assumption that a steady state has been reached, $U(r,t)$ will for the moment be left unspecified. It will only be assumed that the Reynolds number $Re = 2rU/\nu$ increases monotonically with r (ν is the kinematic viscosity of the liquid).

Finally, the gas is assumed to leak out of the bubble at the rate of $\frac{1}{3}F$ units of mass per unit time per unit area. The rate of leakage depends, for a given liquid–gas system, on the rate of ascent, the radius of the bubble and the difference between the gas concentration C in the liquid in contact with the bubble and the uniform concentration very far away from it, C_∞. The concentration, C, may itself be influenced by the presence of surface active materials on the bubble. The mass conservation equation is written

$$(d/dt)\,\rho r^3 = -r^2 F, \tag{5}$$

where $F = F(C - C_\infty, r, U)$. No specific form for F is introduced at this point. Only the following, highly plausible, conditions are imposed: (i) F increases monotonically with $(C - C_\infty)$ and vanishes when the concentration difference vanishes; (ii) as r tends to zero, F vanishes more slowly than the Reynolds number.

Eliminating ρ and z from (1) to (5) we obtain the two differential expressions

$$\frac{dr}{dt} = -\left(F - \frac{\rho_0 g M}{RT} U r\right) \bigg/ \frac{M}{RT}\left(3P - \frac{2\sigma}{r}\right) \tag{6}$$

$$\frac{dP}{dt} = 2\sigma\left(F - \frac{\rho_0 g M}{RT} U r \frac{3P}{2\sigma/r}\right) \bigg/ \frac{Mr^2}{RT}\left(3P - \frac{2\sigma}{r}\right), \tag{7}$$

from which the evolution of r and P can be obtained by integration once U and F are specified.

We note that the denominators of the differential quotients in (6) and (7) never vanish, since, by (2), $3P - 2\sigma/r$ is always positive. The qualitative behaviour of the r and P variations is thus entirely determined by the sign of the numerators. Eliminating the time variable from (6) and (7) and writing $\alpha = \rho_0 g M/RT$ we find that

$$\frac{dr}{dP} = -(F - \alpha U r) \bigg/ \frac{2\sigma}{r^2}\left(F - \alpha U r \frac{3P}{2\sigma/r}\right). \tag{8}$$

This equation contains, in a very concise form, the essential physics of the problem. When the numerator of the differential quotient vanishes, $dr = 0$, and gas leaks out of the bubble just fast enough to counteract the expansion associated with the decrease in hydrostatic pressure. When the denominator vanishes, $dP = 0$, and the bubble ascends at a rate such that the increase in pressure brought about in a shrinking bubble by the influence of surface tension is exactly balanced by the decrease in hydrostatic pressure. The relative importance of leakage and rate of ascent on the volume of the bubble thus determines the sign of the numerator, whereas the relative roles of surface tension (i.e. increase in internal pressure due to shrinkage brought about by rapid leakage of the gas) and ascent on the pressure in the bubble determine the sign of the denominator.

Only the case $F > 0$ (outward leakage from the bubble) will be discussed. The case $F < 0$ is not very interesting (at least not when there is only one gas in the bubble); the bubble simply expands as it rises, no matter what the initial conditions are. For $r \neq 0$ the numerator and the denominator of (8) cannot vanish simultaneously since $3P - 2\sigma/r > 0$. This is of course quite as expected; since a bubble must already be shrinking for the denominator to vanish, its radius cannot simultaneously be stationary. If two critical radii $r_a(P)$ and $r_b(P)$ are defined on which $dr = 0$ and $dP = 0$ respectively, it follows that, if they are both non-zero, $r_a(P)$ and $r_b(P)$ are never equal. The two critical radii, under the conditions imposed on F and U, can coincide only when $C = C_\infty$, in which case they both vanish. The only singular point in the (P, r)-plane is at $[P(C = C_\infty), r = 0]$. To decide whether $r_a(P) > r_b(P)$ or vice versa, it is then sufficient to investigate a limiting case for which explicit expression for F and U are available (that of small Reynolds number). As we shall see below, $r_a(P) > r_b(P)$.

For arbitrary velocity and gas leakage functions (except for the restrictions mentioned earlier) spherical bubbles fall quite naturally into three categories according to the type of trajectory which they follow in the (P, r)-plane. The condition that F vanish more slowly than the Reynolds number at small r, together with $r_a(P) > r_b(P)$ divides the (P, r)-plane into three regions:

$$r > r_a(P): \frac{dr}{dt} > 0, \quad \frac{dP}{dt} < 0;$$

$$r_a(P) > r > r_b(P): \frac{dr}{dt} < 0, \quad \frac{dP}{dt} < 0;$$

$$r < r_b(P): \frac{dr}{dt} < 0, \quad \frac{dP}{dt} > 0.$$

The reader may refer to figure 1 which shows the trajectories in an example specifically worked out to illustrate the three types of behaviour. For $r(t = 0) > r_a(t = 0)$ the bubbles grow monotonically in size as they ascend; gas leakage is not predominant in the volume balance and surface tension is relatively insignificant. For $r(t = 0) < r_b(t = 0)$ on the other hand, leakage and surface tension dominate the volume and pressure balance; the gas pressure increases and the bubbles shrink and ultimately collapse. Bubbles with initial radius intermediate between $r_a(t = 0)$ and $r_b(t = 0)$ follow trajectories along which, at first, the pressure and the volume both decrease. Ultimately these trajectories must cross either the $r_a(P)$ or the $r_b(P)$ curve and the bubble must either expand or disappear. Whenever the liquid is not saturated with gas under atmospheric pressure $P_0(H)$, some of these trajectories may reach the surface before crossing the r_a or r_b curves.

We finally note that since F and U are single valued functions of P and r, dr/dP is uniquely specified at all points of the (P, r)-plane except at the singular point $[P(C = C_\infty), r = 0]$. As bubbles of identically zero radius are not very interesting, that point will be excluded from further consideration. Thus the trajectories traced by ascending bubbles in the (P, r)-plane never intersect each other. Each pair of values of pressure and radius lies on one and only one trajectory and can be reached from only one initial radius.

Bubbles in practice will start from rest. No matter what the initial size of the bubble gas leakage will always dominate the volume balance, and surface tension the pressure balance, during some fraction of the acceleration period, since when $U = 0, r_a = r_b = 0$. For a very short time, even a large bubble will shrink slightly and for an even shorter time (since $r_b < r_a$) the pressure within it will rise, as the bubble departs from rest. The effective initial radius, attained when the bubble has reached terminal velocity, and on which calculations are usually based, will thus be slightly smaller than the actual initial radius. Since terminal velocity is reached quite quickly (in a displacement of a few bubble radii) these transient effects should have only a minor importance.

The qualitative results derived in this section are considered to be the most significant part of this paper. Quantitative results will now be derived for a special case.

3. The Stokes law régime

For small Reynolds numbers, explicit expressions for U and F are available. The Rybczynski–Hadamard formula gives (Levich 1962, § 70), for the rate of fall of a gas sphere through a liquid, $U(r) = \frac{1}{3}gr^2/\nu$. It is however known (Levich 1962, § 80) that in all but the most meticulously cleaned liquids gas bubbles behave at low Reynolds numbers like solid spheres, with terminal velocity given by the Stokes formula: $U(r) = \frac{2}{9}gr^2/\nu$. We will use the subscript c (clean) for the ideally clean system and d (dirty) for systems where surface contaminants are present.

If the Péclet number $Ur/D \gg 1$, with D the diffusivity of the gas in the liquid, a thin concentration boundary layer is formed on the surface of the bubble and diffusion from C to C_∞ occurs across a small distance $\delta \simeq Dr/U$. Since D is typically about three orders of magnitude less than ν, there is an appreciable range of bubble radii over which the Péclet number is large and the Reynolds number small. For that case, F_c and F_d are given by (Levich 1962, §§ 72 and 14)

$$F_c = 8\left(\frac{\pi g D}{2\nu}\right)^{\frac{1}{2}} r^{\frac{1}{2}}(C - C_\infty),$$

$$F_d = 24\left(\frac{2}{9}\frac{gD^2}{\nu}\right)^{\frac{1}{3}} r^{\frac{4}{3}}(C - C_\infty).$$

If we assume that the liquid in contact with the bubble surface is always saturated with gas under the pressure prevailing inside the bubble we can write the concentration C (in g cm^{-3}) as $C = KP$, where K is the coefficient of absorption for the liquid–gas system (Dorsey 1940, p. 529). If some surface active material retards gas diffusion through the bubble surface, K may be only a fraction of the absorption coefficient. Putting

$$\gamma = \frac{C_\infty}{K}, \quad \beta_c = 8\left(\frac{\pi g D}{2\nu}\right)^{\frac{1}{2}} K \quad \text{and} \quad \beta_d = 24\left(\frac{2}{9}\frac{gD^2}{\nu}\right)^{\frac{1}{3}} K,$$

F is given as a function of r and P by

$$F_c = \beta_c r^{\frac{1}{2}}(P-\gamma),$$

$$F_d = \beta_d r^{\frac{4}{3}}(P-\gamma).$$

In the Stokes law régime, F and U clearly satisfy the mild restrictions imposed upon their behaviour in the previous section. In particular it is seen that F does vanish less rapidly than U at small r. Substituting for F_c and U_c into (8), one finds that for a clean system

$$\frac{dr}{dP} = -\left[\beta_c r^{\frac{1}{2}}(P-\gamma) - \frac{\alpha g r^3}{3\nu}\right] \bigg/ \frac{2\sigma}{r^2}\left[\beta_c r^{\frac{1}{2}}(P-\gamma) - \frac{\alpha g r^4}{3\nu}\frac{3P}{2\sigma}\right], \tag{9a}$$

from which the critical radii $r_a(P)$ and $r_b(P)$ are given by

$$\left.\begin{aligned} r_a(P) &= \left[\frac{3\nu}{\alpha g}\beta_c(P-\gamma)\right]^{\frac{2}{5}}, \\ r_b(P) &= \left(\frac{2\sigma}{3P}\right)^{\frac{2}{7}}[r_a(P)]^{\frac{5}{7}}. \end{aligned}\right\} \tag{10a}$$

For a contaminated bubble, substitution of F_d and U_d in (8) gives

$$\frac{dr}{dP} = -\left[\beta_d r^{\frac{4}{3}}(P-\gamma) - \frac{2\alpha g}{9\nu}r^3\right] \bigg/ \frac{2\sigma}{r^2}\left[\beta_d r^{\frac{4}{3}}(P-\gamma) - \frac{2\alpha g}{9\nu}\frac{P}{2\sigma}r^4\right], \tag{9b}$$

from which

$$\left.\begin{aligned} r_a(P) &= \left[\frac{9\nu\beta_d}{2\alpha g}(P-\gamma)\right]^{\frac{3}{5}}, \\ r_b(P) &= \left(\frac{2\sigma}{3P}\right)^{\frac{3}{8}}[r_a(P)]^{\frac{5}{8}}. \end{aligned}\right\} \tag{10b}$$

For both conditions (10a) and (10b) $r_a(P)$ and $r_b(P)$ coincide only when $P-\gamma = 0$, in which case they both vanish. Also, since $r_b/r_a = (2\sigma/3Pr_a)^{\frac{2}{7}}$ for a clean bubble, $(2\sigma/3Pr_a)^{\frac{3}{8}}$ for a dirty bubble, $r_b < r_a$ for all $P > \gamma$. Values of r_b and r_a are listed in table 1 for some liquid–gas systems under a surface pressure $P_0(H)$ of one atmosphere, at a depth of 1 m.

The pressure inside the bubble at the depth of release depends through (2) on the initial radius. The critical radii r_a and r_b are thus different for bubbles of different sizes at the same depth. Values are listed in table 1 for two initial radii: first for bubbles for which $r \gg 2\sigma/P_0$ and for which $P \simeq P_0$, and secondly for bubbles with $r = \sigma/P_0$, for which surface tension contributes twice as much as the hydrostatic head to the total pressure.

Stokes law gives reasonable results up to about $Re = 1$; this corresponds to $r = 7{\cdot}7 \times 10^{-3}$ cm in water, to $r = 1{\cdot}3 \times 10^{-2}$ cm in alcohol. Some of the r_b and most of the r_a listed in table 1 exceed these values, and little weight should be put on them since they fall outside the range of Reynolds numbers for which the

Liquid	Gas	D $10^{-5}\,\text{cm}^2$ sec^{-1}	K $10^{-6}\,\text{g}$ $\text{cm}^{-3}/\text{atm}$	γ atm		Clean system r_b 10^{-3} cm	Clean system r_a 10^{-2} cm	Contaminated r_b 10^{-3} cm	Contaminated r_a 10^{-2} cm
Water	H_2	4·5	1·7	0·5	A	8·1	6·2	1·3	1·0
					B	8·4	6·9	1·4	1·2
Water	N_2	2·0	21	0·5	A	6·5	4·6	1·0	0·7
					B	6·7	5·2	1·0	0·8
Water	CO_2	1·6	2000	0·5	A	21	23	4·5	7·3
					B	22	26	4·8	8·6
Water	O_2	2·0	49	0·5	A	2·3	1·1	1·7	1·6
					B	2·4	1·2	1·8	1·9
Water	O_2	2·0	49	0·5	A	1·3	0·5	0·9	0·5
					B	1·7	0·8	1·3	1·0
Ethyl alcohol	CO_2	3·2	360	0·5	A	8·6	1·1	4·8	7·9
					B	8·9	1·2	5·1	9·5

TABLE 1. Critical radii r_a and r_b calculated from (10a) and (10b) for liquid-gas systems at 15 °C at a depth of 1 m. Two sets of results are shown: those following the letter A are for large radii; those following B for an initial radius equal to $\sigma/P_0(0)$. Data from *Handbook of Chemistry and Physics* (48th ed.), *Int. Critical Tables* (1928) and Dorsey (1940).

formulae from which they were derived apply. As a matter of fact, those r_a and r_b which fall outside the Stokes law régime should be expected to be underestimates of the correct values, since $U(r)$ does not increase as fast as r^2 for $Re > 1$. For example, Deindoerfer & Humphrey (1961) report that a CO_2 bubble of radius 0·48 cm, ascending in water, still shrinks. This value is about twice the r_a calculated from (10a) for clean bubbles.

For oxygen bubbles in water and saturated under one atmosphere (fifth entry in the table) both r_a and r_b are within the Stokes law domain for a clean system. This case has been singled out for more detailed calculations, mainly to illustrate the general behaviour of the trajectories in the (P, r)-plane, as discussed in the preceding section.

The differential quotients (6) and (7) take particularly simple forms if we introduce for a clean system non-dimensional variables as follows:

$$\begin{aligned} P' &= P/P_0(0), \\ \gamma' &= \gamma/P_0(0), \\ r' &= r/r_{a0}, \\ t' &= g^2\rho_0 r_{ao}^2 t/3\nu P_0(0), \end{aligned}$$

where $P_0(0)$ is the initial value of the hydrostatic pressure and r_{a0} is the value of r_a at $t = 0$ for $r \gg \sigma/P_0(0)$:

$$r_{a0} = [(3\nu/\alpha g)\,\beta_c(P_0(0)-\gamma)]^{\frac{2}{5}}.$$

Substituting for F_c and U_c, (6) and (7) become

$$\frac{dr'}{dt'} = \frac{1}{3}\left[r'^4 - \frac{P'-\gamma'}{1-\gamma'}r'^{\frac{3}{2}}\right]\bigg/\left[P'r' - \frac{2\sigma}{3r_{a0}P_0(0)}\right], \tag{11}$$

$$\frac{dP'}{dt'} = \left[\frac{2\sigma}{3r_{a0}P_0(0)}\,\frac{P'-\gamma'}{1-\gamma'}r'^{-\frac{1}{2}} - P'r'^3\right]\bigg/\left[P'r' - \frac{2\sigma}{3r_{a0}P_0(0)}\right]. \tag{12}$$

A similar formulation is possible for the contaminated system with t' multiplied by $\frac{2}{3}$ and r_{a0} written from (10 *b*). One notes that besides initial conditions on r' and P', only two parameters must be specified to describe the behaviour of bubbles in a given liquid–gas system: γ' and $2\sigma/3r_{a0}P_0(0)$. In a clean system under the conditions of the fifth entry in table 1 (O_2 bubbles in water) these parameters take the values 0·91 and $8{\cdot}8\times10^{-3}$ respectively;

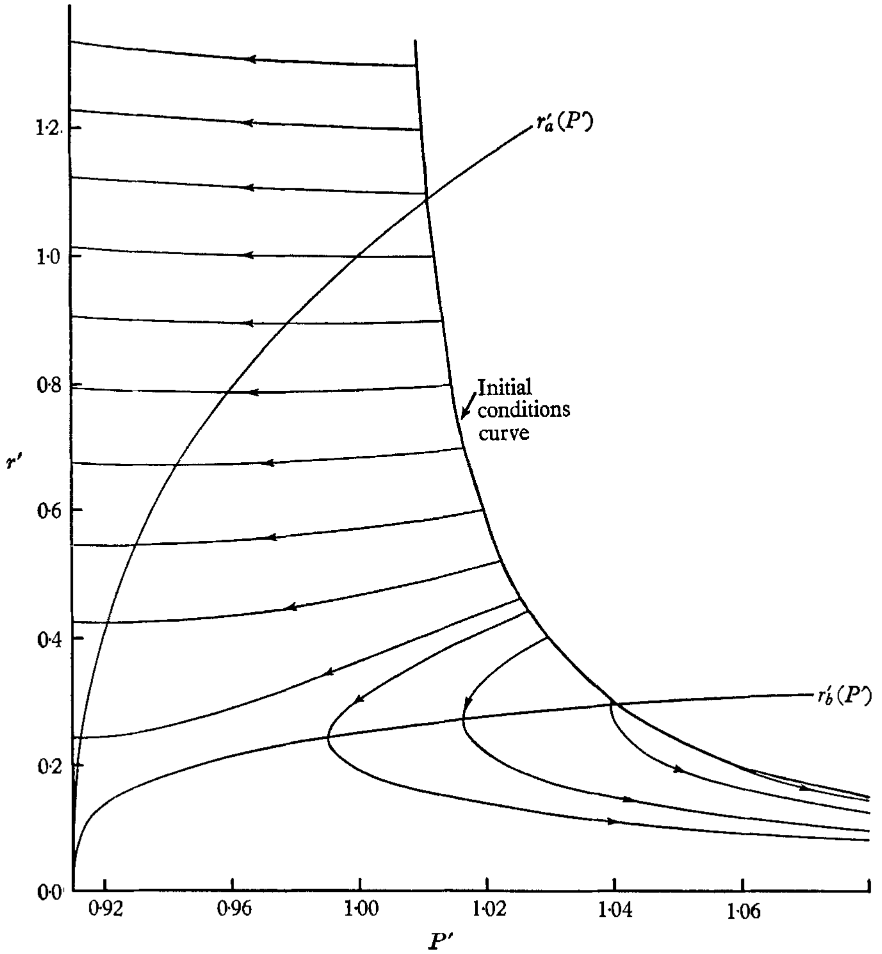

FIGURE 1. The evolution of radius and pressure of oxygen bubbles ascending from a depth of 1 m in clean water saturated with that gas under atmospheric pressure. The radius r' is in units of $r_{a0} = 5{\cdot}0\times10^{-3}$ cm and the pressure P' in units of $P_0(0) = 1{\cdot}1\times10^6$ dynes/cm. The bubbles start with initial conditions given by a point on the 'initial conditions' line; time increases along the trajectories in the direction indicated by the arrows. Atmospheric pressure is at $P' = 0{\cdot}91$.

$$r_{a0} = 5{\cdot}0\times10^{-3}\,\text{cm} \quad \text{and} \quad P_0(0) = 1{\cdot}1\times10^6\,\text{dynes/cm}^2.$$

Trajectories are plotted in figure 1 for values of initial radii chosen so as to show the different types of behaviour described in § 2.

4. Conclusions

The results of the above analysis for the Stokes law régime are of course of limited practical application since they hold only for very small bubbles. The more qualitative results on spherical bubbles are however quite general, do not depend critically on the ascent velocity or on the gas exchange function and still hold well beyond the Stokes law régime, provided only that the bubbles are not too distorted. Extension of these arguments to larger spherical and to non-spherical bubbles and to situations where many gases diffuse through the bubble surface should also prove profitable.

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