# The initiation of Guinness

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**Abstract**

Guinness Draught is a distinctive beer, having a black body and a thick white head of foam. It is unusual in that it is always dispensed with a gas mixture of about 21 mole % carbon dioxide and 79 mole % nitrogen. Consequently, it does not foam spontaneously but must instead be 'initiated'. The initiation methods employed by Diageo in canned and bottled Guinness Draught add a significant cost to the final product. Hence, Diageo asked the Study Group to develop a mathematical model for the initiation of Guinness, focusing on any of the current initiation methods.

We decided to focus on the 'surger' unit, which vibrates ultrasonically to initiate Guinness. It does so mainly by the process of rectified diffusion, although concepts from passive and convective diffusion are also important.

In this paper, we briefly review the initiation methods currently employed, the theory of bubble nucleation and growth, and passive, rectified and convective diffusion. A qualitative explanation of how Guinness is initiated is given. Finally, a mathematical model for the initiation of Guinness by the surger unit is developed, the solutions of which are quantitatively reasonable.

# 1  The problem with draught Guinness

Guinness is a distinctive beer that originated in the brewery of Arthur Guinness (1725–1803) at St. James's Gate, Dublin, Ireland [1]. It is based on the 'porter' that first appeared in London in the early 18th century. Porter incorporated roasted barley for the first time and it is this ingredient which endows Guinness with its characteristic burnt or roasted flavour.

The perfect pint of *draught* Guinness is black, or officially a very dark shade of ruby, with a thick 'creamy' head of foam. The head is an integral part of the experience of drinking Guinness. It is created as a result of gas bubbling out of the beer when it is being served (the famous 'surge and settle'). Guinness Draught is unusual in that it is packaged and dispensed using a gas mixture of carbon dioxide ($CO_2$) *and* nitrogen ($N_2$), in contrast to Guinness Extra Stout, and indeed most beers, which use only carbon dioxide. There seems to have been two motivating factors for the use of nitrogen. First, the introduction of metal kegs allowed beer to be stored and served at high pressures ($2-4$ times atmospheric pressure). For most beers this pressure is achieved using only $CO_2$ and, consequently, the $CO_2$ concentration can be relatively high in the beer ($\sim 6\,g\,l^{-1}$). An acidic 'fresh' taste is associated with the dissolved $CO_2$ (as it reacts with water to form carbonic acid), which is not to everyone's liking [2]. In contrast, the gas mixture used to dispense Guinness is mainly $N_2$. In particular, at $3.8\,$bar and $8\,°C$ the gas mixture is about $79$ mole % $N_2$ and $21$ mole % $CO_2$. This yields the desired $CO_2$ concentration of $\sim 2\,g\,l^{-1}$ and the desired $N_2$ concentration of $\sim 0.072\,g\,l^{-1}$ (Section 8). For comparison, a beer dispensed at the same pressure using only $CO_2$ would have a $CO_2$ concentration of $\sim 9.5\,g\,l^{-1}$. Clearly, the Guinness would have the less acidic flavour, the nitrogen being tasteless. In fact, to avoid over-carbonation when high gas pressures are required, such as when pushing beer through long lines or up vertical lifts, a gas mixture of nitrogen and carbon dioxide is used to dispense *all* beers, the proper gas blend being chosen from the supplier's blend selection chart.

The second advantage to using nitrogen is related to its low solubility. $N_2$ is $100$ times less soluble than $CO_2$ at $8\,°C$. Consequently, the $N_2$ concentration in Guinness is very low. The $CO_2$ concentration is also low but this is because the gas mixture is mainly $N_2$. Once bubbles form in Guinness, they remain small due to the low dissolved gas concentrations and, consequently, low growth rates. The small bubbles give Guinness Draught a finer 'creamier' head of foam than that on a carbonated beer like Guinness Extra Stout. Furthermore, the head is longer-lasting since Ostwald ripening, the main process by which foam becomes coarser, is slowed down by a factor of $100$ due to the lower solubility of $N_2$ [3]. The relative concentrations of $CO_2$ and $N_2$ in air also helps: air is about $79$ mole % $N_2$ and only $0.03$ mole % $CO_2$, meaning that the tendency for gas molecules to escape from the foam bubbles into the air is weaker for $N_2$ than for $CO_2$.

However, a major disadvantage of using nitrogen is that, unlike carbonated beers which foam spontaneously, the head on Guinness does not form spontaneously and must be 'initiated'. A good example of this is the Guinness from a 'surger-ready' can. If such a can is carefully opened and poured into a clean glass, little or no head forms. However, if the glass is now placed on a 'surger' unit, which vibrates ultrasonically, a surge of bubbles appears in the body of the

Guinness and a thick creamy head forms as these bubbles collect on top of the Guinness.

As well as being available in kegs and surger-ready (widget-free) cans, draught Guinness is also sold in widget cans and widget bottles, the 'widget' being a plastic capsule that initiates the Guinness when the seal on the container is broken. In all these forms, the container is pressurised to $3.8$ bar at $8\,°C$ with a $79$ mole % nitrogen and a $21$ mole % carbon dioxide gas mixture.

In order to better understand the existing initiation methods and motivate new ones, Diageo asked us, at the 70th European Study Group with Industry, to develop a mathematical model describing bubble formation and growth in Guinness. First, we will review the existing methods of initiation.

# 2   Existing methods of initiation

1. Keg Draught Guinness: Draught Guinness first became available to licensed premises around 1959. To dispense the Guinness, a tap with two lines is attached to the keg. One line leads to a premixed gas cylinder containing nitrogen and carbon dioxide. Pressure gauges on this line allow the pressure in the system to be set. The other line leads to the dispensing tap. On its way to the spout of this tap, the Guinness is forced at high speed through an orifice plate with five small holes. From Bernoulli's theorem, the pressure drops in the beer as it passes through the holes. This allows existing microbubbles to expand and also induces cavitation in the beer, as evidenced by the characteristic surge of bubbles seen in the dispensed beer. This initiation method is very effective, the result being a thick creamy head.

2. Canned and Bottled Draught Guinness: To meet the demand for draught Guinness that could be poured at home, bottled draught Guinness was launched in 1979. To initiate the Guinness, a syringe, supplied with the bottles, was used to suck up some of the Guinness. This was then squirted back into the glass of (headless) Guinness creating a surge of bubbles and, consequently, the head. The syringe initiator was replaced by the can 'widget' in 1989. The widget is a plastic capsule with a tiny hole connecting its interior to the surroundings. When the can is opened, a small amount of beer and nitrogen, previously trapped in the widget, shoots out into the beer. Originally, the widget was used only in canned draught Guinness and was in the form of an insert wedged into the bottom of the can. In 1997, the widget became a floating spherical capsule (it can be heard rattling in the can). A floating bottle widget in the shape of a rocket was introduced in 1999. The bottle widget is optimised for drinking straight from the bottle, while the can widget is optimised for pouring into a glass.

   The operation of the widget deserves further explanation. In the case of the can, a controlled amount of liquid nitrogen is added just before it is sealed. When this liquid nitrogen evaporates it pressurises the can to $3.8$ bar. The pressure equalises in the widget,

the headspace and the beer, forcing some beer into the widget as it does so. When the can is opened, the pressure in the headspace and beer rapidly drops to about 1 bar (atmospheric pressure). The contents of the widget then decompress by squirting gas (mainly $N_2$) and some beer into the Guinness. In the case of the bottle, no liquid nitrogen is added: the bottle is sealed in an environment already at the desired gas pressure.

3. Surger-Ready Draught Guinness: The 'surger' was launched in Tokyo in 2004. It is an electrical device that recreates the 'surge and settle' effect without the need for the keg-and-tap dispensing system. The interface of the surger unit is a metal plate that vibrates ultrasonically. First a little water is poured onto a plate to ensure good mechanical contact. Then a can of surger-ready (widget-free) Guinness is poured into a glass and placed on the plate. The Guinness initially has little or no head. When a button is pressed, the plate vibrates ultrasonically. The associated pressure fluctuations in the Guinness almost immediately create a surge of bubbles and, consequently, the head.

# 3  Bubble nucleation and growth

Many good introductions to the formation and growth of bubbles in supersaturated liquids can be found in the literature (e.g. [4, 5, 6, 7, 8]). Let us consider a container (keg, can or bottle) filled to the desired level with Guinness and pressurised by some method. In the case of the can, the container is sealed after a controlled amount of nitrogen has been dropped onto the liquid surface, while the bottle is sealed in a closed environment already at the desired gas pressure.

In either case, after the container is sealed, an equilibrium is established between the dissolved gas in the liquid and the gas in the headspace (and in the widget, if present). This equilibrium obeys Henry's law, which states that the concentration $c_l$ of gas dissolved in a liquid is proportional to the partial pressure $p$ of that gas above the liquid:

$$c_l = Hp. \tag{3.1}$$

Clearly, the solubility of a gas in a liquid increases as the pressure of that gas over the liquid increases. The proportionality constant $H$ is known as the Henry's law constant. It is temperature dependent, decreasing as the temperature increases; that is, for a fixed partial pressure, gas solubility decreases as the temperature increases. This is the reason that bubbles are seen to form on the surface of a glass of water when it is left in the sun and the reason that effervescence (bubbling) is initially greater in a hot carbonated beverage than a cold one.

When the container is opened, the pressure $p$ in the headspace falls abruptly and Henry's law is no longer satisfied. The liquid is said to be supersaturated with gas molecules. To reestablish equilibrium or, equivalently, to satisfy Henry's law (3.1), the dissolved gas concentration $c_l$ must decrease. The gas molecules can escape either by diffusing through the free (top) surface

of the liquid or by forming bubbles[1].

Although the laws of thermodynamics favour the formation of gas bubbles, there is a kinetic barrier to the production of gas bubbles. To see why, we note that the gas pressure $p_b$ inside a spherical bubble of radius $R$ is given by Laplace's law:

$$p_b = p_l + \frac{2\gamma}{R}, \tag{3.2}$$

where $p_l$ is the pressure in the liquid and $\gamma$ is the surface tension of the liquid in contact with the gas. Laplace's law states that the pressure inside a bubble is greater by $2\gamma/R$ than that in the surrounding liquid due to the fact that the surface tension $\gamma$ of the liquid tends to contract the bubble surface. Clearly, the gas in the bubble is in equilibrium with its concentration $c_l$ in the liquid if Henry's law is satisfied:

$$c_l = Hp_b \equiv c_b, \tag{3.3}$$

If Henry's law is not satisfied then the bubble either shrinks or grows. If $c_l < c_b$ then the bubble shrinks as the gas in it redissolves, whereas if $c_l > c_b$ then the bubble grows as gas diffuses into it from the liquid. Using Laplace's law (3.2) to eliminate $p_b$ yields

$$c_l = H \left( p_l + \frac{2\gamma}{R} \right).$$

Approximating $p_l$ by $p_a$[2] and rearranging terms yields

$$R = \frac{2\gamma}{c_l/H - p_a} \equiv R_c,$$

where $R_c$ is called the critical radius. If $R = R_c$ then the gas bubble is in equilibrium with the gas concentration in the liquid (i.e. $c_l = c_b$) and it neither shrinks nor grows. If $R < R_c$ then $c_l < c_b$ and the bubble shrinks. If $R > R_c$ then $c_l > c_b$ and the bubble grows (Figure 1). The critical radius is often given in terms of the supersaturation ratio $S$ which is defined by

$$S = \frac{c_l}{Hp_a} - 1,$$

so that

$$R_c = \frac{2\gamma}{p_a S}. \tag{3.4}$$

If $p_0$ is the gas pressure over the liquid in the sealed container, then the gas concentration in the liquid is initially $c_l = Hp_0$. Immediately after opening the container, the gas concentration

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[1]What are widely called 'bubbles' in liquids are actually cavities: a true bubble is a region in which gas is trapped by a thin film, whereas a cavity is a gas-filled hole in a liquid.

[2]Strictly speaking, $p_l$ is the sum of the atmospheric pressure $p_a$ and the hydrostatic pressure $\rho_l g \, (h - z)$, the bubble being at a depth $h - z$. Since $p_a \approx 10^5 \, \text{Pa}$ and $\rho_l g h \lesssim 10^3 \, \text{Pa}$, the hydrostatic pressure can be neglected.
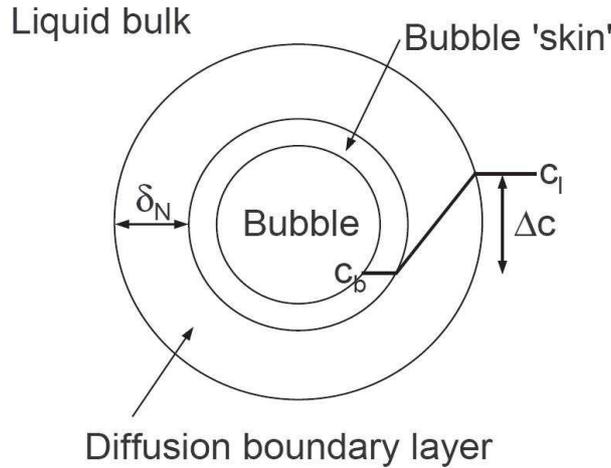
Figure 1: The (idealised) dissolved gas concentration close to a postcritical ($R > R_c$) bubble. $\Delta c$ is the difference between the dissolved gas concentration $c_l$ in the liquid bulk and the dissolved gas concentration $c_b = Hp_b$ in the bubble 'skin', which is a thin layer next to the bubble surface and in equilibrium with the gas pressure in the bubble. The concentration falls from $c_l$ to $c_b$ over a diffusion boundary layer of thickness $\delta_N$.

in the liquid is still $c_l = Hp_0$ so that the initial supersaturation ratio is $S = p_0/p_a - 1$. For beer ($\gamma \approx 40\,\mathrm{mN\,m^{-1}}$ [3]) and an initial supersaturation ratio of 2.8, which is typical for draught Guinness, the critical radius is $0.3\,\mu$m. If enough gas molecules cluster together to form an embryonic bubble with a radius greater than this critical radius, then that bubble will survive and grow. The random thermal motion of the gas molecules is the process that provides these clusters. However, in order to cluster together, the gas molecules must first push their way through the polar water molecules that are strongly attracted to each other. This places a considerable energy barrier before bubble formation. This energy barrier can be lowered by reducing the critical radius, which also increases the likelihood that enough gas molecules will randomly cluster together. To this end, the critical radius can be reduced by lowering the surface tension $\gamma$[3] or by increasing the supersaturation ratio $S$. However, calculations, verified by experiment, show that the random nucleation of bubbles, called homogeneous nucleation, requires a supersaturation ratio of several hundred to over a thousand to be observable [9, 10].

In practice, bubbles form in even weakly supersaturated liquids, such as carbonated soft drinks ($S \sim 1$ [11]) or champagne ($S \sim 5$ [12]). When these liquids are poured into a glass, it is easy to observe that bubbles form on the surface of the glass rather than in the bulk of the liquid. When the bubbles reach a critical size, they detach from the glass surface and rise up through the liquid. Over most of the glass surface, the bubble production is very slow, produces large ($\sim 1\,$mm) bubbles, and soon stops altogether. However, at a few spots on the

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[3]E.g. we found that when washing-up liquid is added to a carbonated soft drink and then placed on the surger unit, a head consisting of small bubbles is formed. Without the washing-up liquid, the head consists of much larger bubbles and also collapses much faster.

Figure 2: Bubbles in a glass of carbonated beverage appear to rise in streams from spots on the surface of the glass. As they rise, they grow larger and spread further apart.

glass surface, the bubble production is very rapid and a continuous stream of small ($< 1\,\mathrm{mm}$) bubbles can be seen rising from these spots. As the bubbles rise, they grow larger and spread further apart (Figure 2). The surface of the glass is assisting bubble formation by providing nucleation sites, which are usually in the form of preexisting gas pockets [13]. This is termed heterogeneous nucleation. The conventional view is that when a glass is filled with liquid, air can become trapped in crevices on the glass surface [13]. If the radius of curvature of any of these gas pockets is greater than the critical radius, then that gas pocket grows into a macroscopic bubble as dissolved gas diffuses into it (Figure 3). Eventually, the increasing buoyancy force on the bubble exceeds the capillary force holding it to the glass surface and it detaches. Some gas may be left behind in the crevice so that the process of bubble production can repeat itself. However, recent work has shown that cellulose fibres, which either fall out of the air or are left after drying with a towel, can be much better nucleation sites than glass crevices [12, 14]. These cellulose fibres are roughly cylindrical and hollow, about $100\,\mu\mathrm{m}$ long and several $\mu$m wide. When a liquid is poured into a glass, air is trapped inside these fibres. Since the radius of curvature of these gas pockets is greater than the critical radius, they grow as dissolved gas diffuses into them. When a gas pocket reaches the tip of a fibre, a bubble is released, but some of the gas is left behind in the fibre so that the process of bubble production can repeat itself (Figure 4). This results in a characteristic bubble stream (Figure 2). As the gas concentration in the liquid decreases, the frequency of bubble formation decreases and the critical radius increases. When the critical radius is equal to the radius of curvature of a gas pocket, bubble production from that gas pocket stops. In summary then, the bubbles in a glass containing a carbonated beverage originate from gas pockets trapped either in glass crevices or cellulose fibres, the bubbles from cellulose fibres being much smaller and more frequent, and thereby forming bubble streams. In passing, we note that a dramatic example of heterogeneous nucleation is the addition of a spoonful of sugar to a carbonated soft drink. The sugar grains most likely contain many small gas pockets.
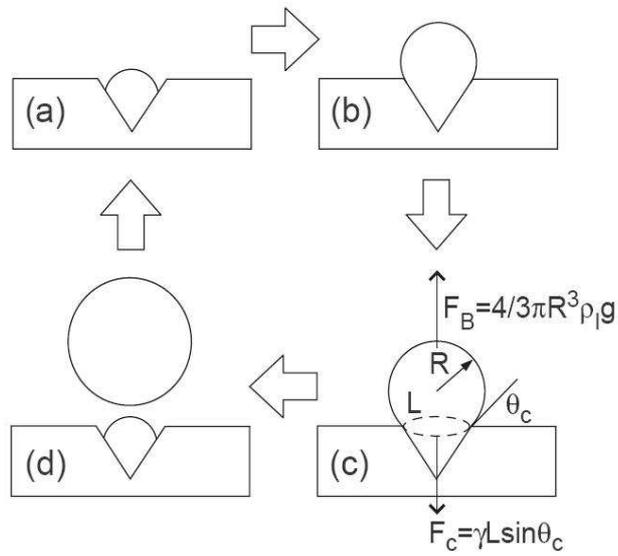
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Figure 3: Bubble production cycle from a crevice in a glass wall. (a) Gas diffuses into trapped air pocket. (b) Bubble forms. (c) Buoyancy force $F_B$ eventually matches the capillary force $F_c$. (d) Bubble detaches. Adapted from [15].
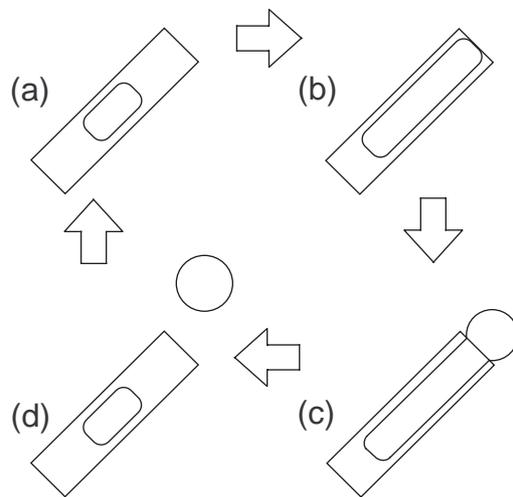


Figure 4: Bubble production cycle from a cellulose fibre. (a) Gas diffuses into trapped air pocket. (b) Pocket reaches tip of fibre. (c) Bubble forms. (d) Bubble detaches.

After a bubble is released from its nucleation site, it grows as it makes its way to the surface. This is due to the continuous diffusion of dissolved gas into the bubble (the drop $\rho_l g h$ in the liquid pressure makes a minor contribution to the expansion of the bubble). The buoyancy force increases as the bubbles grow, causing them to accelerate and spread further apart. The rising bubbles also experience a friction force (i.e. a drag) in the viscous liquid. If the radius of a bubble were fixed, then the bubble would rapidly reach a constant velocity, termed the terminal velocity, at which the upward buoyancy force would be balanced by the downward drag force. However, for a growing bubble, the buoyancy force ($\propto R^3$) always remains slightly larger than the drag force ($\propto R$) so that the bubble continuously accelerates as it rises.

The final size of a bubble is affected by three main factors: (i) the distance the bubble has travelled, (ii) the concentration of dissolved gas, and (iii) the concentration of organic compounds. The first two are obvious factors, whereas the third needs further explanation. Beer contains many organic compounds which have a water-soluble (hydrophilic) part and a water-insoluble (hydrophobic) part. Hence, they like to gather around the surface of a bubble with their hydrophobic ends pointing into the gas bubble and their hydrophilic ends in the liquid. They are thus called surfactants (SURFace-ACTive AgeNTS). As a bubble rises, it collects these surfactants. According to fluid mechanics, a rigid (i.e. solid) sphere rising through a liquid experiences a greater drag than a fluid (e.g. gas) sphere. Essentially, the no-slip condition at the surface of a solid sphere retards its movement, whereas the circulation of gas within a gas bubble 'lubricates' its movement through the liquid. However, surfactants reduce this lubricating effect, causing the drag on the bubble to increase. The bubble continues to grow as it rises and if it grows fast enough then the fraction of the bubble surface that is contaminated by surfactants remains small. This is the case for clear liquids like champagne, which has a relatively high $CO_2$ content ($\sim 12\,\mathrm{g\,l^{-1}}$ [12]) and thus bubble growth rate, and a low surfactant concentration ($\sim 1\,\mathrm{mg\,l^{-1}}$ [12]), so that champagne bubbles experience a drag similar to that which would be experienced by clean bubbles [16]. In contrast, beer bubbles experience a drag similar to that which would be experienced by a solid sphere of the same radius, the combination of low $CO_2$ content ($\sim 6\,\mathrm{g\,l^{-1}}$) and high surfactant concentration ($\sim 100\,\mathrm{mg\,l^{-1}}$ [12]) eliminating the lubricating effect associated with a clean bubble [5, 16]. Furthermore, in liquids with zero or low surfactant concentrations, such as pure water, carbonated soft drinks and champagne, bubbles burst almost immediately on reaching the surface. In beer, the surfactant coating allows the bubbles to collect at the surface of the liquid to form a foam, called the head.

Guinness, being weakly supersaturated, will have no observable homogeneous nucleation within the body of the liquid. Since surger-ready Guinness can be poured with very little or no head forming, the heterogeneous nucleation rate on the surface of the glass must also be very low. It can be made appreciable by adding a spoonful of sugar. The sugar crystals provide many nucleation sites. Furthermore, as the sugar dissolves into the liquid, it readily liberates the bubbles forming at these sites. The result is a surge of small bubbles. Bubbles do form on the surface of the glass but they seem reluctant to detach, probably because the low dissolved gas concentrations in Guinness prevent them from becoming large enough to detach.

# 4 Qualitative explanation of initiation

There are basically two ways to promote bubble formation: (I) we can introduce postcritical ($R > R_c$) bubbles or gas pockets ('seeding'), or (II) we can grow the precritical ($R < R_c$) bubbles that are popping into and out of existence. The methods for achieving type I bubble formation are

- Entrapment of gas bubbles: If a container is shaken, then some of the gas above the liquid level is mixed into the liquid as small bubbles. When the container is opened, the pressure falls and these bubbles expand. Perhaps more importantly, dissolved gas will diffuse into these bubbles if $R > R_c$. This vigorous bubble growth can cause shaken carbonated beverages to spray out of their containers. Splashing a liquid into a glass, rather than pouring it slowly down the side of the glass, can also entrap air bubbles with $R > R_c$, as can banging a glass of liquid down or swirling the glass.

  By opening a can of surger-ready Guinness at an appropriate angle, it is possible to initiate the Guinness. It is likely that as the gas rushes out of the can, it causes waves to form on the liquid surface via the Kelvin-Helmholtz instability. These waves then entrap gas bubbles as they crash against the tab, the walls of the can or back into the liquid. Ocean foam has similar origins, wind creating the crashing waves.

- Cavitation: In the keg-and-tap system, the Guinness is forced through an orifice plate. In accordance with Bernoulli's theorem, the pressure decreases and the velocity increases as the liquid passes through the holes. If the pressure decrease is large enough, then the liquid can be torn apart and cavities (i.e. bubbles) can form in the Guinness. The distinction between type I and type II bubble formation is blurred here since a liquid is more likely to be torn apart where it is weakest, such as where a precritical bubble exists.

- Injection of gas: In widget cans and bottles, a jet of gas shoots from the widget into the Guinness when the container is opened. This jet breaks up into bubbles. If the jet is too short, then some of the Guinness at the bottom of the container remains uninitiated. When the Guinness is poured out of the container, the uninitiated beer passes through or by the foam, providing a fresh supply of nitrogen to existing bubbles and thereby refreshing the head; that is, pouring completes initiation of the Guinness.

The method for achieving type II bubble formation is

- Pressure fluctuations: Precritical bubbles will expand if the local liquid pressure drops. For example, if the expansion is isothermal, then a drop in liquid pressure from $1$ bar to $0.5$ bar causes a precritical Guinness bubble with $R = 0.25 \, \mu$m to expand until $R \approx 0.31 \, \mu$m, while the critical radius drops from $0.29 \, \mu$m to $0.24 \, \mu$m. Hence, dissolved gas in the liquid diffuses into the bubble. If the liquid pressure then returns to its original value, the bubble may or may not survive. It will survive if enough gas has diffused into the

| Initiation method | Method of bubble formation | Type |
|---|---|---|
| Keg-and-tap | Cavitation | I |
| Syringe | Cavitation; entrapment of air bubbles | I |
| Widget | Injection of gas bubbles | I |
| Shaking container | Entrapment of gas bubbles | I |
| Banging glass down | Entrapment of gas bubbles | I |
| Opening can at an angle | Entrapment of gas bubbles | I |
| Ultrasound | Pressure fluctuations | II |

Table 7: Initiation methods classified according to the method and type of bubble formation employed.

bubble to keep its radius greater than the critical radius. Even if this is not the case, the bubble can be encouraged to grow by repeatedly subjecting it to pressure fluctuations. The Guinness surger unit employs this method by vibrating at ultrasonic frequencies.

In table 7, we have classified the initiation methods for Guinness according to the method and type of bubble formation employed. Since the surger unit is the 'cleanest' experiment, we decided at the Study Group to focus on this initiation method.

# 5 The mathematical models

First, we describe a mathematical model for the diffusion of dissolved gas into a bubble which is not rising in the liquid. We call this passive diffusion. By assuming that the gas bubbles are purely nitrogen, we can introduce a small parameter which allows us to obtain some analytical results. These results emphasise the role played by the critical radius. Next, we introduce the effect of a sound field and apply analytical results found in the literature. It is shown that above a critical threshold for the amplitude of the sound field, precritical bubbles grow. This is termed rectified diffusion. Next, we consider how diffusion is altered when the bubble is rising, as it does in practice. We call this convective diffusion, since convection is now assisting the transfer of mass to the bubble. Finally, a mathematical model for describing the initiation of Guinness by the surger unit is described and solved numerically.

## 5.1 Bubble growth by passive diffusion

Consider a spherical bubble of radius $R(t)$ at rest in an infinite incompressible inviscid liquid (Figure 5). Far away from the bubble the pressure in the liquid is $p_\infty(t)$ and this is taken to
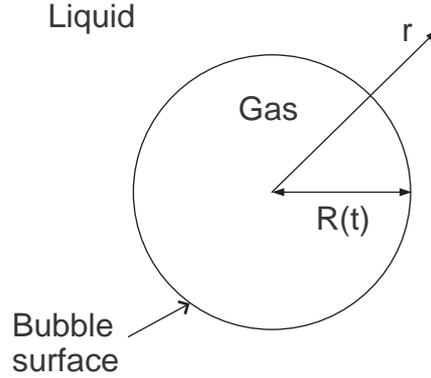
Figure 5: A spherical bubble of radius $R(t)$ in a liquid.

be a known input which regulates the growth or collapse of the bubble. We assume that, as its radius changes in time $t$, the bubble remains spherical so that the bubble surface moves only in the radial direction. It follows that the motion induced in the fluid is also radial:

$$u_r = u(r, t), \quad u_\theta = u_\phi = 0,$$

where $u_r$, $u_\theta$, $u_\phi$ are the components of the fluid velocity expressed in spherical coordinates $(r, \theta, \phi)$. The origin of the coordinate system is taken at the centre of the bubble so that $r$ is distance from the centre of the bubble. Because of the spherical symmetry, all physical quantities are functions of at most $r$ and $t$. Heat transfer is neglected by assuming that the temperature $T$ is constant in time and uniform in space. Furthermore, the pressure $p_b$ in the bubble is taken to be a function only of $t$. We also assume that only one gas species (i.e. nitrogen) is present in the liquid and the bubble.

The governing equations are the incompressibility condition:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 u\right) = 0, \tag{5.1}$$

the radial component of the Navier-Stokes equation governing the motion of the liquid:

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial r} = -\frac{1}{\rho_l}\frac{\partial p_l}{\partial r}, \tag{5.2}$$

and the diffusion-convection equation governing the gas concentration $c(r, t)$ in the incompressible liquid:

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial r} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right). \tag{5.3}$$

The mass flux of gas into the bubble is given by

$$q = 4\pi R^2 D \left.\frac{\partial c}{\partial r}\right|_{r=R(t)},$$

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and can be equated to the rate of increase of the bubble mass:

$$\frac{d}{dt}\left(\frac{4}{3}\pi R^3 \rho_b\right) = 4\pi R^2 D \left.\frac{\partial c}{\partial r}\right|_{r=R(t)}. \tag{5.4}$$

At the bubble surface $r = R(t)$, we also have the following boundary conditions:

$$u = \dot{R} \quad \text{at } r = R(t), \tag{5.5}$$

$$p_l = p_b - \frac{2\gamma}{R} \quad \text{at } r = R(t), \tag{5.6}$$

$$c = Hp_b \quad \text{at } r = R(t). \tag{5.7}$$

The kinematic boundary condition (5.5) holds as the fluid motion is induced by the growth or collapse of the bubble. Equation (5.6) is simply Laplace's law (3.2), and (5.7) is simply an application of Henry's law (3.1). Far away from the bubble at $r = r_\infty$, the pressure and concentration are prescribed by

$$p_l = p_\infty(t) \quad \text{at } r = r_\infty, \tag{5.8}$$

$$c = c_\infty(t) \quad \text{at } r = r_\infty. \tag{5.9}$$

We also require the following initial conditions:

$$R = R_0 \quad \text{at } t = 0, \tag{5.10}$$

$$p_l = p_0 \quad \text{at } t = 0, \tag{5.11}$$

$$c = Hp_0 \quad \text{at } t = 0. \tag{5.12}$$

Here, $p_0$ corresponds to the gas pressure in the sealed container so that (5.12) follows from an application of Henry's law. The contribution of gravity to the liquid pressure is neglected so that the initial liquid pressure can be set equal to $p_0$. From (3.4), the critical radius is

$$R_c = \frac{2\gamma}{\Delta p} = \frac{2\left(4 \times 10^{-2}\,\mathrm{N\,m^{-1}}\right)}{2.8 \times 10^5\,\mathrm{N\,m^{-2}}} \approx 0.3\,\mu\mathrm{m},$$

where $\Delta p = p_0 - p_a$.

Solving (5.1) for $u$ and applying the boundary condition (5.5) yields

$$u = \frac{R^2 \dot{R}}{r^2}. \tag{5.13}$$

Substituting (5.13) into (5.2) yields

$$\frac{\partial}{\partial t}\left(\frac{R^2 \dot{R}}{r^2}\right) + \frac{R^2 \dot{R}}{r^2}\frac{\partial}{\partial r}\left(\frac{R^2 \dot{R}}{r^2}\right) = -\frac{1}{\rho_l}\frac{\partial p_l}{\partial r}.$$

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Hence,

$$\frac{1}{r^2}\frac{d\left(R^2\dot{R}\right)}{dt} - \frac{2\left(R^2\dot{R}\right)^2}{r^5} = -\frac{1}{\rho_l}\frac{\partial p_l}{\partial r}.$$

Integrating from $r = R(t)$ to $r = r_\infty$ yields

$$\frac{d\left(R^2\dot{R}\right)}{dt}\int_R^{r_\infty}\frac{1}{r^2}dr - 2\left(R^2\dot{R}\right)^2\int_R^{r_\infty}\frac{1}{r^5}dr = -\frac{1}{\rho_l}\int_R^{r_\infty}\frac{\partial p_l}{\partial r}dr,$$

and so, applying the boundary condition (5.8) and assuming that $r_\infty \gg R$,

$$\frac{1}{R}\frac{d\left(R^2\dot{R}\right)}{dt} - \frac{\dot{R}^2}{2} = -\frac{p_\infty(t) - p_l(R)}{\rho_l}.$$

This can be rewritten as

$$p_l(R) = p_\infty(t) + \rho_l\left(R\ddot{R} + \frac{3\dot{R}^2}{2}\right).$$

Using (5.6) to eliminate $p_l(R)$, the liquid pressure at the bubble surface, we obtain

$$p_b(t) = p_\infty(t) + \frac{2\gamma}{R} + \rho_l\left(R\ddot{R} + \frac{3\dot{R}^2}{2}\right). \qquad (5.14)$$

This is the well-known Rayleigh-Plesset (RP) equation. In the steady state, it reduces to Laplace's law.

Substituting (5.13) into (5.3) yields

$$\frac{\partial c}{\partial t} + \frac{R^2\dot{R}}{r^2}\frac{\partial c}{\partial r} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right). \qquad (5.15)$$

Assuming that the gas in the bubble behaves as a perfect gas, we have

$$\rho_b = \frac{p_b}{\mathcal{R}_s T}, \qquad (5.16)$$

where $\mathcal{R}_s$ is the specific gas constant. Substituting (5.16) into (5.4) yields

$$\frac{1}{3\mathcal{R}_s T}\frac{d\left(R^3 p_b\right)}{dt} = R^2 D \left.\frac{\partial c}{\partial r}\right|_{r=R(t)}.$$

Using (5.14) to eliminate the bubble pressure $p_b$ finally yields

$$\frac{1}{3\mathcal{R}_s T}\frac{d}{dt}\left\{R^3\left[p_\infty + \frac{2\gamma}{R} + \rho_l\left(R\ddot{R} + \frac{3\dot{R}^2}{2}\right)\right]\right\} = R^2 D \left.\frac{\partial c}{\partial r}\right|_{r=R(t)}. \qquad (5.17)$$

Equations (5.15) and (5.17) govern $c(r, t)$ and $R(t)$. The remaining initial and boundary conditions are

$$R = R_0 \quad \text{at } t = 0, \tag{5.18}$$

$$c = Hp_0 \quad \text{at } t = 0, \tag{5.19}$$

$$c = H\left[ p_\infty + \frac{2\gamma}{R} + \rho_l \left( R\ddot{R} + \frac{3\dot{R}^2}{2} \right) \right] \quad \text{at } r = R(t), \tag{5.20}$$

$$c \approx c_\infty(0) = Hp_0 \quad \text{at } r = r_\infty. \tag{5.21}$$

In condition (5.21), we have assumed that for a single bubble in an infinite liquid, the concentration far away from the bubble remains unchanged from its initial value.

**Initial bubble growth**

We now nondimensionalise the governing equations by letting

$$R^* = \frac{R}{R_c}, \quad r^* = \frac{r}{R_c}, \quad t^* = \frac{t}{\tau}, \quad c^* = \frac{c - Hp_a}{H\Delta p}, \tag{5.22}$$

where asterisks denote dimensionless variables and

$$\tau = \frac{R_c^2}{D\varepsilon}, \quad \varepsilon = \frac{H\Delta p}{\rho_a}, \quad \rho_a = \frac{p_a}{\mathcal{R}_s T}.$$

The time scale $\tau$ corresponds to the time it takes a mass $4\pi\rho_a R_c^3/3$ to enter a sphere of radius $R_c$ if the mass flux density is $DH\Delta p/3R_c$. For nitrogen $\tau \approx 0.8\,\text{ms}$ and $\varepsilon \approx 0.06$. Substituting (5.22) into the governing equations (5.15) and (5.17) yields (asterisks omitted)

$$\varepsilon \left( \frac{\partial c}{\partial t} + \frac{R^2 \dot{R}}{r^2} \frac{\partial c}{\partial r} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right), \tag{5.23}$$

$$\frac{1}{3} \frac{d}{dt} \left\{ R^3 \left[ \frac{p_\infty}{p_a} + \frac{\Delta p}{p_a R} + \delta \left( R\ddot{R} + \frac{3\dot{R}^2}{2} \right) \right] \right\} = R^2 \left. \frac{\partial c}{\partial r} \right|_{r=R(t)}. \tag{5.24}$$

where

$$\frac{\Delta p}{p_a} \approx 2.8, \quad \delta = \frac{\rho_l D^2 \varepsilon^2}{p_a R_c^2} \approx 10^{-9}.$$

Omitting the small terms in (5.23) and (5.24) yields

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) = 0, \tag{5.25}$$

$$\frac{1}{3} \frac{d}{dt} \left[ R^3 \left( \frac{p_\infty}{p_a} + \frac{\Delta p}{p_a R} \right) \right] = R^2 \left. \frac{\partial c}{\partial r} \right|_{r=R(t)}. \tag{5.26}$$

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Dropping the terms of order $\varepsilon$ in (5.23) means that we can no longer satisfy the initial condition (5.19). The other initial and boundary conditions in dimensionless form are (asterisks omitted)

$$R = \frac{R_0}{R_c} \quad \text{at } t = 0, \tag{5.27}$$

$$c = \frac{p_a}{\Delta p} \left( \frac{p_\infty}{p_a} + \frac{\Delta p}{p_a R} - 1 \right) \quad \text{at } r = R(t), \tag{5.28}$$

$$c = 1 \quad \text{at } r = \frac{r_\infty}{R_c}, \tag{5.29}$$

where we have omitted terms of order $\delta$ in (5.28). Since $r_\infty / R_c \gg 1$, we can rewrite (5.29) as

$$c \to 1 \quad \text{as } r \to \infty. \tag{5.30}$$

Solving (5.25) for $c$ and applying the boundary conditions (5.28) and (5.30) yields

$$c = \frac{R p_a}{r \Delta p} \left[ \frac{p_\infty}{p_a} + \frac{\Delta p}{p_a} \left( \frac{1}{R} - 1 \right) - 1 \right] + 1.$$

Hence,

$$\left. \frac{\partial c}{\partial r} \right|_{r=R} = -\frac{p_a}{R \Delta p} \left[ \frac{p_\infty}{p_a} + \frac{\Delta p}{p_a} \left( \frac{1}{R} - 1 \right) - 1 \right]. \tag{5.31}$$

Substituting (5.31) into (5.26) yields

$$\frac{1}{3} \frac{d}{dt} \left[ R^3 \left( \frac{p_\infty}{p_a} + \frac{\Delta p}{p_a R} \right) \right] = -\frac{R p_a}{\Delta p} \left[ \frac{p_\infty}{p_a} + \frac{\Delta p}{p_a} \left( \frac{1}{R} - 1 \right) - 1 \right]. \tag{5.32}$$

When the container is opened, the liquid pressure rapidly equilibrates with the atmospheric pressure so that $p_\infty = p_a$. Then (5.32) becomes

$$\frac{1}{3} \frac{d}{dt} \left[ R^3 \left( 1 + \frac{\Delta p}{p_a R} \right) \right] = R - 1,$$

or

$$\frac{dR}{dt} = \frac{R - 1}{R^2 + 2R \Delta p / (3 p_a)}. \tag{5.33}$$

If $R < 1$ then $\dot{R} < 0$ and the bubble collapses as the gas in it redissolves. If $R > 1$ then $\dot{R} > 0$ and the bubble grows as gas in the liquid diffuses into it. If $R = 1$ then $\dot{R} = 0$ and the bubble is in an unstable equilibrium state; that is, a perturbation from this state results in the bubble either growing or collapsing, depending on whether the perturbation is an increase or decrease in $R$. This confirms that $R_c$ is the critical radius, determining whether the bubble will grow or collapse by diffusion. Solving (5.33) for $R$ and applying the initial condition (5.27) yields

$$\frac{1}{2} \left( R^2 - \frac{R_0^2}{R_c^2} \right) + \left( 1 + \frac{2 \Delta p}{3 p_a} \right) \left[ R - \frac{R_0}{R_c} + \ln \left( \frac{R - 1}{R_0 / R_c - 1} \right) \right] = t.$$

As shown in Figure 6, the bubble collapses if $R_0 < R_c$ and grows if $R_0 > R_c$. For $R_0 > R_c$, $R \to \sqrt{2t}$ as $t \to \infty$.

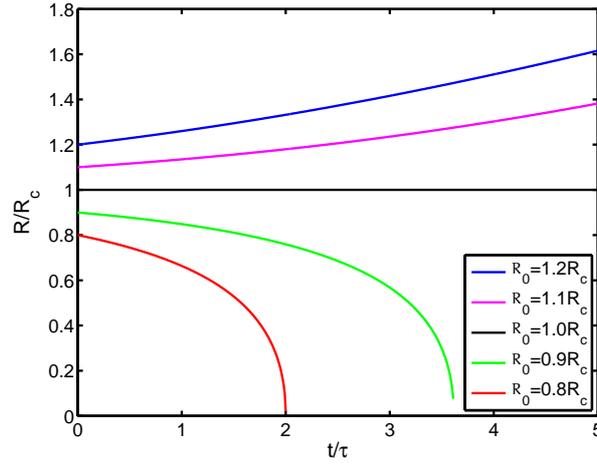157

Figure 6: The bubble collapses if $R_0 < R_c$ and grows if $R_0 > R_c$.

## Bubble maturation

Now consider a finite amount of liquid with many (identical) bubbles in it. Initially, the dissolved gas concentration is $c = Hp_0$, but as the bubbles grow, the dissolved gas concentration falls. Eventually, it is too low and the bubbles stop growing. At this stage, the gas in each bubble is in equilibrium with its concentration in the liquid so that Henry's law is satisfied:

$$c = Hp_b = H\left(p_a + \frac{2\gamma}{R_\infty}\right),$$

where $R_\infty$ is the ultimate radius of each bubble. Also at this stage, the gas in each bubble has been extracted from a volume $\frac{4}{3}\pi r_\infty^3$ of the liquid, where $r_\infty$ is the catchment radius. Ignoring the diffusion of gas across the free surface of the liquid and recalling that the liquid is incompressible, conservation of mass implies

$$\left\{ \begin{array}{c} \text{mass of gas} \\ \text{in bubble} \end{array} \right\} = \left\{ \begin{array}{c} \text{initial mass of} \\ \text{gas in liquid of} \\ \text{volume } \frac{4}{3}\pi r_\infty^3 \end{array} \right\} - \left\{ \begin{array}{c} \text{remaining mass} \\ \text{of gas in liquid} \\ \text{(of same volume)} \end{array} \right\}. \tag{5.34}$$

or, in mathematical notation,

$$\frac{4}{3}\pi R_\infty^3 \rho_b = \frac{4}{3}\pi r_\infty^3 Hp_0 - \frac{4}{3}\pi r_\infty^3 H\left(p_a + \frac{2\gamma}{R_\infty}\right).$$

Solving for $r_\infty$ and assuming that $2\gamma/R_\infty \ll p_a$, we obtain

$$r_\infty = \frac{R_\infty}{\varepsilon^{1/3}}. \tag{5.35}$$

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To study how the bubble grows to its final radius $R_\infty$, we rescale distance and time by letting

$$r^* \to \Lambda r^*, \quad R^* \to \Lambda R^*, \quad t^* \to \Lambda^2 t^*, \tag{5.36}$$

where $\Lambda = R_\infty / R_c$ is a large number ($\Lambda = 200$ for a $60\,\mu\text{m}$ bubble). The length scale is then $R_\infty$ ($\approx 60\,\mu\text{m}$, say) and the time scale is $R_\infty^2 / (D\varepsilon)$ ($\approx 30\,\text{s}$). Substituting (5.36) into (5.23) and (5.24) yields (asterisks omitted)

$$\varepsilon \left( \frac{\partial c}{\partial t} + \frac{R^2 \dot{R}}{r^2} \frac{\partial c}{\partial r} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right),$$

$$\frac{1}{3} \frac{d}{dt} \left\{ R^3 \left[ \frac{p_\infty}{p_a} + \frac{\Delta p}{p_a \Lambda R} + \frac{\delta}{\Lambda^2} \left( R\ddot{R} + \frac{3\dot{R}^2}{2} \right) \right] \right\} = R^2 \left. \frac{\partial c}{\partial r} \right|_{r=R(t)}.$$

Omitting the small terms in these equations, we obtain

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) = 0, \tag{5.37}$$

$$\frac{1}{3} \frac{d}{dt} \left( \frac{R^3 p_\infty}{p_a} \right) = R^2 \left. \frac{\partial c}{\partial r} \right|_{r=R(t)}. \tag{5.38}$$

The appropriate boundary conditions are (asterisks omitted)

$$c = \frac{p_a}{\Delta p} \left( \frac{p_\infty}{p_a} - 1 \right) \quad \text{at } r = R(t), \tag{5.39}$$

$$c = \frac{c_\infty(t) - H p_a}{H \Delta p} \quad \text{at } r = \frac{r_\infty}{R_\infty} = \frac{1}{\varepsilon^{1/3}}, \tag{5.40}$$

where we have neglected terms of order $\Lambda^{-1}$ and $\delta \Lambda^{-2}$ in (5.39). Note that we can no longer approximate $c_\infty(t)$ by $c_\infty(0)$ as we did in (5.21) as we are now considering a finite liquid in which there are many bubbles and the concentration is everywhere falling from its initial value $H p_0$. Although $\varepsilon^{-1/3} \approx 2.6$, we will assume that it is much larger so that (5.40) can be replaced by

$$c \to c_\infty^*(t) \quad \text{as } r \to \infty, \tag{5.41}$$

where

$$c_\infty^*(t) = \frac{c_\infty(t) - H p_a}{H \Delta p}.$$

Solving (5.37) for $c$ and applying the boundary conditions (5.39) and (5.41) yields

$$c = \frac{R p_a}{r \Delta p} \left( \frac{p_\infty}{p_a} - 1 \right) + \left( 1 - \frac{R}{r} \right) c_\infty^*. \tag{5.42}$$

Thus

$$\left. \frac{\partial c}{\partial r} \right|_{r=R} = -\frac{1}{R} \left[ \frac{p_a}{\Delta p} \left( \frac{p_\infty}{p_a} - 1 \right) - c_\infty^* \right]. \tag{5.43}$$

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Substituting (5.43) into (5.38) yields

$$\frac{1}{3}\frac{d}{dt}\left(\frac{R^3 p_\infty}{p_a}\right) = -R\left[\frac{p_a}{\Delta p}\left(\frac{p_\infty}{p_a}-1\right)-c_\infty^*\right]. \tag{5.44}$$

Applying the conservation of mass (5.34) when the radius of the bubble is $R(t)$, we obtain, in mathematical notation and dimensional variables,

$$\frac{4}{3}\pi R^3 \rho_b = \frac{4}{3}\pi r_\infty^3 H p_0 - 4\pi \int_R^{\left(r_\infty^3 + R^3\right)^{1/3}} c(r,t)\, r^2 dr.$$

Using the perfect gas law to eliminate $\rho_b$ and the RP equation to eliminate $p_b$, we obtain

$$\frac{4}{3}\pi R^3 \rho_a \left[\frac{p_\infty}{p_a}+\frac{2\gamma}{p_a R}+\frac{\rho_l}{p_a}\left(R\ddot{R}+\frac{3\dot{R}^2}{2}\right)\right]$$
$$= \frac{4}{3}\pi r_\infty^3 H p_0 - 4\pi \int_R^{\left(r_\infty^3 + R^3\right)^{1/3}} c(r,t)\, r^2 dr.$$

In terms of dimensionless variables (asterisks omitted):

$$R^3\left[\frac{p_\infty}{p_a}+\frac{\Delta p}{p_a \Lambda R}+\frac{\delta}{\Lambda^2}\left(R\ddot{R}+\frac{3\dot{R}^2}{2}\right)\right]$$
$$= \frac{r_\infty^3 \varepsilon p_0}{R_\infty^3 \Delta p} - 3\varepsilon \int_R^{\left(r_\infty^3/R_\infty^3 + R^3\right)^{1/3}}\left(c+\frac{p_a}{\Delta p}\right) r^2 dr.$$

Using (5.35) to eliminate $r_\infty$ and then neglecting small terms yields

$$\frac{p_\infty R^3}{p_a} = \frac{p_0}{\Delta p} - 3\varepsilon \int_R^{\varepsilon^{-1/3}}\left(c+\frac{p_a}{\Delta p}\right) r^2 dr.$$

Substituting (5.42) for $c$ yields

$$\frac{p_\infty R^3}{p_a} = \frac{p_0}{\Delta p} - 3\varepsilon \int_R^{\varepsilon^{-1/3}}\left[\frac{R p_a}{r \Delta p}\left(\frac{p_\infty}{p_a}-1\right)+\left(1-\frac{R}{r}\right)c_\infty^*+\frac{p_a}{\Delta p}\right] r^2 dr.$$

Upon integrating, we obtain

$$\frac{p_\infty R^3}{p_a} = \frac{p_0}{\Delta p} - 3\varepsilon \left[\frac{R p_a}{2\varepsilon^{2/3}\Delta p}\left(\frac{p_\infty}{p_a}-1\right)+\left(\frac{1}{3\varepsilon}-\frac{R}{2\varepsilon^{2/3}}\right)c_\infty^*+\frac{p_a}{3\varepsilon\Delta p}\right]$$
$$+ 3\varepsilon\left[\frac{R^3 p_a}{2\Delta p}\left(\frac{p_\infty}{p_a}-1\right)-\frac{R^3}{6}c_\infty^*+\frac{R^3 p_a}{3\Delta p}\right].$$
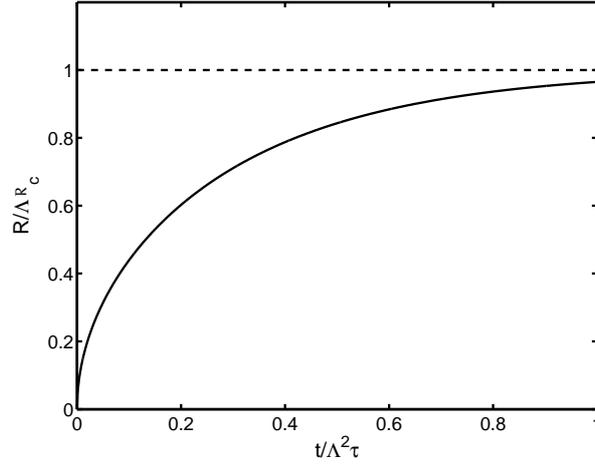
Figure 7: For large times $t \sim \Lambda^2 \tau \sim 30\,\text{s}$, the bubble radius approaches a limiting value $\Lambda R_c = R_\infty$.

Neglecting terms of order $\varepsilon^{1/3}$ and smaller $(\varepsilon)$ and solving for $c_\infty^*$ yields

$$c_\infty^* (t) = 1 - \frac{p_\infty}{p_a} R^3. \tag{5.45}$$

Thus, substituting (5.45) into (5.44) yields

$$\frac{1}{3} \frac{d}{dt} \left( \frac{R^3 p_\infty}{p_a} \right) = -R \left[ \frac{p_a}{\Delta p} \left( \frac{p_\infty}{p_a} - 1 \right) - 1 + \frac{p_\infty}{p_a} R^3 \right]. \tag{5.46}$$

If $p_\infty = p_a$ then (5.46) yields

$$\frac{dR}{dt} = \frac{1 - R^3}{R}. \tag{5.47}$$

Solving (5.47) for $R$ and applying the initial condition $R \to 0$ as $t \to 0$, we obtain

$$\frac{1}{6} \ln \left( R^2 + R + 1 \right) - \frac{1}{\sqrt{3}} \tan^{-1} \left( \frac{2R + 1}{\sqrt{3}} \right) - \frac{1}{3} \ln \left( 1 - R \right) + \frac{\pi}{6\sqrt{3}} = t.$$

As $t \to \infty$, $R \to 1$ as can be seen in Figure 7.

## 5.2 Bubble growth by rectified diffusion

Consider a bubble with $R_0 < R_c$. In the absence of pressure fluctuations (i.e. a sound field), it would gradually dissolve and disappear (Figure 6). However, if a sound field is introduced, then it can cause the bubble to pulsate and this may lead to the diffusion of gas *into* the bubble by a process called 'rectified diffusion'. This process competes with the normal diffusion of gas *out* of

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the precritical bubble. If the amplitude of the sound waves is greater than some threshold value, then rectified diffusion dominates and the bubble grows. Rectified diffusion is composed of three effects [17]: (i) When the bubble contracts, the concentration of gas in the bubble increases and gas tends to diffuse out of the bubble. When the bubble expands, the concentration of gas decreases and gas tends to diffuse into the bubble; (ii) Since the surface area of the bubble is greater during the expansion, more gas will enter during the expansion of the bubble than will leave during the contraction; (iii) During the expansion, the thickness of the diffusion boundary layer adjacent to the bubble decreases. As a result, the concentration gradient across this layer increases. Since the mass flow into the bubble is proportional to the concentration gradient, it is enhanced during expansion. The opposite is true during contraction.

To model the effect of a sound field on a bubble at rest in a liquid, we can set $p_\infty(t) = p_a + p_s(t)$, where $p_s = P_s \sin(\omega t)$ is the sound field. As shown by Eller and Flynn (1965), progress can then be made by first assuming that the instantaneous bubble radius $R(t)$ is periodic with a bubble period $T_b$ and then averaging the equations over one bubble period. This was found to be a valid approximation if $R_e \gg (D/\omega)^{1/2}$, where $R_e$ is the 'equilibrium' radius of the pulsating bubble such that

$$p_b = \left(p_a + \frac{2\gamma}{R_e}\right)\left(\frac{R_e}{R}\right)^3.$$

For $D = 2 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ and $\omega = 250\pi \times 10^3\,\mathrm{rad\,s^{-1}}$, this requires $R_e \gg 0.05\,\mu\mathrm{m}$. The final solution for the rate of change of $R_e$ with time is [18]

$$\frac{dR_e}{dt} = \frac{DH\mathcal{R}_s T}{R_e\left[1 + 4\gamma/(3p_a R_e)\right]}\left\langle\frac{R}{R_e}\right\rangle\left[\frac{p_0}{p_a} - \frac{\langle R/R_e\rangle}{\langle(R/R_e)^4\rangle}\left(1 + \frac{2\gamma}{p_a R_e}\right)\right], \qquad (5.48)$$

where angle brackets denote a time average over one bubble period, and

$$\left\langle\frac{R}{R_e}\right\rangle = 1 + K\alpha^2\left(\frac{P_s}{p_a}\right)^2, \qquad (5.49)$$

$$\left\langle\left(\frac{R}{R_e}\right)^4\right\rangle = 1 + (3 + 4K)\alpha^2\left(\frac{P_s}{p_a}\right)^2, \qquad (5.50)$$

$$\alpha = \frac{1}{3\left[1 + 4\gamma/(3p_a R_e) - \beta^2\right]}, \qquad (5.51)$$

$$K = \frac{(4 - \beta^2)/4 + 4\gamma/(3p_a R_e)}{1 + 4\gamma/(3p_a R_e)}, \qquad (5.52)$$

$$\beta^2 = \frac{\rho_l \omega^2 R_e^2}{3p_a}. \qquad (5.53)$$

In deriving (5.49) and (5.50), it is assumed that that the ratio $P_s/p_a$ is small, an assumption that does not appear to be satisfied in the case of the surger unit.
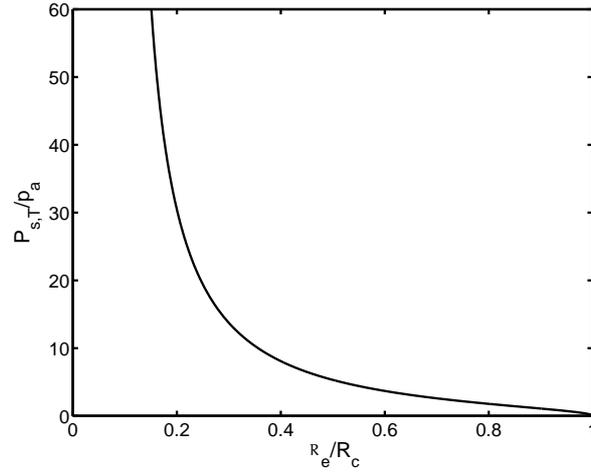
Figure 8: $P_{s,T}$ versus $R_e$ for $p_0 = 3.8\,\text{bar}$, $p_a = 1\,\text{bar}$, $\gamma = 40\,\text{mN}\,\text{m}^{-1}$, $\rho_l = 10^3\,\text{kg}\,\text{m}^{-3}$, $\omega = 250\pi \times 10^3\,\text{rad}\,\text{s}^{-1}$.

The threshold amplitude $P_{s,T}$ for rectified diffusion is obtained by setting $\dot{R}_e = 0$ and solving for $P_s$ to obtain

$$P_{s,T} = \frac{p_a}{\alpha} \sqrt{\frac{1 + 2\gamma/\left(p_a R_e\right) - p_0/p_a}{\left(3 + 4K\right) p_0/p_a - \left[1 + 2\gamma/\left(p_a R_e\right)\right] K}}. \tag{5.54}$$

The threshold amplitude increases as $R_e$ decreases, as shown in Figure 8. Given $R_0$, the initial bubble radius, and $P_s$, (5.48) can be solved for $R_e\left(t\right)$ using the Matlab ODE solver ode15s. Some examples are shown in Figure 9. Those precritical bubbles for which $P_s > P_{s,T}$ grow, while those for which $P_s < P_{s,T}$ shrink.

## 5.3  Bubble growth by convective diffusion

Since the diffusion coefficient $D$ is small ($D \approx 2 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}$ for $N_2$ in water), the rate of mass transfer into a bubble at rest is also small. In practice, the bubble rises in the liquid due to its buoyancy and this motion enhances the rate of mass transfer, just as stirring tea enhances the dissolution of any added sugar. This transport of matter by the combined processes of convection and diffusion will be called convective diffusion.

Consider then a bubble with radius $R\left(t\right) \gg R_c$ rising steadily through a supersaturated liquid. The mass flux $q$ into the bubble would be expected to be proportional to the surface area $4\pi R^2$ of the bubble and to the concentration drop $\Delta c = c_l - c_b$ between the liquid bulk and the bubble 'skin' (Figure 1):

$$q = k4\pi R^2 \Delta c,$$

where the proportionality constant $k$ is known as the mass transfer coefficient. This can be
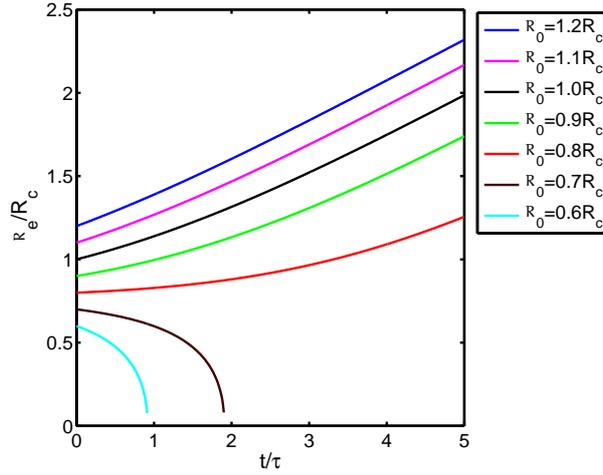
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Figure 9: $R_e$ versus $t$ for $P_s = 2\,\text{bar}$, $p_0 = 3.8\,\text{bar}$, $p_a = 1\,\text{bar}$, $\gamma = 40\,\text{mN}\,\text{m}^{-1}$, $\rho_l = 10^3\,\text{kg}\,\text{m}^{-3}$, $\omega = 250\pi \times 10^3\,\text{rad}\,\text{s}^{-1}$.

equated to the rate of increase of the bubble mass:

$$\frac{d}{dt}\left(\frac{4}{3}\pi R^3 \rho_b\right) = k4\pi R^2 \Delta c. \tag{5.55}$$

Empirically, $k$ is proportional to the diffusion coefficient of the gas in the liquid, so that (5.55) can be rewritten as

$$\frac{d}{dt}\left(\frac{4}{3}\pi R^3 \rho_b\right) = \frac{4\pi R^2 D \Delta c}{\delta_N}. \tag{5.56}$$

Comparing (5.4) and (5.56), the Nernst diffusion layer thickness $\delta_N$ is seen to be given by

$$\left(\frac{\partial c}{\partial r}\right)_{r=R} = \frac{\Delta c}{\delta_N}.$$

As shown in Figure 1, $\delta_N$ is the thickness which the diffusion layer would have if the concentration profile were a straight line with slope $(\partial_r c)_{r=R}$.

If we assume that the gas obeys the perfect gas law $\rho_b = p_b/(\mathcal{R}_s T)$ with $p_b \approx p_a$ as $R \gg R_c$, and if we also assume that $T$ is constant, then $\rho_b$ is also approximately constant. Then

$$\frac{d}{dt}\left(\frac{4}{3}\pi R^3 \rho_b\right) = 4\pi R^2 \rho_b \frac{dR}{dt}. \tag{5.57}$$

Substituting (5.57) into (5.55) yields

$$\frac{dR}{dt} = \frac{k\Delta c}{\rho_b}. \tag{5.58}$$

Experimental evidence suggests that $k$ is approximately constant [5, 12]. During the rise time of the bubble, the gas concentration $c_l$ in the liquid is also approximately constant. Furthermore,

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since $c_b = Hp_b$ and $p_b \approx p_a$, $c_b$ is constant. Integrating (5.58) then yields

$$R = R_0 + \kappa t,$$

where $R_0$ is the initial ($t = 0$) radius of the bubble and the growth rate of the bubble is

$$\kappa = \frac{k\Delta c}{\rho_b}. \tag{5.59}$$

For champagne bubbles originating from cellulose fibres, $R_0 \approx 20\,\mu\text{m}$ and $\kappa \approx 350 - 400\,\mu\text{m s}^{-1}$ [12]. For a carbonated beer, values of $\kappa \approx 100 - 150\,\mu\text{m s}^{-1}$ [12] and $\kappa \approx 40\,\mu\text{m s}^{-1}$ [5] have been reported. The low gas concentrations in Guinness imply smaller values of $\kappa$, as we will see.

In the literature, the mass transfer coefficient $k$ is usually expressed in terms of the Sherwood number (also known as the Nusselt mass transfer number):

$$Sh = \frac{2kR}{D},$$

which is itself a function of the Reynolds number

$$Re = \frac{2\rho_l R U}{\mu},$$

and the Peclet number

$$Pe = \frac{2RU}{D}.$$

If $Pe \ll 1$, then mass transfer is dominated by diffusion. If $Pe \gg 1$, then mass transfer is dominated by convection. In order to determine $k$, we first need to estimate $U$, which we can do by considering the forces on a rising bubble. By Archimedes principle, the buoyancy force on a body immersed in a liquid is equal to the weight of the liquid displaced by that body. Thus, for a spherical bubble, the buoyancy force is

$$F_B = \frac{4}{3}\pi R^3 \rho_l g.$$

Since $\rho_b \ll \rho_l$, the weight of the bubble is negligible in comparsion to the buoyancy force and the bubble rises. As the bubble rises it experiences resistance due friction between its surface and the surrounding viscous liquid. This friction force is expressed as

$$F_d = C_d \frac{\rho_l U^2}{2}\pi R^2,$$

where $C_d$ is the friction factor or drag coefficient. The buoyancy force is nearly always balanced by the drag force so that we can equate them to obtain

$$\frac{4}{3}\pi R^3 \rho_l g = C_d \frac{\rho_l U^2}{2}\pi R^2,$$

or, solving for $C_d$,

$$C_d = \frac{8Rg}{3U^2}. \tag{5.60}$$

This equation can be used to determine $C_d$ experimentally. It is found that beer bubbles ultimately experience a drag similar to that experienced by solid spheres, for which [16]

$$C_d = \frac{24}{Re} \left( 1 + 0.15 \, Re^{0.687} \right), \quad Re < 800.$$

Over the rise time of the bubble though, a good approximation is $C_d \approx 48/\, Re$ [12]. Solving (5.60) for $U$ then yields

$$U = \frac{\rho_l g R^2}{9\mu}. \tag{5.61}$$

As $R$ increases, $U$ increases and the bubble accelerates. Small bubbles rise slower than large bubbles. Hence, they can be entrained in the downward liquid flow at the glass walls and actually sink. These sinking bubbles are easily seen in a pint of Guinness. For bubbles with radii of order $50 \, \mu m$ in Guinness ($\rho_l \approx 10^3 \, kg \, m^{-3}$, $\mu \approx 2 \times 10^{-3} \, Pa \, s$ [19]), $U \approx 0.1 \, cm \, s^{-1}$, $Re \approx 0.07$ and $Pe \approx 68$. In carbonated beers, $U$ is a couple of $cm \, s^{-1}$ in good accordance with Equation (5.61) [5].

For the case of stationary ($U, Re, Pe = 0$) bubbles, $Sh = 2$ as can be verified by rewriting (5.32) in dimensional form. For rising bubbles (nonzero $U, Re, Pe$), flow inside and outside the bubble affects the mass transfer. The Sherwood number can be calculated from the semiempirical expression [8]

$$Sh = 1 + \left( 1 + Pe^{1/3} \right) \left( 1 + \frac{0.096 \, Re^{1/3}}{1 + 7 \, Re^{-2}} \right), \quad Re < 10^5.$$

For large $Pe$, $Sh \approx Pe^{1/3}$ so that, from the definitions of $Sh$ and $Pe$,

$$k = \frac{D}{2R} Pe^{1/3} = \left( \frac{D}{2R} \right)^{2/3} U^{1/3}.$$

Substituting (5.61) for $U$ yields

$$k = \left( \frac{D}{2} \right)^{2/3} \left( \frac{\rho_l g}{9 \mu_l} \right)^{1/3}.$$

Because of the $R^2$ dependence of $U$, $k$ becomes independent of $R$ and hence time, as expected. The growth rate (5.59) becomes

$$\kappa = \left( \frac{D}{2} \right)^{2/3} \left( \frac{\rho_l g}{9 \mu_l} \right)^{1/3} \frac{\Delta c}{\rho_b}$$

Over time $c_l$ drops, so that $\kappa$ drops. For pure nitrogen bubbles in Guinness, we obtain $\kappa \approx 3 \, \mu m \, s^{-1}$, much smaller than the corresponding values for champagne and carbonated beers. Although Guinness bubbles rise slower and therefore have longer to grow, they remain smaller than those in carbonated beverages because of this very low growth rate.

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## 5.4 The surger

In the case of the surger, precritical bubbles are initially grown by rectified diffusion. Once they become postcritical, they grow by convective diffusion as they rise through the Guinness. The equations governing the growth of any individual bubble are much like those we have already seen, except now we must consider the combined effects of a sound field and convection. We must also consider the whole distribution of bubbles within the Guinness, as well as the dissolved gas concentration, if we want to model the formation of the head.

Consider a (pure nitrogen) bubble which is rising steadily through the liquid as it grows. We assume that the rate of increase of mass in the bubble is equal to the sum of the diffusive and the convective fluxes into the bubble:

$$
\left\{
\begin{array}{c}
\text{rate of increase} \\
\text{of mass of gas} \\
\text{in bubble}
\end{array}
\right\}
=
\left\{
\begin{array}{c}
\text{rate of addition} \\
\text{of mass by} \\
\text{diffusion}
\end{array}
\right\}
+
\left\{
\begin{array}{c}
\text{rate of addition} \\
\text{of mass by} \\
\text{convection}
\end{array}
\right\},
$$

or, in mathematical notation,

$$
\frac{d}{dt}\left(\frac{4}{3}\pi R^3 \rho_b\right) = 4\pi R^2 \frac{D\Delta c}{R} + \pi R^2 f U \Delta c. \tag{5.62}
$$

The factor $f$ is unknown initially; through trial-and-error, a value which makes the results quantitatively reasonable is chosen. Of course, if the Sherwood number were known then Equation (5.55) could be used in place of (5.62). Using the perfect gas law to eliminate $\rho_b$ and Henry's law to eliminate $c_b$, we obtain

$$
\frac{1}{3\mathcal{R}_s T}\frac{d\left(R^3 p_b\right)}{dt} = R^2\left(\frac{1}{R} + \frac{fU}{4}\right)(c_l - H p_b). \tag{5.63}
$$

The bubble is assumed to be rising with the Stokes' terminal velocity:

$$
U = \frac{2\rho_l g R^2}{9\mu}, \tag{5.64}
$$

which seems appropriate if wall effects are negligible [16], as they would be for bubbles which originate in the liquid bulk. Neglecting the inertial terms in the Rayleigh-Plesset equation, we have

$$
p_b = p_\infty + \frac{2\gamma}{R}. \tag{5.65}
$$

We set $p_\infty(t) = p_a + p_s(t)$, where $p_s = P_s \sin(\omega t)$ is the ultrasound field. $P_s$ can be estimated as follows: Assuming the plate of the surger unit oscillates sinusoidally with amplitude $A$, its position is given by $z = z_0 - A\sin(\omega t)$. The corresponding acceleration is $g = \ddot{z} = \omega^2 A \sin(\omega t)$. This creates the pressure field

$$
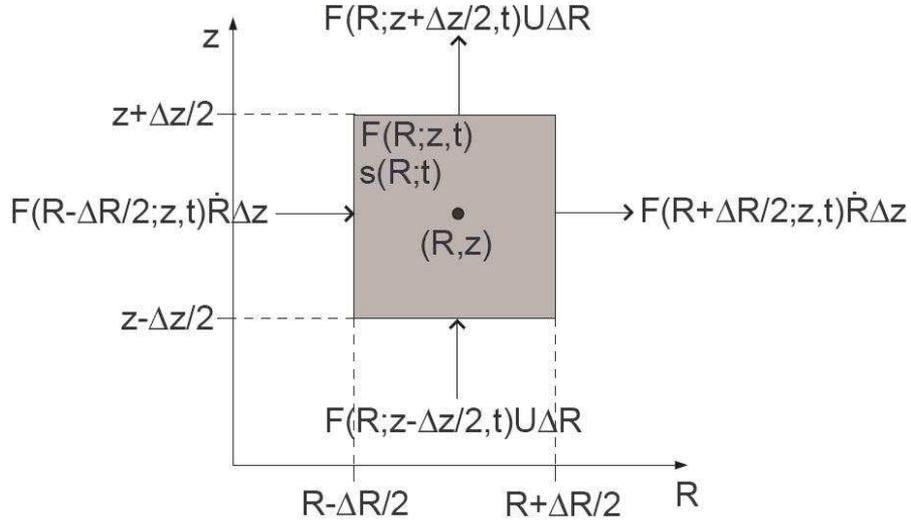p_s = \rho_l g(h - z) = \rho_l \omega^2 A(h - z)\sin(\omega t),
$$

Figure 10: The fluxes into the shaded region $\Delta R \Delta z$ in phase space $(R, z)$.

inside the liquid (as verified experimentally in a vibrating vessel [20]). Inserting appropriate values ($\rho_l = 10^3 \, \text{kg m}^{-3}$, $\omega = 250\pi \times 10^3 \, \text{rad s}^{-1}$, $A = 89 \, \text{nm}$, $h = 10 \, \text{cm}$), we find that $P_s$ varies from $55 \, \text{bar}$ at the bottom ($z = 0$) of the liquid to $0 \, \text{bar}$ at the top ($z = h$). From Figure 8, we can see that $55 \, \text{bar}$ is above the threshold amplitude for most of the precritical bubbles. It does, however, seem like an unusually large pressure and there is uncertainty regarding the exact value of $A$. For simplicity, we ignored the dependence of $p_s$ on $z$.

Now suppose that the bubble distribution in the liquid is given by $F(R; z, t)$ such that $F dR dz$ is the number of bubbles with radii from $R$ to $R + dR$ at heights from $z$ to $z + dz$ at time $t$. As shown in Figure 10, the rate of increase of $F(R; z, t) \Delta R \Delta z$, the number of bubbles in the shaded region, is given by

$$
\left\{ \begin{array}{c} \text{rate of increase} \\ \text{of number of} \\ \text{bubbles in} \\ \text{shaded region} \end{array} \right\} = \left\{ \begin{array}{c} \text{rate of addition} \\ \text{of bubbles due to} \\ \text{bubbles growing} \end{array} \right\}
$$

$$
+ \left\{ \begin{array}{c} \text{rate of addition} \\ \text{of bubbles due} \\ \text{to bubbles rising} \end{array} \right\} + \left\{ \begin{array}{c} \text{rate of addition} \\ \text{of precritical} \\ \text{bubbles by} \\ \text{homogeneous} \\ \text{nucleation} \end{array} \right\},
$$

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or, in mathematical notation,

$$\frac{\partial F}{\partial t}\Delta R\Delta z = \left[ F\left(R - \frac{\Delta R}{2}; z, t\right) - F\left(R + \frac{\Delta R}{2}; z, t\right) \right]\dot{R}\Delta z$$
$$+ \left[ F\left(R; z - \frac{\Delta z}{2}, t\right) - F\left(R; z + \frac{\Delta z}{2}, t\right) \right]U\Delta R + s\left(R; t\right)\Delta R\Delta z,$$

where $s\left(R, t\right)\Delta R\Delta z$ is the number of precritical bubbles being created or destroyed in the shaded region per unit time. Dividing both sides by $\Delta R\Delta z$ and taking the limit as $\Delta R, \Delta z \to 0$ yields

$$\frac{\partial F}{\partial t} = -\frac{\partial F}{\partial R}\dot{R} - \frac{\partial F}{\partial z}U + s\left(R; t\right). \tag{5.66}$$

The dissolved gas concentration is given by

$$\left\{ \begin{array}{c} \text{rate of increase} \\ \text{of mass of gas} \\ \text{per unit volume} \\ \text{of liquid} \end{array} \right\} = \left\{ \begin{array}{c} \text{rate of addition} \\ \text{of mass of gas} \\ \text{per unit volume} \\ \text{by diffusion} \end{array} \right\} - \left\{ \begin{array}{c} \text{rate of loss of} \\ \text{mass of gas per} \\ \text{unit volume by} \\ \text{bubble growth} \end{array} \right\},$$

or, in mathematical notation,

$$\frac{\partial c_l}{\partial t} = D\frac{\partial^2 c_l}{\partial z^2} - \int F\frac{d}{dt}\left(\frac{4}{3}\pi R^3 \rho_b\right) dR.$$

Using the perfect gas law to eliminate $\rho_b$, we obtain

$$\frac{\partial c_l}{\partial t} = D\frac{\partial^2 c_l}{\partial z^2} - \frac{4\pi}{3\mathcal{R}_s T}\int F\frac{d\left(R^3 p_b\right)}{dt}dR. \tag{5.67}$$

Equations (5.63) to (5.67) form a closed set for $\{R, U, p_b, F, c_l\}$ and govern the growth of an initial distribution of bubbles in the presence of an ultrasound field $p_s$ and a source $s$ of precritical bubbles.

However, solving these equations is complicated by the problem of choosing the time step. A naïve simulation would use the ultrasound period $2\pi/\omega \approx 8\,\mu s$ over the duration of the surge and settle ($\sim 1\,\text{min}$). To speed up the simulation, we instead split it into two parts, the first part of which computes the rate at which postcritical bubbles are being produced by the ultrasound field, and the second part of which uses this rate to study the behaviour of the postcritical bubbles. The final results from this part are shown in Figures 11, 12, and 13. Figure 11 shows the bubble radii as a function of time, each bubble corresponding to one cross. Initially, all the bubbles are precritical and thus their radii are clustered together. As time progresses, the radii increase with the maximum radius being about $400\,\mu m$. As bubbles reach the top of the liquid, they are removed from the graph. As time progresses further, the mean bubble radius drops to about $50\,\mu m$ because the bubble growth rate decreases as the dissolved gas concentration in the liquid falls. In Figure 12, the corresponding heights of the bubbles are shown. Finally, the height of the head is shown in Figure 13; it is approximately $12\,\text{mm}$ after $5\,\text{s}$.
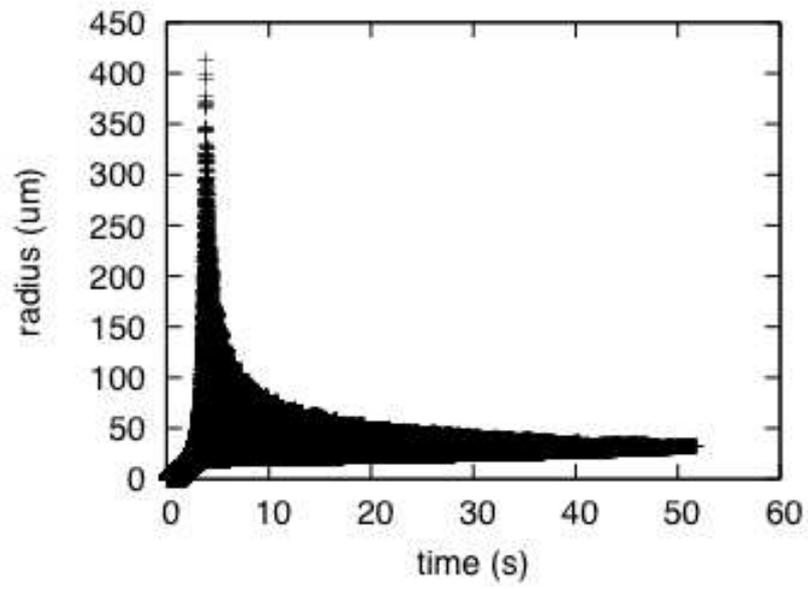
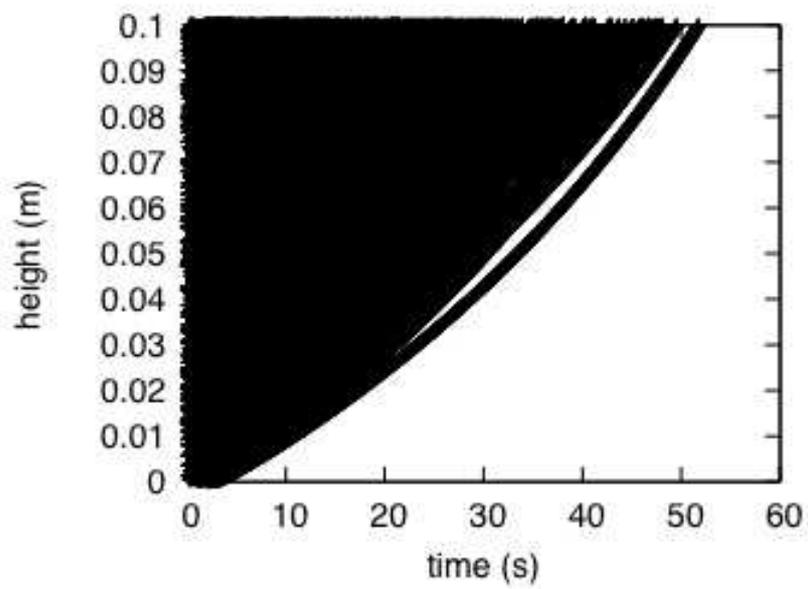Figure 11: Bubble radii as a function of time.



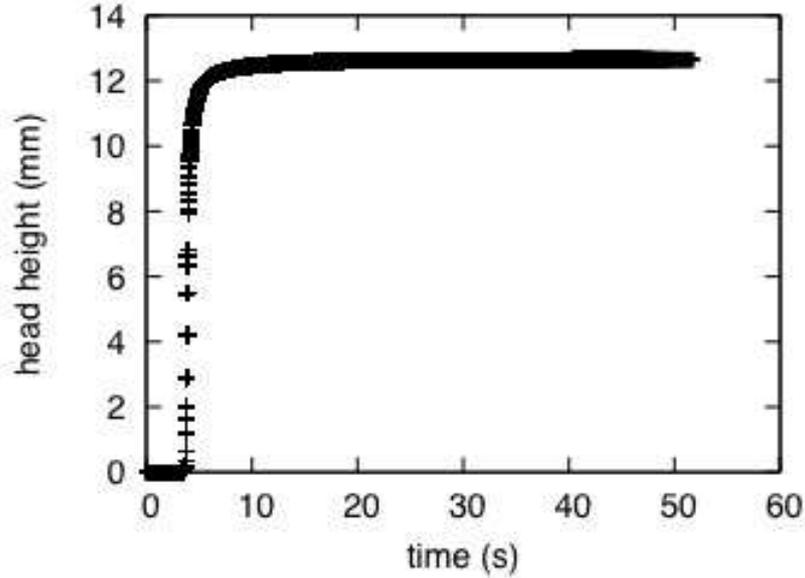Figure 12: Bubble heights as a function of time.

Figure 13: Head height as a function of time.

# 6 Conclusions

Diageo asked us to develop a mathematical model describing bubble formation and growth in Guinness. To this end, we considered the growth of single bubbles by passive, rectified and convective diffusion. In the passive case, the role of the critical radius $R_c$ was emphasised: in the absence of a sound field, precritical ($R < R_c$) bubbles shrink. In the presence of a sound field, we showed that precritical bubbles will grow by rectified diffusion provided that the amplitude of the sound field is above the threshold value given by (5.54). We also considered how the growth of bubbles by convective diffusion is modelled mathematically.

Applying these ideas to the surger unit, and some new ideas regarding the evolution of the bubble distribution and the dissolved gas concentration, we successfully modelled the initiation of Guinness. The results, however, are more qualitative than quantitative since

1. We have completely ignored the dissolved $CO_2$. Since the $CO_2$ concentration is much higher than the $N_2$ concentration, it must surely have a significant effect on the growth of the bubbles (*cf.* Section 8). In particular, a model taking both gases into account should be able to explain quantitatively why the head on Guinness does not form spontaneously. Furthermore, there may also be some water vapour in the bubble, although for low temperatures the ratio of vapour to gas should remain small.

   The surger equations, Equations (5.63) to (5.67), are easily modified to take the $CO_2$ into

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account by replacing Equation (5.63) by

$$\frac{1}{3\mathcal{R}_{s,i}T}\frac{d\left(R^3 x_i p_b\right)}{dt} = k_i R^2 \left(c_{l,i} - H_i x_i p_b\right), \tag{6.1}$$

where we are now using the mass transfer coefficient $k_i$, and Equation (5.67) by

$$\frac{\partial c_{l,i}}{\partial t} = D_i \frac{\partial^2 c_{l,i}}{\partial z^2} - \frac{4\pi}{3\mathcal{R}_{s,i}T}\int F\frac{d\left(R^3 x_i p_b\right)}{dt}dR, \tag{6.2}$$

where $x_i$ is the mole fraction of gas species $i$ in the bubble so that

$$\sum x_i = 1.$$

Equations (6.1) and (6.2) constitute four equations, two each for the $CO_2$ ($i = CO_2$) and the $N_2$ ($i = N_2$).

2. We have not considered the diffusion of gas across the top surface of the Guinness and into the atmosphere. This could be significant: for champagne, 80% of the dissolved $CO_2$ molecules escape by this method [12].

3. For sufficiently large bubbles and high frequencies, the isothermal ($T = $ const) approximation becomes questionable [21].

4. Assuming that the rise velocity is simply the Stokes velocity is an over-simplification. In practice, the high number of bubbles creates a complex flow pattern, with liquid and bubbles rising in the centre of the glass and liquid and small bubbles descending at the edges.

5. The bubble distribution and dissolved gas concentration will vary horizontally as well as vertically.

6. The addition of surfactants significantly affects the accuracy of theoretical predictions regarding rectified diffusion [18].

7. We studied noninteracting spherical bubbles, but bubbles can deform, oscillate, break up and coalesce.

A noticeable feature of using the surger unit is the slight delay ($\sim 1\,s$) before the surge of nitrogen bubbles is seen. It is possible that this delay is due to the so-called Bjerknes force holding the bubbles in place while the surger unit is vibrating [20]. When the surger unit stops vibrating (it only vibrates for $1-2\,s$ after pressing the activation button), there is no Bjerknes force and the bubbles are free to rise. As they rise, some bubbles move towards the glass walls where they become visible.

Although we focused on the surger, the equations we have used can be applied to other methods of initiation simply by modifying the input pressure $p_\infty\left(t\right)$ and the source term $s\left(R;t\right)$.

At the Study Group, some ideas for new initiation methods were discussed. Perhaps the most interesting is the possibility of using a 'nanowidget'; that is, an insert at the bottom of the can which has nanometer features, making it superhydrophobic. When liquid is poured over such a surface, gas is trapped in the cavities between the features. Upon pressurising the can, some of the gas will dissolve. Upon opening the can, the surviving gas pockets will act as nucleation sites, initiating the Guinness. Of course, the effectiveness and cost of such a device would have to be investigated. Another interesting idea is to coat the inside of the can with a surfactant to promote bubble nucleation. For example, it is known that the surfactant coating on Mentos (gum arabic) is partly responsible for the explosivity of the Diet Coke and Mentos reaction [22].

# 7 List of symbols

In the following list of symbols, the corresponding SI unit, if any, is given in brackets.

$A$ amplitude of oscillation of surger plate (m)

$C_d$ drag coefficient

$c$ gas concentration in liquid ($\text{kg}\,\text{m}^{-3}$)

$c_b$ gas concentration in liquid at bubble surface ($\text{kg}\,\text{m}^{-3}$)

$c_l$ gas concentration in liquid bulk ($\text{kg}\,\text{m}^{-3}$)

$c_\infty$ gas concentration in liquid at $r = r_\infty$ ($\text{kg}\,\text{m}^{-3}$)

$D$ diffusivity of gas in liquid ($\text{m}^2\,\text{s}^{-1}$)

$F$ bubble distribution function ($\text{m}^{-2}$)

$F_B$ buoyancy force (N)

$F_c$ capillary force (N)

$F_d$ drag force (N)

$f$ function defined in Equation (5.62)

$g$ acceleration due to gravity ($\text{m}\,\text{s}^{-2}$)

$H$ Henry's law constant ($\text{kg}\,\text{m}^{-3}\,\text{Pa}^{-1}$)

$h$ height of liquid (m)

$K$ function defined in Equation (5.52)

$k$ mass transfer coefficient ($\text{m}\,\text{s}^{-1}$)

$L$ circumference of nucleation site (m)

$\mathcal{M}$ molar mass $(\mathrm{kg\,mol^{-1}})$

$n_b = p_b V_b/(\mathcal{R}_g T)$ number of moles of gas in bubble (mol)

$P_s$ amplitude of sound field (Pa)

$P_{s,T}$ threshold amplitude of sound field (Pa)

$Pe = 2RU/D$ Peclet number

$p$ partial pressure of gas above liquid (Pa)

$p_a$ atmospheric pressure (Pa)

$p_b$ gas pressure in bubble (Pa)

$p_l$ liquid pressure (Pa)

$p_s = P_s \sin(\omega t)$ sound field (Pa)

$p_0$ gas pressure in sealed container (Pa)

$p_\infty$ liquid pressure at $r = r_\infty$ (Pa)

$q$ mass flux $(\mathrm{kg\,s^{-1}})$

$R$ bubble radius (m)

$\dot{R} = dR/dt$ time derivative of $R$ $(\mathrm{m\,s^{-1}})$

$R_c$ critical radius (m)

$R_e$ 'equilibrium' radius of a pulsating bubble (m)

$R_0$ initial radius (m)

$R_\infty$ ultimate radius (m)

$Re = 2\rho_l RU/\mu$ Reynolds number

$\mathcal{R}_g$ universal gas constant $(\mathrm{J\,K^{-1}\,mol^{-1}})$

$\mathcal{R}_s = \mathcal{R}_g/\mathcal{M}$ specific gas constant $(\mathrm{J\,K^{-1}\,kg^{-1}})$

$r$ distance from centre of bubble (m)

$r_\infty$ catchment radius (m)

$S$ supersaturation ratio

$Sh = 2kR/D$ Sherwood number

$s$ precritical bubble source $(\mathrm{m^{-2}\,s^{-1}})$

$T$ temperature (K)

$t$ time (s)

$(u_r, u_\theta, u_\phi)$ liquid velocity components $(m\,s^{-1})$

$u = u_r$ radial component of liquid velocity $(m\,s^{-1})$

$U$ velocity of a rising bubble $(m\,s^{-1})$

$V_b = \frac{4}{3}\pi R^3$ volume of bubble $(m^3)$

$x$ mole fraction of gas

$z$ distance measured upward from bottom $(z = 0)$ of liquid (m)

$\alpha$ function defined in Equation (5.51)

$\beta$ function defined in Equation (5.53)

$\gamma$ surface tension $(N\,m^{-1})$

$\Delta p = p_0 - p_a$ (Pa)

$\Delta c = c_l - c_b$ $(kg\,m^{-3})$

$\delta = \rho_l D^2 \varepsilon^2 / (p_a R_c^2)$ small parameter

$\delta_N$ Nernst diffusion layer thickness (m)

$\varepsilon = H\Delta p / \rho_a$ small parameter

$\theta$ colatitude coordinate in spherical coordinates $(r, \theta, \phi)$ (rad)

$\theta_c$ contact angle (rad)

$\kappa$ bubble growth rate $(m\,s^{-1})$

$\Lambda = R_\infty / R_c$ large parameter

$\mu$ dynamic viscosity of liquid $(Pa\,s)$

$\rho_a = p_a / \mathcal{R}_s T$ density scale $(kg\,m^{-3})$

$\rho_b$ gas density in bubble $(kg\,m^{-3})$

$\rho_l$ liquid density $(kg\,m^{-3})$

$\tau = R_c^2 / (D\varepsilon)$ time scale (s)

$\phi$ longitude coordinate in spherical coordinates $(r, \theta, \phi)$ (rad)

$\omega$ angular frequency of oscillation of surger plate $(rad\,s^{-1})$

# 8   Gas concentrations in Guinness

Dissolved gas concentrations are frequently given in $g\,l^{-1}$ (grams of dissolved gas per litre of solution) or $g\,kg^{-1}$ (grams of dissolved gas per kilogram of solution). They can also be expressed in parts per million (ppm), Volumes (Vol.), or as a volume over volume percentage (% v/v). These three units are defined by

$$\text{ppm of dissolved gas} = (\,g\,kg^{-1} \text{ of dissolved gas}) \times 10^3.$$

$$\text{Vol. of dissolved gas} = \frac{\text{volume of dissolved gas at } 0\,^\circ\text{C and } 1\,\text{atm}}{\text{volume of solution}},$$

$$\text{\% v/v of dissolved gas} = (\text{Vol. of dissolved gas}) \times 100.$$

Thus, to convert from $g\,kg^{-1}$ to ppm, we multiply by $10^3$. For example, the desired $CO_2$ concentration in Guinness is about $2\,g\,l^{-1}$. If $1\,l$ of Guinness has a mass of $1\,kg$, then this is equivalent to $2\,g\,kg^{-1}$ or 2000ppm. To convert to Vol., we must first determine the conversion factor from $g\,l^{-1}$ to Vol.. From the perfect gas law, one mole of gas occupies 22.4 litres at $0\,^\circ\text{C}$ and $1\,\text{atm}$. Thus, one gram of gas occupies $22.4/\mathcal{M}$ litres, where $\mathcal{M}$ is the molar mass of the gas in $g\,mol^{-1}$. Hence,

$$\text{Vol. of dissolved gas} = \,g\,l^{-1} \text{ of dissolved gas} \times \frac{22.4}{\mathcal{M}}.$$

Since the molar mass of $CO_2$ is $44.0\,g\,mol^{-1}$,

$$\text{Vol. } CO_2 = \,g\,l^{-1}\ CO_2 \times 0.509.$$

Thus, to convert from $g\,l^{-1}\ CO_2$ to Vol. $CO_2$, we multiply by 0.509, so that $2\,g\,l^{-1}\ CO_2$ is equivalent to 1.02Vol. $CO_2$. This means that the $CO_2$ in one litre of Guinness would occupy 1.02 litres if brought to a temperature of $0\,^\circ\text{C}$ and a $CO_2$ gas pressure of $1\,\text{atm}$. Since the molar mass of $N_2$ is $28.0\,g\,mol^{-1}$,

$$\text{Vol. } N_2 = \,g\,l^{-1}\ N_2 \times 0.800.$$

To obtain more accurate conversion factors, the deviation from perfect gas behaviour must be taken into account. To convert from Vol. to % v/v, we multiply by 100. Thus, the desired $CO_2$ concentration is 102% v/v.

Henry's law relates the solubility $c$ of a gas to its partial pressure $p$ above the solution:

$$c = Hp,$$

where $H$ is the Henry's law constant. The Henry's law constants of $CO_2$ and $N_2$ in pure water are given in table 8 for different temperatures.

The desired $CO_2$ concentration is about $2\,g\,l^{-1}$ From Henry's law this requires a partial pressure of

$$p_{CO_2} = \frac{c_{CO_2}}{H_{CO_2}} = \frac{2\,g\,l^{-1}}{2.5\,g\,l^{-1}\,\text{bar}^{-1}} = 0.8\,\text{bar}\,.$$

| Temperature (°C) | $H_{CO_2}$ $(g\,l^{-1}\,bar^{-1})$ | $H_{N_2}$ $(g\,l^{-1}\,bar^{-1})$ |
|---|---|---|
| 0 | 3.42 | 0.0283 |
| 8 | 2.50 | 0.0241 |
| 15 | 2.05 | 0.0209 |
| 20 | 1.76 | 0.0192 |

Table 8: Henry's law constants for $CO_2$ and $N_2$ in pure water. Sources: [23] and [24].

In the sealed container the total pressure is $3.8$ bar. Thus the partial pressure of $N_2$ in the headspace (and widget) is $p_{N_2} = 3$ bar. From Henry's law this yields a solubility of

$$c_{N_2} = H_{N_2} p_{N_2} = \left(0.0241\,g\,l^{-1}\,bar^{-1}\right)(3\,bar) = 0.0723\,g\,l^{-1},$$

or $5.78\%$ v/v. If $1\,l$ of Guinness has a mass of $1\,kg$, then the solubility of $N_2$ is $72.3$ppm. The mole fractions in the gas phase are

$$x_{CO_2} = \frac{0.8\,bar}{3.8\,bar} = 0.21, \quad x_{N_2} = \frac{3\,bar}{3.8\,bar} = 0.79,$$

so that the gas mixture is $21$ mole $\%$ $CO_2$ and $79$ mole $\%$ $N_2$.

Suppose now that the container is opened and the gas concentrations are allowed to come to equilibrium with their partial pressures in the atmosphere at $15\,°C$. The partial pressures of $CO_2$ and $N_2$ in air are about $3 \times 10^{-4}$ bar and $0.78$ bar, respectively. Hence, from Henry's law, the corresponding solubilities are

$$c_{CO_2} = \left(2.05\,g\,l^{-1}\,bar^{-1}\right)\left(3 \times 10^{-4}\,bar\right) = 0.0006\,g\,l^{-1},$$

$$c_{N_2} = \left(0.0209\,g\,l^{-1}\,bar^{-1}\right)(0.78\,bar) = 0.016\,g\,l^{-1}.$$

It follows that about $0.0282\,g$ of $N_2$ and $1\,g$ of $CO_2$ must escape from every pint ($\sim 500\,ml$) of Guinness to bring the dissolved gas concentrations into equilibrium with their atmospheric partial pressures. This corresponds to about one billion $50\,\mu m$ radius bubbles, $50\,\mu m$ being close to the average bubble radius [19]:

$$\left\{ \begin{array}{c} \text{total number} \\ \text{of bubbles} \end{array} \right\} = \frac{\text{total number of excess moles of gas in liquid}}{\text{total number of moles in one bubble}}$$
$$= \frac{1\,g\,/\mathcal{M}_{CO_2} + 0.0282\,g\,/\mathcal{M}_{N_2}}{n_b} \approx 10^9 \text{ bubbles.}$$

This number of bubbles would create a head $14\,cm$ thick! In practice, most of the $CO_2$ cannot escape as bubbles and must instead diffuse through the free liquid surface. To see why, let us consider what the $CO_2$ partial pressure, $x_{CO_2} p_b$, in a postcritical bubble tends towards. From Henry's law $CO_2$ will diffuse into the bubble if the dissolved $CO_2$ concentration $c_{CO_2}$ in the liquid is greater than $H_{CO_2} x_{CO_2} p_b$. Noting that initially $c_{CO_2} = H_{CO_2}\,(0.8\,bar)$ and that for a postcritical bubble $p_b \approx 1$ bar, we find that dissolved $CO_2$ diffuses into the bubble if
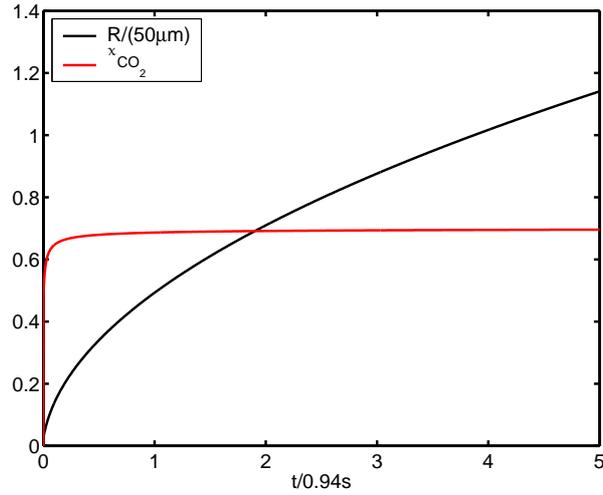
$$x_{CO_2} < 0.8.$$

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Figure 14: $R$ and $x_{CO_2}$ versus $t$ for $R(0) = 1\,\mu m$ and $x_{CO_2}(0) = 0.0003$.

The $CO_2$ mass flux into the bubble will be greater than the $N_2$ mass flux because of the higher concentration of $CO_2$. Hence, the $CO_2$ mole fraction in the bubble will tend towards $0.8$. In fact, solving (6.1) for the case of stationary bubbles ($Sh = 2$, $k_i = D_i/R$) and constant dissolved gas concentrations ($c_{l,i} = const$), we find that the $CO_2$ mole fraction tends towards $0.7$ (figure 14). It is therefore appropriate to consider how many bubbles, each with $x_{N_2} = 0.3$ and $R = 50\,\mu m$, can be created before the $N_2$ runs out:

$$\left\{ \begin{array}{c} \text{total number} \\ \text{of bubbles} \end{array} \right\} = \frac{\text{total number of excess } N_2 \text{ moles in liquid}}{\text{total number of } N_2 \text{ moles in one bubble}}$$
$$= \frac{0.0282\,\text{g}\,/\mathcal{M}_{N_2}}{x_{N_2} n_b} \approx 1.5 \times 10^8 \text{ bubbles.}$$

This reduces the height of the head to about $2\,cm$, which is reasonably close to the observed value of about $1\,cm$ considering the approximations made. The amount of excess $CO_2$ left dissolved in the liquid when the $N_2$ runs out is given by

$$\left\{ \begin{array}{c} \text{dissolved mass of} \\ \text{excess } CO_2 \text{ left} \end{array} \right\} = \left\{ \begin{array}{c} \text{initial excess} \\ CO_2 \text{ mass} \end{array} \right\} - \left\{ \begin{array}{c} CO_2 \text{ mass in} \\ \text{one bubble} \end{array} \right\}$$
$$\times \left\{ \begin{array}{c} \text{number} \\ \text{of bubbles} \end{array} \right\}$$
$$= 1\,\text{g} - \left( \mathcal{M}_{CO_2} x_{CO_2} n_b \right) \left( 1.5 \times 10^8 \right) \approx 0.9\,\text{g}\,.$$

Hence, $90\%$ of the excess $CO_2$ remains and can only escape by diffusing through the free surface.

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