

Dissolution or growth of soluble spherical oscillating bubbles: the effect of surfactants

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A new theoretical formulation is developed for the effects of surfactants on mass transport across the dynamic interface of a bubble which undergoes spherically symmetric volume oscillations. Owing to the presence of surfactants, the Henry's law boundary condition is no longer applicable; it is replaced by a flux boundary condition that features an interfacial resistance that depends on the concentration of surfactant molecules on the interface. The driving force is the disequilibrium partitioning of the gas between free and dissolved states across the interface. As in the clean surface problem analysed recently (Fyrillas & Szeri 1994), the transport problem is split into two parts: the smooth problem and the oscillatory problem. The smooth problem is treated using the method of multiple scales. An asymptotic solution to the oscillatory problem, valid in the limit of large Péclet number, is developed using the method of matched asymptotic expansions. By requiring that the outer limit of the inner approximation match zero, the splitting into smooth and oscillatory problems is determined unambiguously in successive powers of $\mathcal{P}^{-1/2}$, where \mathcal{P} is the Péclet number. To leading order, the clean surface solution is recovered. Continuing to higher order it is shown that the concentration field depends on $R_I \mathcal{P}^{-1/2}$, where R_I is the (dimensionless) interfacial resistance associated with the presence of surfactants. Although the influence of surfactants appears at higher order in the small parameter, surfactants are shown to have a very significant effect on bubble growth rates owing to the fact that the magnitude of R_I is approximately the same as the magnitude of $\mathcal{P}^{1/2}$ at conditions of practical interest. Hence the higher-order 'corrections' happen numerically to be of the same magnitude as the leading-order, clean surface problem. This is the fundamental reason for major increases in the bubble growth rates associated with the addition of surfactants. This is in contrast to the case of a still, surfactant-covered bubble, in which the first-order correction to the growth rate is of order $R_I \mathcal{P}^{-1}$ and presents a $\mathcal{P}^{-1/2}$ correction. Finally, although existing experimental results have shown only enhancement of bubble growth in the presence of a surfactant the present theory suggests that it is possible for a surfactant, characterized by weak dependence of interfacial resistance on surface concentration, to inhibit rather than enhance the growth of bubbles by rectified diffusion.

1. Introduction

It is of fundamental importance in the study of bubbles to understand the exchange of gases across the interface between the free state within the bubble and the dissolved state outside the bubble. It is well known that if a bubble undergoes volume oscillations, the usual tendency to dissolve in undersaturated liquids may be reversed

through a phenomenon known as rectified diffusion. In addition, the clear indications of preliminary experimental work are that surfactants have a very pronounced effect on the growth of bubbles by rectified diffusion. However no theoretical explanation has yet been developed that accounts for the dramatic increase in bubble growth rates via rectified diffusion in the presence of surfactants.

The phenomenon of rectified diffusion was first identified by Blake (1949), who used a quasi-static solution of the diffusion problem to compare with his experimental results. Following Blake, many analyses of the phenomenon were undertaken, restricted either to the assumption of infinitesimal bubble oscillations or of equilibrium exchange of gas, or both. A detailed review of this work can be found in Plesset & Prosperetti (1977). Recently, Fyrrilas & Szeri (1994) (hereinafter referred to as FS) reviewed more recent work and developed a theoretical description of the phenomenon of rectified diffusion across a clean bubble surface that suffers from neither restriction.

Still, however, satisfactory agreement between theory and experiment remains elusive. The theory tends to underpredict bubble growth rates, particularly for large bubbles. The discrepancy was first attributed to bubble resonances; however the importance of resonances has been shown to be an artifact of the polytropic model (FS). Crum (1980), Crum & Hansen (1982) and Church (1988) speculated that the ubiquitous presence of surfactants might be the reason for the disagreement. This is supported by experimental evidence reported by Crum (1980, 1984). Bubbles intentionally contaminated by surfactants were observed to have much larger growth rates when undergoing rectified diffusion.

In the absence of surfactant contamination, rectified diffusion is brought about in the following way. When a bubble undergoing volume oscillations is in the collapsed phase, the internal gas pressure is high – this leads to a flow of gas out of the bubble through the interface. When the bubble is in the expanded phase, the internal pressure is low and the bubble gains gas from the surrounding liquid through the dynamic interface. However, these two phenomena may not be in balance; bubble growth is favoured because the pressure is roughly proportional to $R^{-3\eta}$ where R is the bubble radius and η is the polytropic exponent.

When there is, in addition, interfacial resistance associated with the presence of surfactant, the imbalance that leads to rectified diffusion may be exacerbated. Because the surface area of the bubble changes by a large amount over a typical bubble oscillation, the surface concentration of surfactant molecules is highly variable. When the bubble is contracted, and there is a tendency of the bubble to lose gas, the interfacial resistance is high as a consequence of high surface concentration of surfactant. In contrast, the interfacial resistance is low when the bubble is expanded and the tendency is to gain dissolved gas from the surrounding liquid.

Actually, associated with the presence of surfactants at a gas–liquid interface are two effects: (i) most importantly, surfactants present a barrier to mass transport, and (ii) surfactants reduce the surface tension (Borwankar & Wasan 1983), reflected in a minor change in the dynamics of bubble oscillations. Although it is generally accepted that certain monolayers have been shown through experiment to inhibit mass transport through an interface (Barnes 1986), the understanding of this phenomenon is somewhat limited. Theoretical efforts include the work of Whitaker & Pigford (1966), who assumed an interface of zero thickness but with finite capacity for the solute and an adsorption/desorption process at the interface. Nguyen Ly, Carbonell & McCoy (1979) considered an interfacial region of finite thickness with capacity for the dissolved gases greater than the solubility in water but with much reduced diffusivity. Plevan & Quinn (1966) developed an interfacial resistance model which

has received some theoretical justification by Borwankar & Wasan (1986). The latter authors do not rule out, however, the validity of the other models. Their justification is the leading-order solution to the microscopic equations of mass transport of Brenner & Leal (1982).

Experimental determination of interfacial resistance to gas transport is complicated by the need to isolate interfacial resistance from the overall resistance to transport. Thus, the monolayer resistance must be determined by comparison of two measurements: one performed on the system with the monolayer present and one performed on the system without the monolayer. A detailed review of the evaporation of liquids and transport of gases in the presence of monolayers is given by Barnes (1986). There is a paucity of data that relates interfacial resistance to surface concentration of surfactant molecules. One exception is the work of Caskey & Barlage (1971, 1972). In the first paper (1971) the authors report results of dynamic surface tension versus surface concentration for several surfactants; in the second paper (1972) are the results of interfacial resistance versus surface concentration for the same surfactants. In reporting the predictions of the theory we shall develop, we make use of the interfacial resistances determined by Caskey & Barlage.

The plan of the paper is as follows. We begin by briefly describing the formulation of the problem. Next we turn to an analysis of the oscillatory problem; we concentrate on the splitting of the boundary condition into the parts ascribed to the oscillatory and smooth problems. Next we give the formal solution to the smooth problem. Thereafter we specify the dependence of the interfacial resistance on the surface concentration of surfactant. Finally, we present numerical predictions of the growth rates of bubbles contaminated with surfactants.

2. Formulation

In this section we formulate the problem for dissolution or growth of a soluble, spherical bubble undergoing volume oscillations in response to some external forcing, in a liquid contaminated with surfactants. The differential equation governing the convection and diffusion of a dissolved gas in a liquid outside a spherically symmetric bubble is, in spherical polar coordinates,

$$\frac{\partial \tilde{C}}{\partial t} + \frac{R^2(t)\dot{R}(t)}{r^2} \frac{\partial \tilde{C}}{\partial r} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \tilde{C}}{\partial r} \right), \quad (2.1)$$

where \tilde{C} is the mass fraction of gas dissolved in the liquid, $R^2(t)\dot{R}(t)/r^2$ is the radial velocity field in the liquid associated with the bubble oscillations, D is the diffusivity of the gas in the liquid, and the bubble radius R is a function of time t . $R(t)$ may be obtained by integration of the equations of motion of the bubble. We defer any specification of these equations to §7 on numerical results. The bubble is assumed to be created in a fluid which initially has a uniform concentration of the gas \tilde{C}_∞ . Hence the initial condition and the far-field conditions are

$$\tilde{C}(r, t = 0) = \tilde{C}(r \rightarrow \infty, t) = \tilde{C}_\infty. \quad (2.2)$$

In the clean surface problem, the boundary condition is developed by application of Henry's law which relates the concentration of a gas in a liquid to the partial pressure of the gas above the liquid. In the presence of surfactants Henry's law is no longer applicable. The surfactant monolayer affects the mass transfer characteristics of the interface, both at the microscopic and at the macroscopic level, a fact established by

numerous experiments (Nguyen Ly *et al.* 1979; Emmert & Pigford 1954; Whitaker & Pigford 1966; Plevan & Quinn 1966). The Henry's law boundary condition of the clean surface problem is replaced by a flux boundary condition in which the non-equilibrium partitioning of the gas across the interface is the driving force behind mass transport through the surfactant monolayer. In the present analysis we employ the interfacial resistance model suggested by Plevan & Quinn (1966). This model was placed on firmer theoretical ground by Borwankar & Wasan (1986) using the microscopic approach of Brenner & Leal (1982). The result is that the flux through the interface is proportional to the difference of the surface concentration and the equilibrium concentration (given by Henry's law); this is expressed mathematically as

$$D \frac{\partial \tilde{C}(r = R(t), t)}{\partial r} = \frac{1}{\tilde{R}_I} \left(\tilde{C}(r = R(t), t) - \frac{p_G(t)}{k} \right).$$

Here $p_G(t)$ is the partial pressure of the gas and k is the (equilibrium partition) constant of Henry's law. The constant of proportionality \tilde{R}_I measures the resistance of the monolayer, i.e. if $\tilde{R}_I \rightarrow 0$ the clean surface problem is recovered. In general, \tilde{R}_I depends strongly on the concentration of surfactants on the interface; for the present we shall treat it as a general function of time, $\tilde{R}_I = \tilde{R}_I(t)$. We develop an explicit form for $\tilde{R}_I(t)$ in § 6 below.

As in FS the transport problem is recast in dimensionless, Lagrangian coordinates to yield

$$\frac{\partial C}{\partial \tau} = \frac{1}{\mathcal{P}} \frac{\partial}{\partial \sigma} \left((3\sigma + x^3(\tau))^{(4/3)} \frac{\partial C}{\partial \sigma} \right), \quad (2.3)$$

with boundary and initial conditions

$$\frac{x^2(\tau)R_I(\tau)}{\mathcal{P}} \frac{\partial C(\sigma = 0, \tau)}{\partial \sigma} = C(\sigma = 0, \tau) - (C_{sb} p_G^*(\tau) - C_\infty), \quad (2.4)$$

$$C(\sigma, \tau = 0) = C(\sigma \rightarrow \infty, \tau) = 0.$$

The scales for non-dimensionalization are a , the radius of the undisturbed bubble, and Ω_0^{-1} , the inverse natural frequency of radial oscillations of the bubble about the undisturbed state. The dimensionless parameters introduced are the Péclet number ($\mathcal{P} = a^2 \Omega_0 / D$), which is the ratio between the time scales for convection and diffusion; the dimensionless bubble radius $x(\tau)$; and the dimensionless interfacial resistance, $R_I(\tau) = \tilde{R}_I(t \Omega_0) a \Omega_0$. As explained in FS, if the initial pressure inside the bubble is used to non-dimensionalize Henry's constant we get the dimensionless parameter $C_{sb} = p_{Gi}/k$, which corresponds to the saturation concentration in the liquid separated from a gas within a spherical bubble with initial pressure p_{Gi} . The dimensionless Lagrangian coordinate is

$$\sigma \equiv \frac{1}{3} \left(\frac{r^3}{a^3} - x^3(\tau) \right).$$

We have subtracted the concentration at infinity from the concentration field, i.e. $C = \tilde{C} - \tilde{C}_\infty$.

3. Oscillatory problem

Following FS we shall split the problem in two, in order to handle the complicated boundary condition. We proceed to split the time-dependent boundary condition into a constant and an oscillating part, making use of the linearity of the problem for the

concentration field. The constant part of the boundary condition is associated with the *smooth problem* (C_{sm}) and the oscillating part of the boundary condition with the *oscillatory problem* (C_{osc}).

Because the convection diffusion equation for C is linear, the splitting is not unique. In FS we defined the splitting by requiring the solution to the oscillatory problem to be different from zero only in a thin layer near the bubble surface in a way that is uniformly valid in time. This was accomplished to leading order in the small parameter $\mathcal{P}^{-1/2}$. In effect, this procedure places a restriction on what part of the total boundary condition we can ascribe to the oscillatory solution, in order that it should be non-zero in only a thin layer near the bubble surface. The remainder of the boundary condition is satisfied by the smooth solution, which is permitted to be non-zero away from the bubble surface. We treat the oscillatory problem using the method of matched asymptotic expansions. The outer approximation to the solution of the oscillatory problem is identically zero by construction if we restrict the boundary condition of the oscillatory problem in such a way as to make the outer limit of the inner approximation zero. In this case, the inner approximation to the solution of the oscillatory problem is uniformly valid in space.

To begin the splitting, we transform the problem (2.3) into the oscillatory form using (i) the nonlinear time $\hat{\tau}$, developed by Plesset & Zwick (1952) and later used by Eller & Flynn (1965):

$$\hat{\tau} \equiv \int_0^\tau x^4(\theta) d\theta,$$

and (ii) the re-scaled Lagrangian coordinate $s = \mathcal{P}^{1/2}\sigma$. The result is

$$\frac{\partial C_{osc}}{\partial \hat{\tau}} = \frac{\partial}{\partial s} \left(\left(\frac{3s}{x^3(\hat{\tau})\mathcal{P}^{1/2}} + 1 \right)^{(4/3)} \frac{\partial C_{osc}}{\partial s} \right). \tag{3.1}$$

Next we assume an expansion of the form

$$C_{osc} = C_{osc}^0(s, \hat{\tau}) + \frac{1}{\mathcal{P}^{1/2}} C_{osc}^1(s, \hat{\tau}) + \frac{1}{\mathcal{P}} C_{osc}^2(s, \hat{\tau}) + \dots,$$

together with a similar expansion for the smooth problem, and use the binomial theorem to expand equation (3.1) for large \mathcal{P} (small $\mathcal{P}^{-1/2}$). To zeroth and first order we have

$$\left. \begin{aligned} \frac{\partial C_{osc}^0}{\partial \hat{\tau}} &= \frac{\partial^2 C_{osc}^0}{\partial s^2}, \\ C_{osc}^0(s=0, \hat{\tau}) &= C_{sb} p_G^*(\hat{\tau}) - C_\infty - C_{sm}^0(\sigma=0, \hat{\tau}) \end{aligned} \right\} \tag{3.2}$$

and

$$\left. \begin{aligned} \frac{\partial C_{osc}^1}{\partial \hat{\tau}} &= \frac{\partial^2 C_{osc}^1}{\partial s^2} + \frac{4}{x^3(\hat{\tau})} \frac{\partial}{\partial s} \left(s \frac{\partial C_{osc}^0}{\partial s} \right), \\ C_{osc}^1(s=0, \hat{\tau}) &= x^2(\hat{\tau}) R_I(\hat{\tau}) \frac{\partial \bar{C}_{osc}^0(s=0, \hat{\tau})}{\partial s} - C_{sm}^1(\sigma=0, \hat{\tau}) \end{aligned} \right\} \tag{3.3}$$

respectively. In (3.2) and (3.3) we have introduced the extra terms, $C_{sm}^0(\sigma=0, \hat{\tau})$ and $C_{sm}^1(\sigma=0, \hat{\tau})$ to aid in splitting the problem. Effectively, in (3.2) and (3.3) we write the boundary condition of the oscillatory problem at a given order in $\mathcal{P}^{-1/2}$ as the full boundary condition at that order minus the boundary condition of the smooth problem at that order. $C_{sm}^0(\sigma=0, \hat{\tau})$ and $C_{sm}^1(\sigma=0, \hat{\tau})$ are the constant parts of

the boundary condition that we shall use in order to satisfy the conditions for the splitting.

The next step is to ensure that the long-time asymptotic solutions (indicated by an overbar), \bar{C}_{osc}^0 and \bar{C}_{osc}^1 , are uniformly valid in space and do not require an outer expansion. This is achieved by forcing the ‘outer’ limit of \bar{C}_{osc}^0 and \bar{C}_{osc}^1 , i.e. as $s \rightarrow \infty$, to be zero. As a result, the outer approximation for the oscillatory problem leads to a homogeneous problem with both boundary conditions and initial condition zero.

As we shall see, the oscillatory problem contributes very little to the mass transport across the bubble surface. An expression for the amount of mass transfer is

$$m_G^*(\hat{\tau}) - m_G^*(0) = \frac{1}{\mathcal{P}} \int_0^{\hat{\tau}} \frac{\partial C(\sigma = 0, \hat{\tau}')}{\partial \sigma} d\hat{\tau}',$$

where m_G^* is the mass of the gas in the bubble divided by the mass of liquid displaced by the undisturbed bubble. A more useful expression can be easily obtained from the differential equation for the concentration field (2.3) by two integrations: one in s from zero to infinity and one in $\hat{\tau}$

$$m_G^*(\hat{\tau}) - m_G^*(0) = - \int_0^\infty C(\sigma', \hat{\tau}) d\sigma'. \tag{3.4}$$

3.1. Zeroth-order oscillatory problem

The zeroth-order problem is presented in detail in FS where it was shown that the outer limit of the zeroth-order oscillatory problem is zero, if the average of the boundary condition with respect to the time $\hat{\tau}$ is zero, i.e. $\langle C_{osc}^0(0, \hat{\tau}) \rangle_{\hat{\tau}} = 0$. Here the average $\langle \cdot \rangle_{\hat{\tau}}$ is defined by

$$\langle f(\sigma, \hat{\tau}) \rangle_{\hat{\tau}} \equiv \frac{1}{\hat{\tau}(T)} \int_0^{\hat{\tau}(T)} f(\sigma, \hat{\tau}) d\hat{\tau} = \frac{1}{\int_0^T x^4(\tau) d\tau} \int_0^T f(\sigma, \tau) x^4(\tau) d\tau,$$

where T is the dimensionless period of bubble oscillation. Hence the boundary conditions for C_{osc}^0 and C_{sm}^0 are determined from (3.2) to be

$$C_{osc}^0(s = 0, \hat{\tau}) = C_{sb} [p_G^*(\hat{\tau}) - \langle p_G^*(\hat{\tau}) \rangle_{\hat{\tau}}]$$

and

$$C_{sm}^0(\sigma = 0, \tau) = C_{sb} \langle p_G^*(\hat{\tau}) \rangle_{\hat{\tau}} - C_\infty, \tag{3.5}$$

respectively. The asymptotic solution \bar{C}_{osc}^0 is very quickly approached within a few periods of bubble oscillation; it is easily computed using Fourier series. The result is

$$\begin{aligned} \bar{C}_{osc}^0(s, \hat{\tau}) = & \sum_{m=1}^\infty \exp \left[- \left(\frac{\omega_m}{2} \right)^{1/2} s \right] \\ & \times \left\{ a_m \cos \left[\omega_m \hat{\tau} - \left(\frac{\omega_m}{2} \right)^{1/2} s \right] + b_m \sin \left[\omega_m \hat{\tau} - \left(\frac{\omega_m}{2} \right)^{1/2} s \right] \right\}, \end{aligned} \tag{3.6}$$

where a_m and b_m are the expansion coefficients of the boundary condition

$$\begin{aligned} \bar{C}_{osc}^0(s = 0, \hat{\tau}) = & C_{sb} [p_G^*(\hat{\tau}) - \langle p_G^*(\hat{\tau}) \rangle_{\hat{\tau}}] \\ = & \sum_{m=1}^\infty [a_m \cos(\omega_m \hat{\tau}) + b_m \sin(\omega_m \hat{\tau})] \end{aligned}$$

and

$$\omega_m = \frac{2m\pi}{\hat{\tau}(T)}.$$

The long-time rate of mass transport is determined from (3.4). The zeroth-order oscillatory problem \bar{C}_{osc}^0 does not contribute to any net bubble growth or dissolution, because the mass transport is a periodic function of time ($\hat{\tau}$) with zero mean.

3.2. First-order oscillatory problem

The condition for uniform validity of \bar{C}_{osc}^1 (3.3) is not so straightforward to obtain as a consequence of the inhomogeneous term. In the Appendix we show that the condition for uniform validity of the oscillatory problem is

$$\langle C_{osc}^i(s = 0, \hat{\tau}) \rangle_{\hat{\tau}} = \int_0^\infty \int_\infty^{s'} \langle F^i(s'') \rangle_{\hat{\tau}} ds'' ds'$$

where F^i is the inhomogeneous term (forcing term) associated with i th-order oscillatory problem. The resulting condition for the C_{osc}^1 problem is

$$\langle \bar{C}_{osc}^1(0, \hat{\tau}) \rangle_{\hat{\tau}} = - \left\langle \frac{4}{x^3(\hat{\tau})} \int_0^\infty \bar{C}_{osc}^0(s', \hat{\tau}) ds' \right\rangle_{\hat{\tau}}. \tag{3.7}$$

Hence the parts of the total boundary conditions ascribed to C_{osc}^1 and C_{sm}^1 are determined from (3.3) to be

$$C_{osc}^1(s = 0, \hat{\tau}) = x^2(\hat{\tau})R_f(\hat{\tau}) \frac{\partial \bar{C}_{osc}^0(s = 0, \hat{\tau})}{\partial s} - \left(\left\langle x^2(\hat{\tau})R_f(\hat{\tau}) \frac{\partial \bar{C}_{osc}^0(s = 0, \hat{\tau})}{\partial s} \right\rangle_{\hat{\tau}} + \left\langle \frac{4}{x^3(\hat{\tau})} \int_0^\infty \bar{C}_{osc}^0(s', \hat{\tau}) ds' \right\rangle_{\hat{\tau}} \right)$$

and

$$C_{sm}^1(\sigma = 0, \tau) = \left\langle x^2(\hat{\tau})R_f(\hat{\tau}) \frac{\partial \bar{C}_{osc}^0(s = 0, \hat{\tau})}{\partial s} \right\rangle_{\hat{\tau}} + \left\langle \frac{4}{x^3(\hat{\tau})} \int_0^\infty \bar{C}_{osc}^0(s', \hat{\tau}) ds' \right\rangle_{\hat{\tau}}, \tag{3.8}$$

respectively. The asymptotic solution \bar{C}_{osc}^1 is not required in the present analysis as our intent is to solve the smooth problem up to order $\mathcal{P}^{-1/2}$. The solution can be obtained using Fourier series.

To compute the amount of mass transfer due to the first-order oscillatory problem we use (3.4) and recall that the mean part of the long-time asymptotic solution \bar{C}_{osc}^1 decays exponentially as shown in the Appendix. Hence, the first-order oscillatory problem contributes very little to the transport, and then only in the initial stages.

4. The smooth problem

The *smooth problem* is defined by

$$\frac{\partial C_{sm}}{\partial \tau} = \frac{1}{\mathcal{P}} \frac{\partial}{\partial \sigma} \left((3\sigma + x^3(\tau))^{(4/3)} \frac{\partial C_{sm}}{\partial \sigma} \right), \tag{4.1}$$

with the boundary condition (obtained by the sum of (3.5) and (3.8)) and initial condition

$$\frac{x^2(\tau)R_I(\tau)}{\mathcal{P}} \frac{\partial C_{sm}(\sigma = 0, \tau)}{\partial \sigma} = C_{sm}(\sigma = 0, \tau) - [C_{sb} \langle p_G^*(\hat{\tau}) \rangle_{\hat{\tau}} - C_{\infty}] - \frac{1}{\mathcal{P}^{1/2}} \left[\left\langle x^2(\hat{\tau})R_I(\hat{\tau}) \frac{\partial C_{osc}^0(s = 0, \hat{\tau})}{\partial s} \right\rangle_{\hat{\tau}} + \left\langle \frac{4}{x^3(\hat{\tau})} \int_0^{\infty} C_{osc}^0(s', \hat{\tau}) ds' \right\rangle_{\hat{\tau}} \right] + O(\mathcal{P}^{-1}), \quad (4.2a)$$

$$C_{sm}(\sigma, \tau = 0) = C_{sm}(\sigma \rightarrow \infty, \tau) = 0. \quad (4.2b)$$

The smooth boundary condition (4.2) includes terms of order $\mathcal{P}^{-1/2}$ and represents a higher-order correction to our earlier solution in FS in the case of a clean surface. In the clean surface problem ($R_I(\tau) = 0$) the additional term presents a small correction as it is multiplied by $\mathcal{P}^{-1/2}$ which is very small at conditions of practical interest. As we shall demonstrate, the correction is not small in the surfactant-covered surface problem because $R_I(\tau)$ happens to be of the same magnitude as $\mathcal{P}^{1/2}$ in the physical problems of interest.

The smooth problem is treated by the method of multiple scales in time. We introduce a second time scale $\lambda \equiv \tau/\mathcal{P} = tD/a^2$, which captures the slow diffusive behaviour and define a second (conventional) time average with respect to the fast time τ ,

$$\langle f(\sigma, \tau) \rangle_{\tau} \equiv \frac{1}{T} \int_0^T f(\sigma, \tau) d\tau. \quad (4.3)$$

Equation (4.1) transforms to

$$\frac{\partial C_{sm}}{\partial \tau} + \frac{1}{\mathcal{P}} \frac{\partial C_{sm}}{\partial \lambda} = \frac{1}{\mathcal{P}} \frac{\partial}{\partial \sigma} \left((3\sigma + x^3(\tau))^{(4/3)} \frac{\partial C_{sm}}{\partial \sigma} \right).$$

Next we expand

$$C_{sm}(\sigma, \tau) = C_{sm}^0(\sigma, \lambda, \tau) + \frac{1}{\mathcal{P}^{1/2}} C_{sm}^1(\sigma, \lambda, \tau) + \frac{1}{\mathcal{P}} C_{sm}^2(\sigma, \lambda, \tau) + \frac{1}{\mathcal{P}^{3/2}} C_{sm}^3(\sigma, \lambda, \tau) + \dots$$

Note that we must expand the smooth problem in powers of $\mathcal{P}^{-1/2}$ in view of the asymptotic sequence in the boundary condition (4.2). Upon substituting in our expansion for C_{sm} and equating coefficients of like powers of $\mathcal{P}^{-1/2}$, we obtain a sequence of problems for C_{sm}^i for $i = 0, 1, 2, \dots$. We remark that the $C_{sm}^0 - C_{sm}^2$ problems decouple from $C_{sm}^1 - C_{sm}^3$. To zeroth and first order in the small parameter $\mathcal{P}^{-1/2}$, we have the systems

$$\frac{\partial C_{sm}^i}{\partial \tau} = 0, \quad \text{where } i = 0, 1, \quad (4.4)$$

with boundary and initial conditions

$$C_{sm}^0(\sigma = 0, \lambda, \tau) = C_{sb} \langle p_G^*(\hat{\tau}) \rangle_{\hat{\tau}} - C_{\infty},$$

$$C_{sm}^1(\sigma = 0, \lambda, \tau) = \left[\left\langle x^2(\hat{\tau})R_I(\hat{\tau}) \frac{\partial C_{osc}^0(s = 0, \hat{\tau})}{\partial s} \right\rangle_{\hat{\tau}} + \left\langle \frac{4}{x^3(\hat{\tau})} \int_0^{\infty} C_{osc}^0(s', \hat{\tau}) ds' \right\rangle_{\hat{\tau}} \right],$$

$$C_{sm}^i(\sigma, \lambda = 0, \tau = 0) = C_{sm}^i(\sigma \rightarrow \infty, \lambda, \tau) = 0, \quad i = 0, 1.$$

The solution to the zeroth- and first-order problems (4.4) is simply $C_{sm}^i(\sigma, \lambda, \tau) = C_{sm}^i(\sigma, \lambda)$, $i = 0, 1$. However C_{sm}^i is further determined by ensuring that there is no secular behaviour in C_{sm}^{i+2} , lest the expansion become disordered as τ increases. Hence we force the right-hand side of the second- and third-order problems to have zero

τ -average (defined in (4.3)); this leads to a second equation for C_{sm}^i ($i = 0, 1$):

$$\frac{\partial C_{sm}^i}{\partial \lambda} = \frac{\partial}{\partial \sigma} \left(\left\langle (3\sigma + x^3(\tau))^{(4/3)} \right\rangle_{\tau} \frac{\partial C_{sm}^i}{\partial \sigma} \right).$$

The smooth problem has a very straightforward asymptotic solution $\bar{C}_{sm}^i(\sigma)$ (indicated by an overbar) in the limit $\lambda \rightarrow \infty$, developed in FS:

$$\bar{C}_{sm}^i(\sigma) = C_{sm}^i(\sigma = 0) \left[1 - \frac{\int_0^{\sigma} \frac{d\sigma'}{\left\langle (3\sigma' + x^3(\tau))^{(4/3)} \right\rangle_{\tau}}}{\int_0^{\infty} \frac{d\sigma}{\left\langle (3\sigma + x^3(\tau))^{(4/3)} \right\rangle_{\tau}}} \right], \tag{4.5}$$

which is valid for any nonlinear periodic bubble oscillation. The asymptotic solution for the (smooth) concentration field and for the rate of mass transport up to first order in $\mathcal{P}^{-1/2}$ may be expressed as

$$\bar{C}_{sm}(\sigma) = \bar{C}_{sm}(0) \left[1 - \frac{\int_0^{\sigma} \frac{d\sigma'}{\left\langle (3\sigma' + x^3(\tau))^{(4/3)} \right\rangle_{\tau}}}{\int_0^{\infty} \frac{d\sigma}{\left\langle (3\sigma + x^3(\tau))^{(4/3)} \right\rangle_{\tau}}} \right] \tag{4.6}$$

and

$$\frac{d\bar{m}_{G_{sm}}^*(\lambda)}{d\lambda} = -3 \frac{\bar{C}_{sm}(0)}{\int_0^{\infty} \frac{d\sigma}{\left\langle (3\sigma + x^3(\tau))^{(4/3)} \right\rangle_{\tau}}}, \tag{4.7}$$

respectively, where $\bar{C}_{sm}(0)$ is the threshold condition for rectified diffusion

$$\begin{aligned} \bar{C}_{sm}(0) = C_{sb} \langle p_G^*(\hat{\tau}) \rangle_{\hat{\tau}} - C_{\infty} + \frac{1}{\mathcal{P}^{1/2}} & \left[\left\langle x^2(\hat{\tau}) R_I(\hat{\tau}) \frac{\partial \bar{C}_{osc}^0(s=0, \hat{\tau})}{\partial s} \right\rangle_{\hat{\tau}} \right. \\ & \left. + \left\langle \frac{4}{x^3(\hat{\tau})} \int_0^{\infty} \bar{C}_{osc}^0(s', \hat{\tau}) ds' \right\rangle_{\hat{\tau}} \right] + O(\mathcal{P}^{-1}) \end{aligned} \tag{4.8}$$

and \bar{C}_{osc}^0 is the zeroth-order asymptotic solution (3.6) of the oscillatory problem. In § 6 we turn to consideration of $R_I(\tau)$ before evaluating these expressions for specific physical problems.

5. Effect of surfactants on a still bubble

In the absence of pressure oscillations the bubble is still; the transport problem (2.3) simplifies because $x(\tau) = 1$ and $R_I(\tau)$ is constant. At steady state, i.e. $\frac{\partial C}{\partial \tau} = 0$, the rate of mass transport is readily determined:

$$\frac{dm_G^*}{d\lambda} = -3 \frac{C_{sb} - C_{\infty}}{1 + R_I/\mathcal{P}}.$$

Because R_I is a positive number, the effect of a surfactant is to reduce mass transport and hence to suppress growth or dissolution.

When \mathcal{P} is large the growth rate simplifies to

$$\frac{dm_G^*}{d\lambda} = -3 [C_{sb} - C_\infty] \left(1 - \frac{R_f}{\mathcal{P}} \right) \quad (5.1)$$

which reveals two important differences between a still and an oscillating bubble. For the former, surfactants inhibit mass transport and their effect appears at $O(\mathcal{P}^{-1})$. In the case of an oscillating bubble however, the effect of a surfactant appears at $O(\mathcal{P}^{-1/2})$ and as we show in § 7, surfactants might enhance or reduce mass transport depending on the way in which R_f depends on the surface concentration of the surfactant.

6. Interfacial resistance

A surfactant molecule consists of a hydrophobic and a hydrophilic portion; as a consequence surfactant molecules tend to accumulate at a gas–liquid interface. In a set of experiments of great significance to the present work, Crum (1980) demonstrated that the addition of small amounts of surfactant to the liquid in which a bubble was suspended had a very significant effect on the growth rate of the bubble by rectified diffusion. These were preliminary experiments; it appears that the intentional addition of surfactants was for the purpose of supporting speculation on the inability of the theory adequately to explain the large growth rates of large bubbles by rectified diffusion. Crum made use of a commercially available surfactant known by the trade name *Photoflo 200* –which is commonly employed in photographic processing. We are advised that this formulated product contains a number of other, unspecified components in addition to the surfactant ethoxylated octylphenol (P. Schwartz 1994, personal communication). Moreover, there are statistical distributions of chain length of the hydrophobic end and of the oxyethylene hydrophilic end of the surfactants. The interfacial resistance properties of this product do not appear to have been characterized. Therefore it does not seem possible to compare the theoretical predictions we can now make regarding bubble growth rates in the presence of surfactants with the experimental results of Crum. Clearly this is an area to pursue in future work.

In the present paper, we shall have to content ourselves with the development of theoretical predictions of bubble growth rates for surfactant systems that are well-characterized. We shall show that the theoretical prediction for these surfactant systems yields growth rates of bubbles that are significantly larger than growth rates for clean bubbles.

Therefore, using experimental results by Caskey & Barlage (1971, 1972), we shall obtain simple expressions that relate surfactant surface concentrations with interfacial resistances and surface tensions for three surfactant systems. The former is needed for the calculation of the mass transport (4.7) and threshold (4.8) and the latter in the model for the dynamical equations for bubble oscillations.

A general treatment for surfactant transport along a deforming interface presents a formidable task. This would require a transport equation for the bulk and surface-excess quantities of surfactant and a constitutive relation for non-equilibrium partitioning of a soluble surfactant between interface and bulk (Edwards, Brenner & Wasan 1991). Assuming that the forward rate constant is much larger than the diffusion coefficient, this problem can be identified as the diffusion-controlled case. In the diffusion-controlled limit surfactant is transported slowly by diffusion through the bulk to the interface. In contrast, the adsorption step appears to occur instantaneously; hence an equilibrium adsorption relation may be assumed – which for

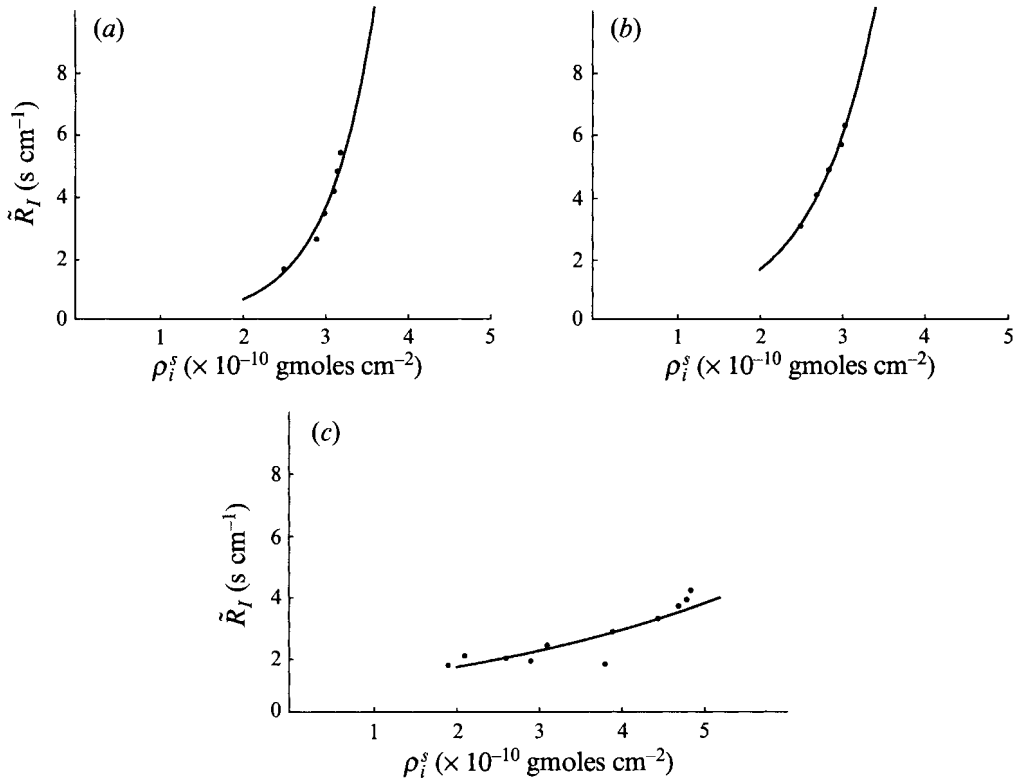


FIGURE 1. Interfacial resistance \tilde{R}_I in s cm^{-1} versus surfactant surface concentration ρ_i^s in 10^{-10} gmol cm^{-2} . The points correspond to the experimental data of Caskey & Barlage (1972) and the solid line to an exponential curve fit. The surfactants are (a) dodecyltrimethylammonium chloride ($\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$), (b) hexadecyltrimethylammonium chloride ($\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Cl}$) and (c) dodecyl sodium sulphate ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$). The fits are (a) $\tilde{R}_I = 0.022 \exp(1.68 \rho_i^s)$, (b) $\tilde{R}_I = 0.13 \exp(1.26 \rho_i^s)$, (c) $\tilde{R}_I = 0.72 \exp(0.36 \rho_i^s)$.

an ideal surface reduces to the Langmuir isotherm. For surface-excess concentrations much smaller than the surface-excess saturation density (which corresponds to the maximum realizable surface-excess density) or large adsorption coefficients the resulting equation for the surface concentration yields

$$\rho_i^s(\tau)x(\tau)^2 = \text{const} = \rho_i^s(\tau = 0)$$

where $\rho_i^s(\tau)$ is the surface surfactant concentration, $x(\tau)$ is the dimensionless bubble radius and $\rho_i^s(\tau = 0)$ the initial concentration. Note that the same expression can be obtained by assuming the surfactant to be insoluble (Stone 1990). Finally, we note that $R_I(\tau)$ is then a function of $\rho_i^s(\tau)$, or equivalently of $\rho_i^s(\tau = 0)/x(\tau)^2$.

We shall make use of experimental results for three surfactants:

- (a) dodecyltrimethylammonium chloride ($\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$),
- (b) hexadecyltrimethylammonium chloride ($\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Cl}$) and
- (c) dodecyl sodium sulphate ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$).

To obtain an expression for the interfacial resistance as a function of surface concentration we developed straightforward exponential fits to the data in figure 3 of Caskey & Barlage (1972); this procedure seems to yield adequate approximations, as shown in figure 1.

Finally, a remark concerning the numerical results we present below is in order. When we make use of the experimental data of Caskey & Barlage, we take great care in remaining within the ranges of surfactant surface concentration at which the interfacial resistance is known. This implies a restriction on the amplitudes of driving pressure that we may consider; however, it is important to base our numerical results on hard evidence rather than on pure extrapolation.

Because interfacial tension does not vary significantly with surfactant surface concentration we use an average value of 60 dynes cm^{-1} obtained from figure 5 of Caskey & Barlage (1971).

7. Theoretical predictions of bubble growth rates

Now we shall evaluate the expression we have developed for the growth rate of a surfactant-covered bubble via the mechanism of rectified diffusion. The last component required for the evaluation of the growth rate is the periodic bubble motion $R(t)$. There are numerous mathematical models for bubble oscillations as reviewed by Plesset & Prosperetti (1977). For rectified diffusion calculations, polytropic models have been used in the vast majority of studies. However, a recent comparison in FS showed a dramatic difference near resonance in the solution of the clean surface transport problem between the polytropic and a more accurate non-polytropic model. Consequently, in this paper, as in FS, we shall use the four-term Galerkin formulation of Kamath & Prosperetti (1989) in which the polytropic assumption for the bubble internal pressure is relaxed and thermal effects are included. This model, like the polytropic models, assumes that the pressure field within the bubble is uniform. However a spatially non-uniform temperature field is allowed. This requires solution of the energy equation for the gas within the bubble, which is a partial differential equation.

Hence, to the bubble dynamical equations we append four ordinary differential equations for the amplitude coefficients of the Galerkin expansion of the temperature field. The pressure inside the bubble is given explicitly by an equation based on constant mass of gas within the bubble. These equations are given in the Appendix of the paper by Kamath & Prosperetti (1989). The bubble dynamical equations are $x_1 \equiv x$,

$$\frac{dx_1}{d\tau} = x_2,$$

and

$$\begin{aligned} \frac{dx_2}{d\tau} = & \left[3 x_2^2 \left(\frac{x_2}{3 c^*} - 1 \right) + \left(1 + \frac{x_2}{c^*} \right) (p_B^* - p^*) \right. \\ & \left. + \frac{x_1}{c^*} \left(\frac{8 x_2}{We x_1^2} + \frac{8 x_2^2}{Re x_1^2} - p_{Gi}^* \frac{dp_G^*(\tau)}{d\tau} \right) \right] \left[2 \left(1 - \frac{x_2}{c^*} \right) x_1 + \frac{8}{Re c^*} \right]^{-1} \end{aligned}$$

where

$$\begin{aligned} p_B^* &= p_{Gi}^* p_G^*(\tau) - \frac{8}{We x_1} - \frac{8 x_2}{Re x_1}, \\ p^* &= p_\infty^* \left[1 - \frac{p_A^* (\Omega_0^{-1} [\tau + x_1/c^*])}{p_\infty^*} \right], \end{aligned}$$

c^* is the dimensionless sound speed, We denotes the Weber number and Re the Reynolds number. Finally, we add two more nonlinear ODEs which yield the

oscillatory part of the background pressure that drives the bubble oscillation. The details are in FS. The system of eight nonlinear ODEs is integrated numerically using the software AUTO (Doedel 1986). To ensure that the four-term Galerkin expansion is accurate enough we stop the calculation if one of the amplitude coefficients is not at least one order of magnitude less than the preceding one. For the bubble radii used in our calculations, i.e. 20, 40 and 60 μm , we had to stop the integration at dimensionless pressure amplitude of 0.5.

Following Eller (1969), the dimensional rate of growth of the equilibrium bubble radius is related to the mass transfer as follows:

$$\begin{aligned} \frac{da}{dt} &= a \Omega_0 \frac{R_G T_\infty \rho}{3 M p_0} \frac{1}{\mathcal{P}} \left(1 + \frac{16}{3 We p_0^*} \right)^{-1} \frac{d\bar{m}_{Gsm}^*}{d\lambda} \\ &= a \Omega_0 \frac{R_G T_\infty \rho}{M p_0} \frac{1}{\mathcal{P}} \left(1 + \frac{16}{3 We p_0^*} \right)^{-1} \frac{-3\bar{C}_{sm}(0)}{\int_0^\infty \frac{d\sigma}{\langle (3\sigma + x^3(\tau))^{(4/3)} \rangle_\tau}}, \end{aligned} \quad (7.1)$$

where $\bar{C}_{sm}(0)$ is the threshold condition given by equation (4.8); $R_G = 8314 \text{ J kmol}^{-1} \text{ K}^{-1}$ is the universal gas constant, $T_\infty = 300 \text{ K}$ is the temperature of the liquid at the far field, $\rho = 1.0 \text{ gm cm}^{-3}$ is the liquid density, $M = 29 \text{ kmol kg}^{-1}$ is the molecular weight of the gas and $p_0 = 1 \times 10^6 \text{ dynes cm}^{-2}$ is the background pressure.

In figures 2–4 we show plots of predicted bubble growth rates versus dimensionless pressure amplitude for bubbles of radius 20, 40 and 60 μm respectively. The upper plot in each of these figures consists of a magnification of the vertical axis near zero growth rate (which corresponds to the threshold for rectified diffusion). In all cases, the curves showing bubble growth rates correspond to dynamic surfactant surface concentrations within the ranges over which we know the interfacial resistance from the work of Caskey & Barlage.

The solid curves show the effect of the three different surfactants on the bubble growth rates. As we mentioned previously, surfactants can affect bubble growth rates through two mechanisms: (i) reduction of interfacial tension, and (ii) interfacial resistance to mass transfer. Of these, the latter is the far more significant effect, as demonstrated in the figures where we plot the growth rates as modified by both mechanisms (solid curves) and by only the reduction in surface tension (long-dashed curves). The clean surface results are shown using the short-dashed curves. Reduction of surface tension contributes only a small upward shift of the growth rate curve, a result first noted by Crum (1980), and cannot justify the high bubble growth rates observed in experiments. This suggests that the ‘missing physics’ which accounts for the difference between theoretical predictions and experimental results for growth rates by rectified diffusion is the effect of interfacial resistance on mass transfer. This would appear to bear out the speculations of Crum and of Church, to which we made earlier reference, on the importance of surfactants to the phenomenon of rectified diffusion.

It is also of considerable interest to note that surfactants are not only responsible for higher growth rates but might tend to favour dissolution of bubbles as one can see in figure 2 curve (c). This fact is further clarified by the following investigation. In figure 5 we show the effect of initial surface concentration of the surfactant hexadecyltrimethylammonium chloride ($\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Cl}$) on bubble growth rates, for a bubble of radius 20 μm . There is a dramatic effect of a slight increase of initial surface concentration on bubble growth rates. Clearly, higher concentration

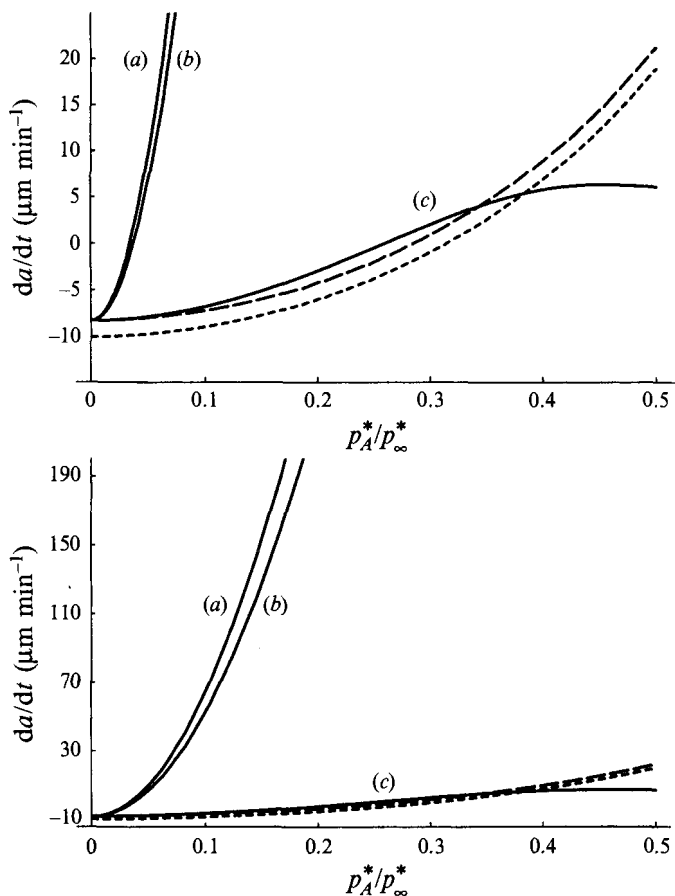


FIGURE 2. The rate of bubble growth in $\mu\text{m min}^{-1}$ versus dimensionless pressure amplitude p_A^*/p_∞^* . The solid curves correspond to (7.1) for the surfactant (a) $\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$, (b) $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Cl}$ and (c) $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$, each with initial surface concentration 2.9×10^{-10} gmol cm^{-2} . The two dashed curves correspond to (7.1) with R_I set to zero. The diffusivity of the gas in the liquid is 2.0×10^{-5} $\text{cm}^2 \text{s}^{-1}$. The bubble is of equilibrium radius $20 \mu\text{m}$ and is driven at a frequency of 26.6 kHz. The interfacial tension is 60 dynes cm^{-1} except for the short-dashed curve which corresponds to the clean surface with interfacial tension 73 dynes cm^{-1} . The upper plot consists of a magnification of the vertical axis near zero growth rate which corresponds to the threshold for rectified diffusion. Note that the presence of surfactant is associated with a reduction in the threshold pressure amplitude for rectified diffusion.

of surfactant appears to favour growth of bubbles for this surfactant. The principal effect of changing the initial concentration of surfactant is to move up or down the exponential curve of interfacial resistance. At larger concentrations, the interfacial resistance changes more rapidly with concentration. This leads one to conclude that if the interfacial resistance versus surface concentration curve for one surfactant is steeper than for another, then the first surfactant will tend to promote bubble growth more than the second. These statements are in agreement with the predictions we have made thus far, and with the following.

We shall assume a general form for the interfacial resistance

$$\tilde{R}_I(\tau) = \exp\left(\frac{\alpha}{x^2(\tau)}\right), \quad (7.2)$$

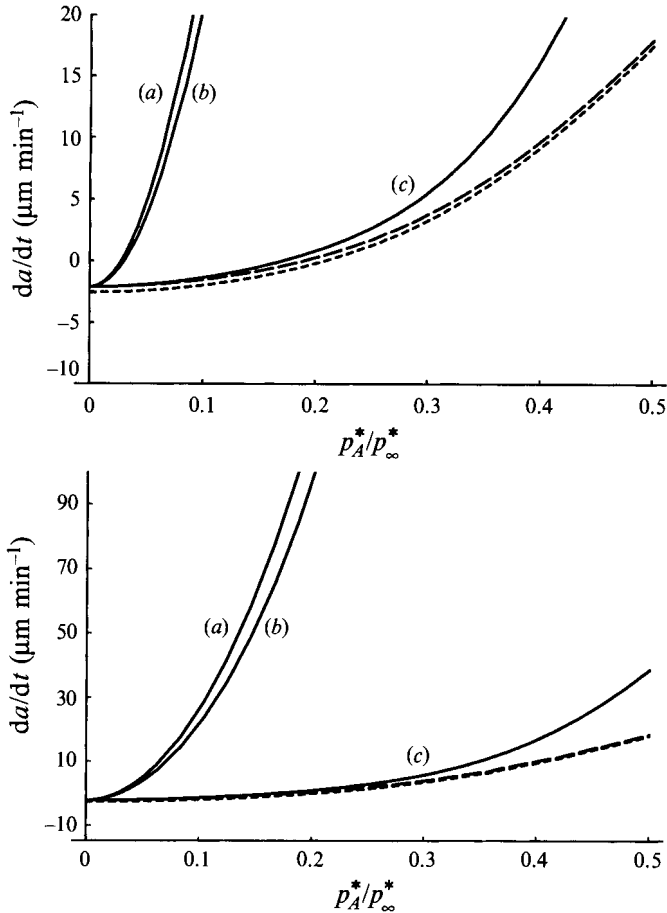


FIGURE 3. The rate of bubble growth in $\mu\text{m min}^{-1}$ versus dimensionless pressure amplitude p_A^*/p_∞^* . The data are the same as for figure 2 except the bubble is of equilibrium radius $40\ \mu\text{m}$.

and investigate the effect of interfacial resistance on bubble growth rates for different values of the exponent α and a fixed bubble oscillation. For these calculations we use equation (7.1) but include only the interfacial resistance term in $\bar{C}_{sm}(0)$:

$$\frac{1}{\mathcal{P}^{1/2}} \left[\left\langle x^2(\hat{\tau}) R_I(\hat{\tau}) \frac{\partial \bar{C}_{osc}^0(s=0, \hat{\tau})}{\partial s} \right\rangle_{\hat{\tau}} \right].$$

Figure 6 demonstrates that there is a critical exponent α_c for which interfacial resistance does not contribute to bubble growth rate, i.e. the bubble surface behaves like a clean surface. Interfacial resistance enhances bubble growth rates for $\alpha > \alpha_c$ and inhibits growth rates for $\alpha < \alpha_c$.

A comparison of the magnitude of the terms in $\bar{C}_{sm}(0)$ (4.8) reveals that the interfacial resistance term is the most significant one for bubble oscillations of practical interest. The fact that the first-order problem presents a significant correction to the zeroth-order problem does not suggest a breakdown of the perturbation scheme because the expansions remain well-ordered as $\mathcal{P} \rightarrow \infty$. Furthermore, in the second-order correction the resistance term, R_I , appears multiplied by \mathcal{P}^{-1} . Since $R_I \mathcal{P}^{-1/2}$ is of order one, then $R_I \mathcal{P}^{-1}$ is of order $\mathcal{P}^{-1/2}$ and presents a small correction to the

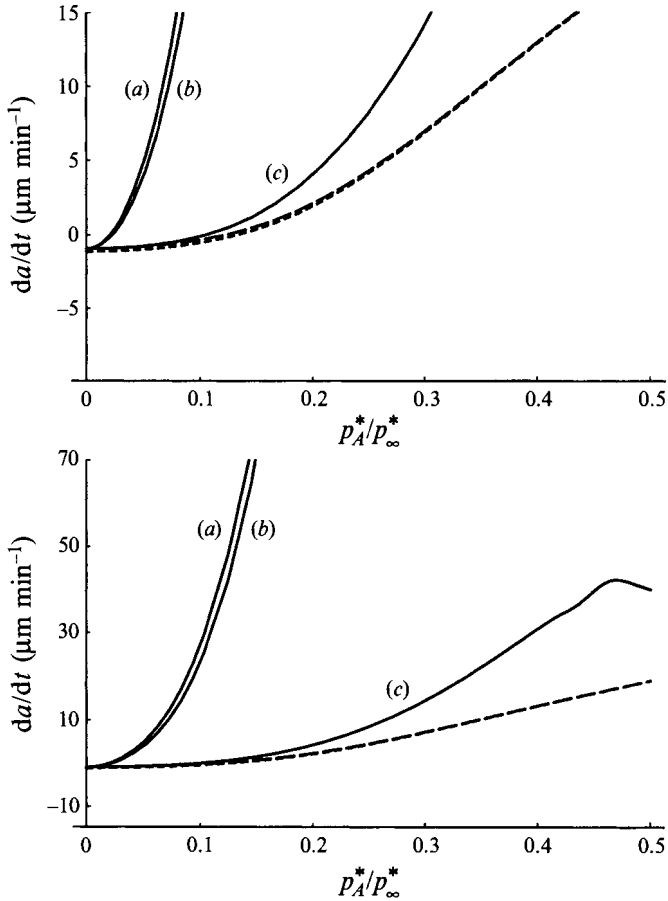


FIGURE 4. The rate of bubble growth in $\mu\text{m min}^{-1}$ versus dimensionless pressure amplitude p_A^*/p_∞^* . The data are the same as for figures 2 and 3 except the bubble is of equilibrium radius $60 \mu\text{m}$.

first-order term. In contrast the first-order correction to the clean surface problem involves the factor $\mathcal{P}^{-1/2}$ and is therefore very small.

8. Conclusions

We have developed a theory to explain the observed effects of surfactants on the problem of mass transport across the dynamic interface of a soluble spherical gas bubble undergoing volume oscillations in a liquid. The difference between the surfactant problem and the clean surface problem is that, in the former, the Henry's law boundary condition is no longer applicable. Surfactants present an interfacial barrier to mass transport, accounted for using a flux boundary condition featuring interfacial resistance.

The clean surface problem was treated to leading order in our earlier paper (FS) by splitting the problem into two parts: the oscillatory problem and the smooth problem. As in the case of the clean surface, the surfactant problem is split into the same two parts. The oscillatory problem is treated using the method of matched asymptotic expansions in a way such that the outer approximation to the oscillatory solution is identically zero. This serves to define the splitting in successive powers in $\mathcal{P}^{-1/2}$.

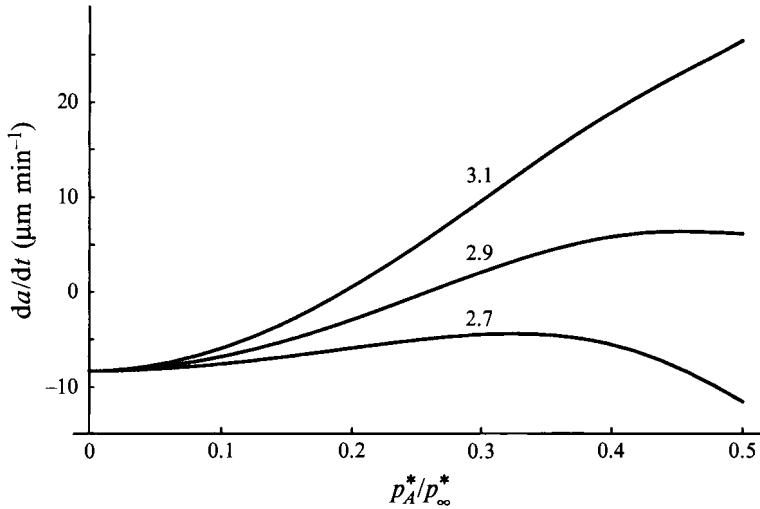


FIGURE 5. The rate of bubble growth in $\mu\text{m min}^{-1}$ versus dimensionless pressure amplitude p_A^*/p_∞^* . The curves correspond to (7.1) for the surfactant $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ for initial surface concentrations 2.7, 2.9 and 3.1×10^{-10} gmole cm^{-2} on a 20 μm bubble. The other data are the same as for figures 2-4.

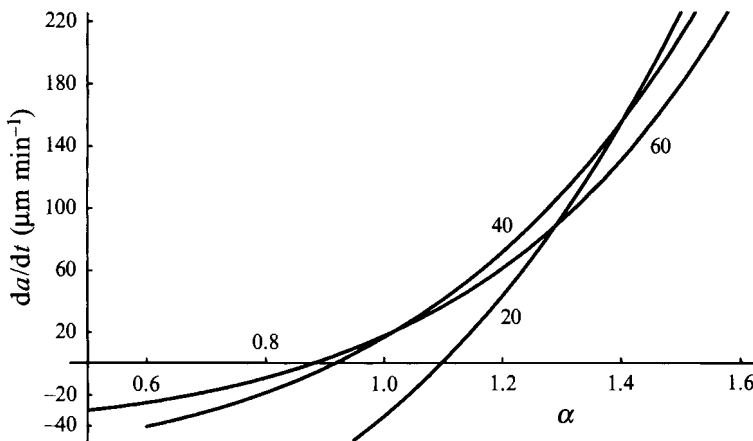


FIGURE 6. The rate of bubble growth in $\mu\text{m min}^{-1}$ versus the exponent α . The curves correspond to (7.1) but include only the effect of interfacial resistance (see text). The bubbles considered are of radius 20, 40 and 60 μm (as shown), forced at a dimensionless pressure amplitude of 0.5. The other data are the same as for figures 2-4.

The oscillatory solution is valid everywhere in the liquid but differs from zero only in a thin layer in the neighbourhood of the bubble surface. Furthermore it does not contribute to bubble growth or dissolution because it accounts for only a finite amount of mass transfer at initial times. The smooth solution is also valid everywhere in the liquid and evolves via convection-enhanced diffusion which is treated by the singular perturbation method of multiple scales.

To leading order, the clean surface solution is recovered. Continuing to higher order it is shown that the concentration field depends on $R_l \mathcal{P}^{-1/2}$, where R_l is the (dimensionless) interfacial resistance due to the presence of surfactants. Although the influence of surfactants appears at higher order in the small parameter, surfactants

are shown to have a large effect on bubble growth rates owing to the fact that the magnitude of R_I is approximately the same as the magnitude of $\mathcal{P}^{1/2}$ at conditions of practical interest. Hence the 'corrections' are numerically of the same magnitude as the leading-order, clean surface problem. This is in contrast to the case of a still, surfactant-covered bubble, in which corrections to the bubble growth rate due to surfactants are smaller by $\mathcal{P}^{-1/2}$.

Based on experimental data of Caskey & Barlage (1971), an exponential dependence between interfacial resistance and surfactant surface concentration was assumed. For the case of diffusion-controlled surfactant transport or insoluble surfactants, the resistance is of the form $R_I \propto \exp(\alpha/x^2(\tau))$ where α is a constant which depends on the surfactant and the initial concentration and $x(\tau)$ is the dimensionless bubble radius. It was observed that for a fixed bubble oscillation, there is a critical exponent (α_c), which determines the effect of the surfactant on the growth rate. If $\alpha > \alpha_c$ the bubble grows more quickly (or dissolves more slowly); if $\alpha < \alpha_c$ the bubble grows more slowly (or dissolves more quickly) as a consequence of the presence of surfactants.

For the case of an oscillating bubble the enhancement of bubble growth by rectified diffusion when surfactants are present is predicted to be at least as significant as was observed in the experiments of Crum (1980).

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Appendix. Splitting

In general the asymptotic solution to the oscillatory problem to any order $i = 1, 2, \dots$ (\bar{C}_{osc}^i) leads to the following partial differential equation:

$$\frac{\partial C_{osc}^i}{\partial \hat{\tau}} - \frac{\partial^2 C_{osc}^i}{\partial s^2} = F^i(x(\hat{\tau}), s, C_{osc}^0, \dots, C_{osc}^{i-1}) \quad (\text{A } 1)$$

with boundary condition

$$C_{osc}^i(s = 0, \hat{\tau}) = B^i(x(\hat{\tau}), C_{osc}^{i-1}(s = 0, \hat{\tau})),$$

where F^i is the inhomogeneous term associated with the i th-order oscillatory problem. In this Appendix, we shall determine restrictions on the boundary conditions necessary for the outer limit of the inner approximation of the oscillatory solution to be zero. In other words, we need to verify that the boundary layer solution of the oscillatory problem decays to zero as $s \rightarrow \infty$.

The asymptotic solution \bar{C}_{osc}^i can be represented as a Fourier series of the form

$$\bar{C}_{osc}^i(s, \hat{\tau}) = \sum_{m=-\infty}^{\infty} c_m(s) \exp[\omega_m i \hat{\tau}],$$

where

$$\omega_m = \frac{2m\pi}{\hat{\tau}(T)}.$$

Similarly F^i and B^i can be expanded in a Fourier series with Fourier coefficients f_m and b_m respectively. This can be shown inductively for all $i \geq 0$ beginning from $i = 0$ and (3.6).

Next we substitute these complex Fourier expansions into (A 1); this leads to the following system of ordinary differential equations for $m = -\infty$ to ∞ :

$$\frac{d^2 c_m(s)}{ds^2} - i\omega_m c_m(s) = -f_m(s) \tag{A 2}$$

with boundary condition

$$c_m(s = 0) = b_m. \tag{A 3}$$

The general solution of equation (A 2) which is zero as $s \rightarrow \infty$ is

$$c_m(s) = A_m \exp \left[-\left(\frac{\omega_m}{2}\right)^{1/2} s \right] \exp \left[-i \left(\frac{\omega_m}{2}\right)^{1/2} s \right] - \frac{1}{(1+i)(\omega_m/2)^{1/2}} \int_s^\infty f_m(s') \sinh \left[(1+i) \left(\frac{\omega_m}{2}\right)^{1/2} (s-s') \right] ds'. \tag{A 4}$$

Note that the exponential decay for large s of $f_m(s')$ ameliorates the exponential growth of the sinh in the integrand. Finally, we use the boundary condition at $s = 0$ (A 3) to obtain an expression for A_m :

$$A_m = b_m + \frac{1}{(1+i)(\omega_m/2)^{1/2}} \int_0^\infty f_m(s') \sinh \left[-(1+i) \left(\frac{\omega_m}{2}\right)^{1/2} s' \right] ds'. \tag{A 5}$$

Equations (A 4), (A 5) give the expression for the Fourier coefficients of the asymptotic oscillatory problem to any order.

The differential equation for $m = 0$, however, is somewhat different in view of $\omega_0 = 0$:

$$\frac{d^2 c_0(s)}{ds^2} = -f_0(s)$$

with boundary condition

$$c_0(s = 0) = b_0.$$

The solution that is zero as $s \rightarrow \infty$ is

$$c_0(s) = \int_s^\infty \int_\infty^{s'} f_0(s'') ds'' ds'.$$

If we try to implement the boundary condition at $s = 0$ we get

$$b_0 = \int_0^\infty \int_\infty^{s'} f_0(s'') ds'' ds'.$$

In other words the inhomogeneous term of the $m = 0$ equation restricts the boundary condition that can be satisfied in order to have a solution of the oscillatory problem which differs from zero only near the bubble. Recognizing that b_0 and f_0 are just the averages (with respect to $\hat{\tau}$) of the boundary condition and the inhomogeneous term, we have developed the following condition, which actually defines the splitting:

$$\langle C_{osc}^i(s = 0, \hat{\tau}) \rangle_{\hat{\tau}} = \int_0^\infty \int_\infty^{s'} \langle F^i(s'') \rangle_{\hat{\tau}} ds'' ds'. \tag{A 6}$$

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