The Fundamentals of Bubble Evolution

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1 Introduction

Bubbles appear in all sorts of unexpected places; sometimes welcome, but often unwelcome. The pleasant tingle of carbon dioxide bubbles in carbonated drinks – or the rapid emptying of the contents of the container over the person opening the drink typify the distinction. Other rather more important examples include the gushing of oil wells, as the high pressure from the reservoir is relieved at the well-head, the rapid (often violent) release of trapped gases in steel making, the fobbing of beers at the dispenser, and the damage caused to ships' propellers by cavitation, and the 'bends' which can ensue upon too rapid a decompression after diving to great depths. Perhaps more significant from an economic standpoint are the release of gas during electrolysis, where the presence of bubbles can have a very significant influence on the efficiency of the process, and ebullition and the effects of bubbles on heat and mass transfer in heat exchangers and boilers. It is surprising that really very little is known about the details of bubble evolution; truly this subject is in its (albeit rather protracted) infancy.

Conceptually, bubble evolution consists of various stages: nucleation, growth, detachment (if the nucleation was heterogeneous), rise, and bursting. In practice, these processes will be happening concurrently, and it may prove difficult if not impossible to separate them experimentally. For the purposes of this review, it is convenient to examine each separately, and to imagine that there is no coupling between them, an approximation likely to be poor when the bubble volume density (or density per unit area on an electrode) is large. We set out in this review to ask the following questions for each of the five conceptually separate stages in the evolution process, namely: What is the current state of our understanding in terms of the theory and experimental techniques and data? What are the outstanding challenges?

1.1 General Background

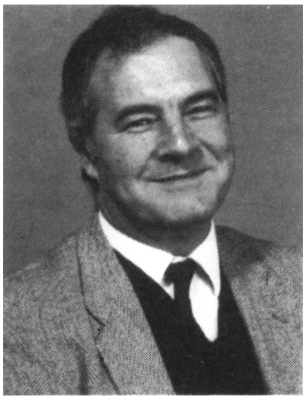
There are two main ways in which bubbles can be generated, depending on whether we are dealing with a unary or an *n*-ary system. In a unary system, bubbles are generated by boiling (ebullition) or cavitation, whereas in an *n*-ary system, in addition to ebullition and cavitation, one or more components may be supersaturated, and bubbles of this component (together with vapour from other components in the system) may be formed at ambient pressures and temperatures. Typical of such systems are carbonated drinks, where CO_2 is dissolved to greater than atmospheric pressure, and the system is then sealed. Upon release of the pressure by opening the bottle or can, bubbles of CO_2 form spontaneously. A simple observation raises an interesting question here. If the container has been agitated by dropping or shaking, and is then opened, the release of excess CO_2 pressure is much more vigorous than if the container has been quiescent. Why? It seems difficult to find an explanation in terms of nucleation theory. Are vast numbers of relatively stable nucleation centres formed by the shaking? This seems exceedingly improbable if these centres are identified as being supercritical sized bubbles – the energy input is simply insufficient to account for such a profusion of sites. A more likely explanation appears to be that areas of the container are exposed to gas by the liquid being violently moved around in the container, and that these gas-filled sites then act as Harvey nuclei (see below) for subsequent bubble generation. This explanation appears flawed by the fact that leaving the container for a period restores the *status quo ante*. How do these Harvey nuclei become deactivated[1]?

In this review, we will concentrate on bubbles formed by supersaturating the solution with a gaseous component, either by *in situ* gas generation (usually by electrolysis) or by prior saturation at elevated pressures followed by pressure release to a lower (but not necessarily atmospheric) pressure. In these systems, the saturation ratio, α (where α is defined as the ratio of the ambient vapour pressure, p divided by the equilibrium vapour pressure under the prevailing conditions, p_0, or $\alpha = p/p_0$) is of prime importance. In three out of the five stages identified in the first paragraph, α is the controlling parameter, whilst in one more, it is a significant factor – only for bursting is supersaturation not important.

With the exception of the nucleation stage, very little attention has been paid in the past to the effects of departure from equilibrium. Here we examine both the effect of a spatially uniform non-equilibrium distribution of a surface active (dissolved gas) species, and look at the dynamic effects of a non-spatially uniform non-equilibrium distribution of the surface active gas. The latter gives rise to the Marangoni effect, and as far as bubble evolution is concerned, has been ignored up to the present time; and we will see that this omission is likely to be quite serious in certain cases.

2 Nucleation

In general, there is an energy barrier to the nucleation process. The height of this barrier may be strongly influenced by the presence of an interface which participates in the process, and by the physicochemical properties of the interface. If there is no interface involved, then the nucleation is said to be homogeneous, and the height of the barrier can be evaluated using nucleation theory. Where the saturation ratio α is relatively low, then the classical treatment is adequate, and other theoretical treatments (for example, the atomistic theory) are not needed. We will assume that this is so here. Cases where this may be an insufficient assumption are where very substantial supersaturations are expected (for example, where the nucleation is from molecular beams, or by direct impingement of metal atoms on cooled substrates). The reason for the importance of the correct



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selection of the theoretical model is mainly due to the altered calculated size of the critical nucleus, a subject revisited below. If this nucleus is sufficiently small, then the exact number of atoms (growth units) is important in evaluating the free energy of formation of this growing cluster. This can be most clearly understood in terms of the change in free energy associated with the addition of a single monomer to the growing nucleus: if this free energy can be treated as a continuous variable, *i.e.*, where the number of monomers is essentially rather large (say $> \sim 100$), then the error in ignoring the discrete nature of the addition process to the sub-critical nucleus is unimportant.

The theory of nucleation of liquids from the vapour is particularly well-developed. The so-called classical theory developed by Volmer[2] and Becker and Döring,[3] although refined in a number of ways, still forms the basis of our understanding and the modifications needed when discussing bubble nucleation are relatively minor: these will be elaborated below. We will use the nucleation of liquid drops as a vehicle for illustrating the theory.

2.1 Homogeneous Droplet Nucleation

The classical theory rests upon the assumption that the macroscopic meanings of quantities such as the interfacial tension can be successfully attributed to microscopic droplets at and even below the critical size, and is manifested in the use of the Gibbs–Thompson (Kelvin) equation

$$\ln(p/p_0) = 2\gamma v/rRT$$

to describe the vapour pressure p of the growing germ or sub-critical nucleus of radius r. The other quantities in the equation are γ, the interfacial tension, v the molar volume, and p_0, the vapour pressure of a flat sample (of infinite radius). The validity of this assumption, together with the related one that the surface tension is definable and has close to its bulk value when applied to sub-critical droplets has long been a source of unease, particularly with theoretical physicists working in this area. The reliable measurements of Fisher,[4] surprisingly show that when the macroscopic values of the interfacial tension and other variables are inserted into an expression for the force of adhesion between two curved mica surfaces, where the predicted adhesive force is directly obtained from the Gibbs–Thompson equation, accurate values (to within a few percent) are obtained for radii of curvature of 0.5nm for non-polar liquids, and for water, for radii of about 2nm, thus showing that for these liquids at least, such fundamental worries are groundless.

In order to calculate J (cm^{-3}s^{-1}), the number of droplets of the new phase appearing per unit time per unit volume, two things are needed; the energy barrier to the formation of a critical sized cluster ΔG^*, and thence the number of such clusters, n^*, formed per unit time per unit volume, and then the rate, g^*, at which such clusters acquire a single growth unit and so become essentially free-growing.

First, we deal with the question of the energy barrier. The formation of a droplet of the more stable (liquid) phase from a supersaturated vapour requires the expenditure of energy to form the new interface, and in compensation, the return of some energy since the new, liquid phase is more thermodynamically stable than the old, supersaturated vapour. Since this latter quantity, ΔG_v depends on the volume of new phase formed, whilst the former depends upon the surface area, we can see immediately that as the radius of the drop changes, so will the energy balance: one term is negative, the other positive, one depends on the square of the radius and the other on its cube. The function describing the total energy therefore goes through a maximum, since $\Delta G_{tot} = 4\pi r^2\gamma - 4\pi r^3\Delta G_v/3$. Differentiation and setting equal to zero, and thus finding the turning point, provides the definition of the 'critical' size, r^*

$$r^* = 2\gamma\Omega/kT\ln\alpha = 2\gamma\Omega/kT\ln(p/p_0), \tag{1}$$

where p is now the vapour pressure in an unstable equilibrium with the critical sized nucleus, r^*. The corresponding free energy, ΔG^*, essentially constitutes the barrier to the phase change, since once a critical size nucleus of the new, liquid daughter phase is present, the stability of the supersaturated mother (vapour) phase is threatened – should the nucleus gain one further atom (molecule) it will become free growing, and a macroscopic liquid drop will appear. The number of such critical sized nuclei is given by:

$$n^* = A\exp(-\Delta G^*/kT), \text{ where } \Delta G^* = 16\pi\gamma^3\Omega^2/3k^2T^2ln^2\alpha \tag{2}$$

The second step in calculating the rate of nucleation, J cm^{-3}s^{-1} is to assess how rapidly such critical sized nuclei acquire one more monomer unit, and thus become free-growing. The simplest method is to evaluate the surface area, O of the metastable critical nucleus, and so to calculate the rate of impingement of monomer species onto this area. The Hertz–Knudsen expression for the rate of impingement is satisfactory for a simple assessment, and relates the ambient vapour pressure, p to the impingement rate, $g^* = pO/(2\pi mkT)^{1/2}$. This actually hides the significant problem of thermal accommodation – each condensing monomer unit liberates the latent heat per monomer, and it is far from easy to see how the cluster gets rid of this excess energy without itself disintegrating.
Now, overall, $J = n^*g^*$, so

$$J = C\exp(-\Delta G^*/kT), \text{ or } J = C\exp(-16\pi\gamma^3\Omega^2/3k^3T^3\ln^2\alpha) \tag{3}$$

where C is not actually a constant, but changes relatively slowly with the other variables, particularly α. The word 'relatively' here is important: it is the extreme sensitivity of J to the terms in the exponential which make it permissible to assume that the pre-exponential terms are indeed constant. This is not a universal truth, and under certain circumstances, it could give rise to serious errors. It is also worth pointing out that the formal similarity of the expression (equation 3) above with the Arrhenius law

$$R = A\exp(-E_a/kT) \tag{4}$$

is quite misleading. In Arrhenius' law, the exponential quantity E_a, the activation energy, is essentially independent of the temperature (the usual experimental variable), but in equation 3, ΔG^* is a strong function of the independent variable, α.

2.2 Heterogeneous Droplet Nucleation

The presence of a participating interface can affect the nucleation process by decreasing the energy barrier to nucleation. It does this by decreasing the volume of the critical sphere needed for nucleation. Consider a part-spherical cap sitting on a uniform, flat substrate with which the liquid forms a finite contact angle (*i.e.*, partial wetting, with θ non-zero) The larger the size of the critical nucleus, the smaller the probability of its formation by random fluctuations (see Dunning[5]). The fraction of the volume of the spherical critical nucleus which needs to be formed is a function of the contact angle, θ of the liquid on the solid, and has commonly been designated $\Phi(\theta)$, which is given by:

$$\Phi(\theta) = (1 - \cos\theta)^2(2 + \cos\theta)/4, \tag{5}$$

and the expression for the rate of nucleation becomes:

$$\begin{aligned} &J = C'\exp(-\Phi(\theta)\Delta G^*/kT),\\ &\text{or } J = C'\exp(-16\pi\gamma^3\Phi(\theta)\Omega^2/3k^3T^3\ln^2\alpha). \end{aligned} \tag{6}$$

Comparing equation 3 with 6, it is clear that the exponential term in the case of hetero-nucleation will be smaller than the homo case by a factor of $\Phi(\theta)$. For small values of $\theta \sim 0$, then $\Phi(\theta)\Delta G^* \rightarrow 0$, and the nucleation barrier tends to zero, whilst at the opposite extreme, as $\theta \rightarrow \pi$, then the barrier tends to that required for homogeneous nucleation, and the interface is not catalytic for the phase change

2.3 Homogeneous and Heterogeneous Bubble Nucleation

The fundamental ideas developed above for droplet nucleation apply when considering the case of a gas bubble nucleating from a supersaturated liquid phase Three chief modifications need to be made to the theory for droplets, when considering bubbles These are (1) The pressure inside the bubble, p_b is a function not just of the curvature (i e , $1/r$) as was the case for drops, but also of the hydrostatic pressure due to the depth of liquid above the level at which the nucleation is taking place In appropriate cases the partial pressure of the dissolved gas as well as the partial (vapour) pressure of the solvent (often water) needs to be taken into account (2) There is equality of chemical potential of the nucleus with the surrounding liquid at all sizes of the sub-critical bubble, whilst for drops this condition only holds for the critical sized drop, conversely there is always mechanical equilibrium for drops, but for bubbles this equilibrium obtains only at the critical size (3) We denote by $\Phi'(\theta)$ the fractional reduction in the volume of the critical sized bubble when it forms on a surface with which it has a contact angle, θ For *drops*, the function $\Phi(\theta) = (1 - \cos\theta)^2(2 + \cos\theta)/4$ gave the required fraction but for bubbles, we define $\Phi'(\theta) = (1 + \cos\theta)^2(2 - \cos\theta)/4$ This function goes from 0 at $\theta = \pi$ to 1 when $\theta = 0$, which is the reverse of the case for droplets Note that the contact angle, θ is always measured through the liquid

With these changes, we now write the equation (analogous to equation 3) for the rate of homogeneous bubble nucleation

$$J = C''\exp(-\Delta G^*/kT), \qquad (7)$$

where $\Delta G^* = 16\pi\gamma^3\Omega^2/3(p_b^* - P)^2$

For the heterogeneous case, with contact angle, θ,

$$J = C \exp(-\Phi'(\theta)\Delta G^*/kT) \qquad (8)$$

2.4 Current State of Understanding and Experiment

For the nucleation of drops of liquid from a supersaturated vapour phase, 'classical' homogeneous nucleation theory has provided a generally good agreement with experimental data The arguments about the so-called replacement factor are now settled, but for a time, this rather large factor appeared to have removed the agreement between the classical theory and experiment Much of the experimental work on homogeneous vapour nucleation has been done by Reiss, and by Katz[6] using a thermal diffusion cloud chamber, and the data are generally accepted as being good However, when the case of heterogeneous nucleation is examined, then the situation is not quite so satisfactory The chief reason for the doubt is the uncertainty about the effects of the hetero-surface for example, what exactly do we mean by the contact angle? Is it the macroscopic or the microscopic angle, the advancing or receding angle? How seriously should we take the usual strictures about the establishment of equilibrium before the contact angle is taken to be meaningful, especially since most nucleation events take place on very short time-scales, and are non-equilibrium phenomena in any case? Unless the nucleation is taking place at a liquid surface, then flatness (or indeed any other well-defined geometry for the nucleation site) cannot be assumed Even for a liquid, transient changes in interfacial geometry might occur and could be catalytic for the appearance of the new phase, but would remain undetected The calculations of Wilt[7] are illustrative, but can easily become misleading For example, combinations of conical pit half angle β, and θ (the contact angle) such that $\theta - \beta > 90°$ leads to $p_b < P$ (the applied hydrostatic pressure), and thus the incipient bubble cannot grow When there is a solid surface present, then there will usually be nucleation sites with a broad spread of geometries, and hence of catalytic potencies (see for example Deutscher and Fletcher[8]) To complicate matters further, it is not just the geometry of the sites which will vary, but also the chemistry, and particularly, the surface chemistry, thus giving rise to a spread of contact angles and interfacial free energies, not only between various sites, but probably from place to place within a given site

Besides reducing the free energy barrier to nucleation, the presence of a solid surface is expected to increase the rate of nucleation by providing a route for enhanced diffusion to the growing germ on the substrate, as expressed by the additional factor involving ΔG_{des} the free energy for desorption, and ΔG_{sd} the free energy for surface diffusion

$$\exp[(\Delta G_{des} - \Delta G_{sd})/kT] \qquad (9)$$

incorporated into the equation for hetero nucleation, as noted by Hirth and Pound [9] Experimentally, the sign of the quantity in round brackets in equation 9 above has been found to be negative by at least two independent authors, which suggests that this part of the theory is in error The solid surface is obviously going to exercise its greatest effect when the concentration is smallest, and thus is expected to play a major role in vacuum deposition experiments, for example, but is not likely to be influential in bubble nucleation

Most methods of measurement of nucleation rates depend upon counting the macroscopic products of nucleation followed by growth – for example, visible bubbles which are detected during their rise through the solution Accurate estimates of the time required for nucleation depend upon reliable knowledge of the rate of growth from a just supercritical size up to the size at which the observations are made If there is a possibility of a change of mechanism and hence of rate, which in many such cases there may be, a simple back-extrapolation of the growth rate may give rise to substantial errors in the calculated nucleation time

The literature on bubble nucleation is rather sparse Findlay[10] was a pioneer, but restricted his quantitative measurements to the solubility of gases (particularly CO_2) in various solutions and suspensions His observations on bubble formation were of a qualitative nature As a group, the electrochemists have made the largest single contribution to the study of the nucleation of supersaturated gas solutions usually of O_2, H_2, or Cl_2 (see for example Sides[11]) whilst CO_2 has been investigated by Lubetkin [12]

An aspect of bubble nucleation which has not had the attention it deserves is that the supersaturated gas acts as a surfactant, and this has many consequences for bubble evolution At 21 °C, the molarity of a solution of carbon dioxide supersaturated to $\alpha = 4$ (i e , typical of carbonated drinks) in water is about 0 15 mole dm^{-3}, and the surface tension is[13] 62 3 mNm^{-1} This represents a considerable surface activity, with a surface pressure, $\pi = 9$ mNm^{-1} Next, let us examine what are the expected results of having such a reduced interfacial tension When calculating the rate of nucleation, J, the interfacial tension, γ, appears to the third power in the exponent, so that small changes in γ can give rise to large variations in J As an example, if the pre-exponential factor is 10^{20}, to give a nucleation rate of 1 cm^{-3} s^{-1}, a value of $\exp(-\Delta G/kT) \sim 10^{-20}$ is required, and this requirement is satisfied by a numerical value of about -46 for the exponent With this condition, and assuming that all the variation is due only to changes in the value of γ, then for the carbonated water referred to above ($\alpha = 4$) the rate of nucleation would be enhanced by a factor of about 4×10^6 by the 14% decrease in surface tension referred to above, compared to the calculated result if the interfacial tension of the water remained unaffected by the presence of the dissolved CO_2 Wilt made allowance for a reduction in the interfacial tension with pressure, based upon the behaviour of N_2, using $d\gamma/dp = -0$ 7 mNm^{-1} atm^{-1}, and this corrects the calculation to the extent that the discrepancy would now be 'only' a factor of about 10^5

It should be noted that it is not only the interfacial tension which is affected by the surfactant properties of the CO_2, but so also is the contact angle Changes in the contact angle can have similarly dramatic consequences for the nucleation rate, through the direct effect on the exponential term of the factor $\Phi'(\theta) = (1 + \cos\theta)^2(2 - \cos\theta)/4$ For the water/CO_2/316 stainless steel system, the contact angle changes about 13% (from 77 to 64°) as the applied pressure goes from 1 to 4 bar, which gives roughly a 40% change in $\Phi'(\theta)$ As discussed above, the surface tension also changes from about 72 mNm^{-1} for pure water to $\gamma_0 - \gamma = \pi$, so $\gamma = \gamma_0 - \pi = 63$ $\text{mNm}^{\ 1}$ ($\sim$ 13%), and this changes the exponential by about 40% Fortuitously, therefore, the effect of pressure of CO_2 gas on the nucleation rate on 316 stainless steel is roughly self-compensating clearly, this is not expected to be generally true

2.5 What are the Outstanding Challenges?

All the methods so far used to detect bubble nucleation, and the events associated with detachment, rise, and bursting depend on macroscopic and therefore observable (and measurable) bubble sizes To deduce the nucleation rate, an assumption has to be made about the rate of growth from a just supercritical bubble to the size at which it is measured, in order to back-calculate the time at which the nucleation event took place The assumption most commonly made is that the bulk (macroscopic) growth rate is given by $R \alpha t^{1\ 2}$, for diffusion-controlled growth This is an approximation (probably a good one), since it is known that early in the bubble lifetime, the growth rate is controlled by inertia, surface tension, and forces that rapidly become unimportant as the bubble develops Thus, measuring the sub-critical cluster distribution as a function of supersaturation, is one of the important experimental objectives Only in mass spectrometer methods for vapour condensation has this aim been met, but for bubbles this method is impractical, and essentially no progress has been made towards this goal Since ultrasound is scattered very efficiently by the gas/liquid interface of bubbles, it is likely that this method will be used to study bubble nucleation at some time in the future, this has not yet be done, as far as the author is aware

Thermal accommodation at the surface of the growing sub-critical cluster is still an issue in the nucleation of liquids from the vapour, although not for bubbles, where thermal accommodation is guaranteed Probably the biggest outstanding issue for bubble nucleation is the (as yet unanswered) question Where exactly does the bubble form in electrolysis? No method has yet definitively answered this question, although one would expect on theoretical grounds that the surface of the electrode should be implicated The potentially strong interaction of the electrostatic charges on the bubble and the electrode may overcome the energy disadvantage in some circumstances, and lead to homogeneous nucleation in the Stern layer, (or even further into the electrolyte), becoming kinetically preferred over the heterogeneous nucleation on the electrode surface A second, equally fundamental question which has not been fully resolved Is nucleation actually implicated at all in the formation of bubbles at low supersaturations? Generally, bubbles will be nucleated at specific sites in the interface, and such sites will have specific microtopographies such that nucleation is facilitated for whatever reason (particularly favoured geometry, or surface chemistry, or contact angle, or most likely, a combination of these) It is worth remarking that nucleation is an *extremely* sensitive probe for selecting just those sites which will produce bubbles, so even a very unlikely combination of features will (given the large number of potential surface sites) give rise to substantial numbers of bubbles The apparent rarity of such a specific set of requirements being met is therefore not a decisive argument against nucleation as the source of bubbles The fundamental question – is nucleation actually responsible for bubble formation at the low supersaturations found for example with carbonated drinks, or is bubble production due mainly or exclusively to Harvey nuclei[14] (which are pre-existing supercritical bubbles of gas, trapped in suitably shaped re-entrant imperfections in the solid surface) under these conditions? – therefore remains unanswered

A question of detail rather than of principle is the undecided effect of various geometries upon bubble nucleation Wilt[7] chose certain simple and readily evaluated geometries for his study Cracks, fissures, scratches and other essentially 'two dimensional' imperfections may have energy advantages over the typically three dimensional examples reported by Wilt

Finally, the Marangoni effect, which predicts the presence of a force as a result of a gradient of surface tension, applies equally to liquid droplets in a vapour environment as it does to bubbles in a liquid continuum The magnitude of the effect is much smaller (chiefly because of the small density of the vapour relative to that of the liquid) but given the sensitivity of nucleation phenomena to subtle changes in the environment, this would seem to be a possible source of error which should be considered by the experimentalists using the thermal diffusion method

3 Detachment

It is convenient to split the processes of detachment into the (quasi) equilibrium, and the dynamic cases, according to whether one can apply thermodynamics or not [Strictly speaking, since detachment is by definition a non-equilibrium phenomenon, no (equilibrium) thermodynamic treatment can properly describe it] For the first case, the classical detachment theories associated with the names of Tate and Bashforth and Adams are available Tate's Law relates the weight, W of a detaching drop to the radius of the tip on which it is formed, r and the surface tension, γ, $W = m\Delta\rho g = 2\pi r\gamma$, Actually, Tate expressed his 'law' as follows 'Other things being equal, the weight of a drop of liquid is proportional to the diameter of the tube in which it is formed' This 'law' may be as much as 40% in error, and empirical correction factors must be used The Bashforth and Adams treatment is based upon the wholly accurate, but unfortunately analytically insoluble dimensionless equation

$$1/(R_1/b) + \sin(\phi)/(x/b) = \beta(z/b) + 2,$$
$$\text{where } \beta = \Delta\rho g b^2/\gamma = 2b^2/a^2$$

here $b = R_1 = R_2$ (the principal radii of curvature) at the apex of the axisymmetric drop, and ϕ is the angle subtended by a general point on the curved interface, with an elevation z above the apex At $z = 0$, $\Delta p = 2\gamma/b$, and as z increases away from the apex, so the change in Δp is given by $\Delta\rho gz$ Bashforth and Adams solved this equation numerically (before the era of computers), and they give tables of x/b against z/b for various values of β

These approaches provide either analytical, simple, and crude (Tate's Law) or numerical but arbitrarily accurate (Bashforth and Adams) assessments of the amount of gas detaching from an orifice of known diameter There is a rich literature on the equilibrium shapes of axisymmetric drops (see for example Hartland and Hartley's book[15]), and since as far as the mathematics are concerned, bubbles are simply drops with an appropriate sign reversal, such treatments apply equally to bubbles As noted before, these calculations are based on an assumption of equilibrium, and thus cannot account for any dissipative processes going on The further from equilibrium we get, the worse this approximation becomes, and thus rapid detachment of bubbles is governed by quite different criteria inertia and viscoelasticity for example There is an intermediate regime in which quasi-equilibrium terms can be successfully combined with dynamic interfacial forces, and the hybrid theory is then at least partly empirical Among the terms that might be included in such a quasi-equilibrium treatment are F_d, F_s, F_i, F_p, and F_b, where F_d is the drag (viscous) force acting to oppose the bouyancy, as does F_s, the surface tension force acting around the contact line of the bubble on the (flat) solid surface F_i represents the inertia force, F_p the excess pressure acting over the area of the bubble foot, and F_b is the bouyancy term, caused by the difference in densities of the liquid and vapour (gas) phases This list is not exhaustive – one might include the energy required to produce new interfacial area against the interfacial tension, and the energy needed to stretch the viscoelastic interface at a rate appropriate to the growth rate of the bubble, though both of these terms are small provided the bubble detachment process is near equilibrium

Particularly for the case of electrolytic bubbles, two forces not previously included in the calculation of the detachment may need to be taken into account in the quasi-static or dynamic force balance, (and even where no detachment takes place, the forces may influence droplet or bubble shape and size) These are due to an electrostatic interaction force, F_e between the bubble and the solid surface from which it is becoming detached (and was discussed in a qualitative way in Brandon and Kelsall[16]), and also the Marangoni effect force, F_M resulting from a gradient of surface tension away from the surface as illustrated in Figure 1

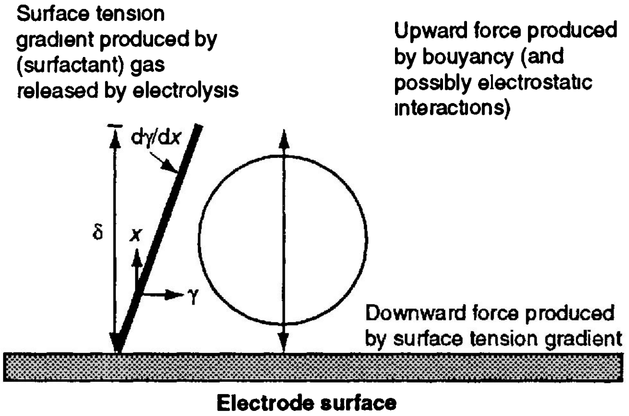

Figure 1 Illustrating the Marangoni effect, and the important parameters governing the force exercised on the bubble $d\gamma/dx$ is a measure of the gradient of the field, and is shown as a straight line function here because the gradient of concentration of the surfactant gas producing the surface tension gradient is usually modelled as being linear in the electrochemical literature This gradient occurs over a distance given approximately by δ the diffusion layer thickness, typically 100 μm for unstirred systems, so that $d\gamma/dx \sim \Delta\gamma/\delta$

Neither of these forces is universal In the case of the electrostatic interaction, it is possible to imagine a set of circumstances in which either the bubble or the surface or (possibly) both are uncharged, though this is deemed extremely unlikely Clearly when the solid surface is an electrode, one of the preconditions for the electrostatic interaction is fulfilled – although the nature of the interaction (whether attractive or repulsive) depends upon the exact circumstances The electrostatic interaction between the surface charge on the bubble and that of the solid surface from which it is becoming detached could be of either sign, depending on the surface chemistry of the various interfaces involved, and the presence of adsorbing species, if any The electrostatic interaction could thus help to retain the bubble on the surface by acting downwards, or cause premature detachment by acting upwards

The Marangoni effect is at first glance likely to be less common, since the prerequisite gradient of surface tension is by no means as universal as the presence of charge at interfaces However, note that during electrolysis in the steady state, electrodes will always produce a gradient of concentration, and if the species being liberated has any surface activity, then the Marangoni effect will be present The liberation of thermal energy at the electrode surface will also have the side effect of producing a surface tension gradient in the adjacent liquid, as a result of a corresponding temperature gradient away from the electrode Thus, it appears that these two forces, F_e and F_M will be of potential importance in electrolysis (particularly where a gas is being liberated) and may be so elsewhere

The prediction is that the electrostatic interaction will reduce the departure diameter when the bubble and surface share the same charge, and will increase it when they are oppositely charged, whilst the Marangoni force will always tend to increase the departure diameter, at least for positively adsorbed (surface active) electrolytic species

3.1 The Interplay of Nucleation and Detachment

It has been noted in Section 2 that heterogeneous nucleation is normally energetically strongly favoured over homogeneous nucleation, and for this reason, surfaces are usually implicated in nucleation processes Overall, the kinetics of release of bubbles in the presence of such a surface would be different from the kinetics in the absence of the surface *even if the nucleation rate itself was artificially adjusted to be the same* The reason for this is that the surface introduces a new kinetic step, detachment, into the overall rate of release, as discussed in Section 4 The ratio of the rate of nucleation to that of detachment is a significant quantity, since it decides which of these two processes becomes rate-determining in the overall release kinetics For heterogeneous nucleation, the three most important experimental variables are the saturation ratio α, the contact angle θ, and the interfacial tension γ, whilst for detachment, the selection of important variables depends upon the treatment of the detachment process In the case of (quasi) equilibrium detachment, a quantitative treatment[17] exists which allows a prediction of the regions in which detachment dominates or is dominated by nucleation It emerges that the contact angle is likely to play an especially important role, since small contact angles ease detachment whilst strongly inhibiting nucleation, thus making nucleation the rate determining step, but large contact angles make detachment difficult whilst promoting heterogeneous nucleation, thus making detachment the rate determining step

3.2 Current State of Understanding and Experiment

Recognizing that the theoretical description of drop and bubble detachment are the same (except for a sign reversal), experiments on drop detachment (which are plentiful) apply equally to bubbles (for which there is rather a sparse literature) So long as the detachment process can be considered to be very close to equilibrium (and provided that there are no strong electrostatic forces, and that the Marangoni effect is not present or at least is of negligible magnitude) then current theory and in particular, the empirical solutions to the Bashforth and Adams equation are of good accuracy Thus, for near equilibrium situations, with the possible exception of electrolytic bubble nucleation/ detachment where the Marangoni and electrostatic forces are expected to be involved, our understanding is good, and excellent experimental data are to be found in the extensive literature (see for example Adamson[18] and the references therein)

As we go farther from equilibrium (which is more typical of conditions found in electrolysis or sparging, for example) the individuality of the bubbles becomes lost in empirical engineering descriptions of gas holdup Here quantitative prediction is crude at best, and knowledge of the detailed mechanisms is lacking

3.3 What are the Outstanding Challenges?

Although the theory of detachment from a plane, smooth surface under near equilibrium conditions is well understood, there are several areas in which our understanding is less than complete

Hetero-nucleation sites (and for that matter, Harvey 'nucleation' sites) will in general have geometrical discontinuities associated with their intersection with the generally flat surface There has been no discussion in the literature on the effects of such geometrical discontinuities on detachment, but clearly, pinning by a surface feature of this sort is expected to stop the lateral growth of a bubble foot, and thus to decrease the departure diameter of the affected bubble. This factor would be expected to mitigate the effects of the difficulty of detachment referred to above in Section 4, and thus to reduce the region in which detachment kinetics dominate the overall release rate. In this connection, it is interesting to note that a drop forming at the vertical end of a tube will have a diameter determined by the internal radius of the tube if it is 'non-wetting' on the tube material, but determined by the outside radius if it 'wets' the tube. The converse is true for bubbles (the bubble is larger if the liquid is non-wetting). Two results follow: if the definition of wetting is that the contact angle of the liquid on the solid is zero or very close to zero, then the detachment diameter of bubbles in this region will be a function of the mouth diameter of the nucleating site (or Harvey site). Information on these sizes could in principle be obtained from nucleation experiments under suitable conditions (see Carr *et al.*[19]). The second question which arises is what degree of departure from zero contact angle is needed for the diameter of the bubble to switch from being equal to that of the inside of the tube to being determined by that of the outside? Could this experiment be a sensitive way of determining contact angle? On a flat surface, it will only be appropriate to apply the analysis of reference 20 when the contact angle is sufficiently far from zero.

Another (although related) area of uncertainty involves the contact angle itself, (which appears in the expression for the detachment rate, exactly as it did for the nucleation rate), and which is not clearly defined. Is the appropriate quantity the macroscopic or the microscopic contact angle, the advancing or the receding contact angle, or none of these?

As noted in the discussion above, two 'new' forces should be taken into account when calculating bubble detachment, these being the Marangoni force where a surface tension gradient exists away from the nucleation site, and the electrostatic force resulting from the interaction of charges at the solid/liquid and liquid/gas interfaces. Whilst these are probably not of great significance in the case of detachment in gas solutions where the supersaturation is achieved by pressure release, in the case of electrolytic bubble evolution there is every reason to expect that these factors will be of significance, and sometimes, of crucial importance as discussed below, in Section 6.

Regardless of the method of imposition of the supersaturation, as we move farther from equilibrium, nothing is well understood, and the greater this departure, the worse our understanding becomes.

4 Growth

If a system is supersaturated sufficiently to produce supercritical bubbles, whether by nucleation (homogeneous or heterogeneous) or by Harvey nuclei, then these bubbles are expected to grow – assuming of course that the nucleation process has not sufficiently depleted the supersaturation to bring the system back to equilibrium (an eventuality with a vanishingly small probability, since in practice this would mean nucleation with arbitrarily small supersaturations). The question is how fast will they grow? The answer depends on a number of factors, but the most important is the supersaturation. Since the supersaturation is directly related to the departure from equilibrium ($\alpha = p/p_0 = \exp(-\Delta\mu/kT)$, one notes that this is equivalent to the statement that the kinetics are governed by the thermodynamic drive ('driving force' seems inappropriate, since there is no force involved), and this is hardly surprising. When inertial and surface tension forces are dominant, which is likely to be the case in the very early stages of bubble growth then the time-dependent bubble radius, $R(t)$ is given by

$$R(t) = At \tag{10}$$

where A is a constant.

Where the growth is determined by how rapidly material can be transported across the interface, Fick's laws apply, and the radial growth rate of a bubble (assumed spherical, or part spherical) is a relatively straightforward calculation, and such a calculation was performed by Scriven in 1959,[20] following the earlier general solution of a spherically symmetrical phase growth (the word 'bubble' was not mentioned) given by Frank.[21] Solution of the diffusion equations with appropriate boundary conditions gives rise to the so-called Scriven equation for the bubble radius $R(t)$

$$R(t) = 2\beta[Dt]^{1/2} \tag{11}$$

This shows the $t^{1/2}$ dependence typical of diffusion-controlled growth, where the interfacial area grows linearly with time. In this equation, β is constant for given conditions of supersaturation.

Under other constraints, for example where direct injection of gas into the bubble is the mechanism for growth, the equation

$$R(t) = Ct^{1/3} \tag{12}$$

is found to apply, where C is constant for a given system, and the volume increases linearly with time.

No substantial advances have been made since these early papers, except to allow for the fact that when a bubble is in contact with an inert (*i.e.*, not an electrode) surface, then some interference in the nominally spherically symmetrical diffusion field occurs as a result of the presence of the surface, resulting in a slowing of the full growth rate by the factor $[1 - \ln(2)] = 0.31$. This is still true for electrode surfaces, but 'direct injection' of gas into bubbles may occur, particularly when bubbles are larger in diameter than the electrode.

4.1 Current State of Understanding and Experiment

Most of the significant experiments on bubble growth rates have been done by electrochemists, and in particular by Westwater and co-workers,[22] although recent advances in instrumental technique reported by Tobias[23] and Carr *et al.*[24] show considerable promise for future improvements in accuracy and spatial resolution. The engineering literature has much material on ebullition, and high speed cinematography has been in use for many years in this connection. Measurements of the kinetics of bubble growth in boiling are somewhat complicated by the omnipresence of convection, a difficulty which is not so acute in the case of electrolysis at low current densities, and is largely absent in the case of bubble growth from pressure release. It is a little surprising that these methods have not yet been fully exploited for kinetic studies.

4.2 What are the Outstanding Challenges?

There are two main areas of uncertainty in bubble growth studies, relating to the role of surfactant films at the liquid/gas interface in slowing diffusion, and thus in reducing the growth rate, and the question of the growth rate of a free bubble. In addition, as mentioned earlier, there has been no reported study of the interaction of growth and the rate of bubble rise.

Ignoring these two rather specific difficulties, there remains the problem of measuring the behaviour of free gas bubbles rising through liquids, which presents a number of experimental difficulties. Among these one might identify the problem of the short duration of bubble rise time on the laboratory scale (for conveniently observable, large bubbles this is typically a few seconds*), the problems of magnification of the usually curved glass containers, and of apparent depth with flat containers, the problems of confining the bubble whilst allowing complete

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*It appears that the possible use of a rotating liquid environment (in much the same way as a spinning drop teniometer produces an effectively zero *g* environment) to eliminate bouyant rise. has not yet been exploited.

freedom for diffusion, and several quite awkward practical difficulties (often of optics or illumination) in precisely measuring the position of the gas/liquid interface when it is strongly curved.

5 Rise

The nucleation and detachment stages of the bubble's evolution are over, and along with growth, rise through the surrounding liquid now takes place. It might be expected that this relatively simple process would be well-understood, and that no significant problems remain. This would be erroneous on both counts. Usually, detachment leads to ascent, but not always. There are a couple of references[25] in the electrochemical literature to observations of detachment being followed rapidly (< 100ms) by re-attachment, and of the bubble jumping back to the electrode surface. This startling behaviour needs an explanation, and is discussed below.

Putting to one side such apparently paradoxical behaviour, the rate of rise of a small gas bubble in a liquid is a classical hydrodynamic problem, and involves solving the Navier–Stokes equation

$$\rho Du/Dt = \rho g - \nabla p + \mu \nabla^2 u, \text{ and } D/Dt = \partial/\partial t + u \cdot \nabla$$

where p is the pressure, ρ is the density, u the velocity, and μ the viscosity of the fluid. Two solutions with different boundary conditions are of concern to us here. These are the Stokes Law, for rigid spheres, which predicts a terminal velocity $U_T = 2gr^2\Delta\rho/9\mu$, and the Hadamard–Rybczynski solution for non-rigid spheres,

$$U_T = 2gr^2\Delta\rho\{(1 + \kappa)/(2 + 3\kappa)\}/3\mu$$

In the absence of surfactant (Hadamard–Rybczynski) the rate of rise is predicted to be 50% more rapid than that of a rigid (Stokes') bouyant sphere.[26] The effect of surfactant in the system is to rigidify the interface, and then the Stokes' law predicted rise is recovered. This latter state of affairs (a rigid interface in the presence of surfactant) is overwhelmingly more common than the former, since unless very special steps are taken to eliminate surface-active species, sufficient will usually be there adventitiously to give the interfacial rigidity required to produce the Stokes' behaviour. It is an interesting but undecided question, whether the surface activity of small gaseous absorbed species such as CO_2 is sufficient to give the interface the needed rigidity – if this was so, then under no conditions would bubbles of (for example) CO_2 obey the Hadamard–Rybczynski prescription, whilst oxygen, nitrogen, and hydrogen are probably insufficiently surface active, and would give the expected non-Stokesian behaviour in the absence of added surfactants.

Both Stokes' Law and Hadamard–Rybczynski solutions of the Navier–Stokes equation assume that the sphere does not change in size with time. In practice, as we have discussed above, bubbles will always grow as they ascend, often because of the supersaturation of the surrounding solution, and (always) because of the relief of hydrostatic pressure during the rise of the bubble. Note that this last results in modest changes in bubble diameter, for example of about 0.33% for a 10cm rise in an aqueous medium, but the former could result in very substantial changes in diameter, depending on the prevailing conditions of supersaturation, and hence growth rate. There is no treatment of this problem in the literature as far as the author is aware. Clearly, there would not be expected to be a terminal velocity for such a system, but rather a monotonic increase in the velocity as the depth decreases.

As with the detachment of bubbles, the Marangoni and electrostatic interactions may have a significant effect on the rise of bubbles, and in particular, on the early stages of this rise, since both effects are linked to the presence of the solid surface. Well away from the surface, in the bulk liquid the rise is governed by the considerations outlined above. In this context, a phenomenon mentioned above, and which has been recorded a couple of times in the literature, is puzzling at first sight, and becomes even more odd upon closer inspection. During electrolysis bubbles sometimes become detached from the (usually horizontal) electrode surface, and immediately (within a few tens of milliseconds) return. Clearly forces other than gravity are involved, and from general principles, one might expect that the gradient of an appropriate field is responsible. It has been suggested that the force involved is electrostatic in origin, but this does not provide an explanation, as will be discussed in greater detail below. If one proposes that the force is due to a Marangoni effect, this also gives rise to a difficulty of a slightly different sort. Essentially, the problem is this, that for the bubble to return to the electrode, a net downward force (of whatever origin) has to be present, but for a bubble to detach from the electrode in the first place, there must be a net upward force. Since these requirements are mutually exclusive, there must be at least one time- or position-dependent force (or both) involved, which acts initially upwards and then becomes unimportant (or zero) or alternatively, a downward force which initially is zero, but grows as the bubble becomes more distant from the electrode. Westwater attributes the departure to coalescence providing a transient upward kinetic energy, and return to electrostatic interactions. The Marangoni effect may thus provide the source of the required downward acceleration.

5.1 Current State of Understanding and Experiment

Clearly, all the difficulties listed in Section 5 which beset the experimentalist in attempting to measure bubble growth will also be present in experiments to measure rise. Perhaps unsurprisingly, therefore, little is known experimentally about the details of bubble rise through liquids. For relatively large bubbles, there is an ample empirical chemical engineering literature on sparging and gas holdup in various types of gas/liquid contactor columns.[27] As the interfacial area is increased, and the bubble size decreases, the rate of rise falls. The Peclet number, is a dimensionless measure of the relative importance of gravity and Brownian diffusion, and a definition is $Pe = 4\pi r^4 \Delta\rho g/3kT$. At sufficiently low Peclet numbers, when the diameter is of the order of 1 μm for aqueous systems, the bubbles will not rise on any convenient time-scale, and the system will be colloidally 'stable' against creaming. In most situations, bubble concentrations are relatively low when compared with other colloidal systems, and coalescence during rise is generally unimportant.

5.2 What are the Outstanding Challenges?

With large bubbles ($>$ 1mm) the shape of the bubble is non-spherical, and the path followed by such a bubble as it rises through a quiescent liquid may be spiral, or oscillatory, or chaotic. At sizes between about 1mm and 1 μm the bubble is approximately spherical, and the rise will generally be rectilinear. The theoretical difficulties are very similar to those involving the trajectory of solid particles sedimenting. The theory of both bubble rise, and of particle sedimentation has been systematically studied by (amongst others) Levitch.[28] Because usually the concentration of bubbles is much lower than of colloidal particles, coalescence will be a rare event during bubble rise, and the focus of much of the current research work (on the interaction between the particles) is not so relevant to the case of bubbles.

6 Bursting

The situation is illustrated in Figure 2, where it is shown that the internal pressure is intermediate between that of a free surfactant bubble (or soap bubble) in air, and that of the same size of bubble completely immersed in a liquid. Essentially, the stability of the bubble once it reaches the free liquid surface is dependent upon the rate of thinning of the liquid layer forming the upper surface of the bubble. In the absence of surfactants, this is a very

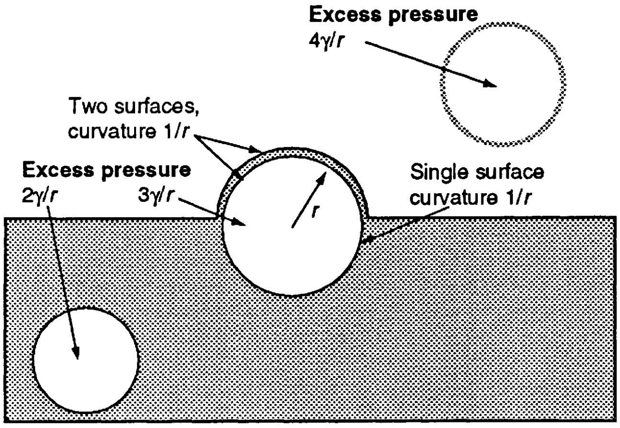

Figure 2 A bubble having completed its rise, intersects the surface The bursting is governed by the rate of thinning of the upper bubble surface The presence of surfactants very considerably slows this otherwise rapid process Since the bubble in the bulk liquid has only one surface, whilst a free bubble in air has two, the excess pressures in the two extreme cases are $2\gamma/r$ and $4\gamma/r$ respectively Depending upon where exactly the bubble intersects the surface it will have an excess pressure intermediate between these extremes Usually, of course, the curvatures of the upper and lower surfaces would be unequal

rapid collapse, opposed only by inertial and viscous forces, since the van der Waals forces are monotonically attractive with decreasing thickness The forces are the same as for two liquid drops approaching across air (gas) because of symmetry of the force expression and the resulting disjoining pressure is negative (attractive) For a surfactant-free system, therefore bubbles will burst very rapidly at the surface An appropriate choice of surfactant will however allow exceedingly long lifetimes at the surface, and foams built up of such bubbles can be very stable (see for example Akers[29])

6.1 Current State of Understanding and Experiment

The general conditions for the stability of a bubble at an interface are either governed by double layer or steric interactions in the thinning lamellæ This is a topic fully covered in general texts on colloid chemistry such as Hunter,[30] and will not be further discussed here

6.2 What are the Outstanding Challenges?

An interesting aspect of bubble bursting which has not been addressed in the literature is how the sound of bursting arises, and what the expected acoustic spectrum might be There are clearly some frequencies which are in the normal audio range (< 16kHz) since the sound of bursting is evident to the human ear FFTs (Fast Fourier Transforms) of the sounds have been reported,[31] but these were recorded with very poor quality microphones It is likely that the sound of the burst is dominated by resonance in the transient but essentially part-spherical cavity produced as the top of the bubble, having penetrated the liquid/air interface, thins and ruptures

7 Conclusions

At the outset, it was remarked how wide the area of potential interest in bubble evolution was, and, paradoxically, how little fundamental work has been done Maybe the reasons are to do with the apparently frivolous nature of investigating Keats' ' beaded bubbles winking at the brim ' Despite the importance of bubbles in Champagne, there are more serious interests at stake, as anyone who has suffered with the bends will attest Bubbles are pretty, scientifically fascinating, and they are important Who needs any other reasons to study them?

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