

Surfactant dynamics and rectified diffusion of microbubbles

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Surfactant transport dynamics and the consequences for rectified diffusion of microbubbles are treated for bubbles undergoing arbitrarily large-amplitude periodic radial oscillations. A perturbation technique is used to reveal averaged equations for the slow convection-enhanced diffusive transport of surfactant molecules. These equations have a readily obtained asymptotic limit in the form of a single nonlinear integral equation – this may be interpreted as a dynamic equilibrium adsorption isotherm. For a lightly populated interface, an explicit solution for the surface excess population of surfactants may be obtained. Bubble oscillations are shown to drive an increased number of surfactant molecules to the interface, if it is lightly populated, but to reduce the maximum possible population of surfactants on the interface. These effects have important consequences for rectified diffusion, in which the interfacial resistance to gas transfer of a surfactant monolayer is a strong function of the surface excess population.

1. Introduction

A surfactant molecule consists of a hydrophobic and a hydrophilic portion; as a consequence surfactants accumulate preferentially at gas–liquid interfaces. This adsorption process introduces a discontinuity to the macroscopic concentration field, and the classical transport equation for the bulk concentration of surfactant needs to be supplemented by appropriate equations to quantify the surface excess. Namely, one requires an appropriate equation to characterize the ‘jump’ in the surfactant surface concentration, known as the surface excess balance equation, and a bulk interphase partition relation that describes the equilibrium between the bulk and surface excess; we refer the reader to Edwards, Brenner & Wasan (1991) for background.

In the case of a static interface the bulk problem can be eliminated by the use of Laplace transforms, and an integral equation for the time evolution of the surface excess can be obtained. This technique was used by several investigators and is outlined by Borwankar & Wasan (1983). A similar technique was used by Joos and Van Uffelen for the surfactant transport associated with surface dilation. The moving interface sets up convection currents that must be accounted for in the diffusion equation. Van Voorst Vader, Erkens & Van Den Tempel (1964) studied the case of an expanding interface, whereas Joos & Van Uffelen (1993) and Van Uffelen & Joos (1993) studied a contracting interface.

In the analysis of an oscillating bubble one must restrict attention to limiting cases owing to the unsteady, spatially inhomogeneous velocity field and the complicated boundary condition. The case of small oscillations was treated by Gottier, Amundson

& Flumerfelt (1986). Johnson & Stebe (1994) improved this analysis to obtain information about the sorption kinetics of surfactants and to measure surface tension and dilational viscosity using the phase lag and amplitude ratio between the gas pressure and bubble radius. Recently, numerical results were reported for small-amplitude axisymmetric bubble oscillations and large-amplitude spherical oscillations by Nadim (1996); however the quantitative results are restricted to specific numerical values of the relevant dimensionless parameters. Relevant to the present work, Nadim observed that the amount of surfactant on an oscillating bubble can be 30% higher than the initial equilibrium value.

Surfactants are known to inhibit gas transport through an interface (Barnes 1986), hence knowledge of the amount of surfactant on the surface is of primary importance when determining gas transport across an interface. For the case of gas transport across the interface of a soluble spherical oscillating bubble, the significance of surfactants on the phenomenon of rectified diffusion was demonstrated by both experiment (Crum 1980) and theory (Fyrillas & Szeri 1994, 1995). Qualitatively, experimental and theoretical results agree that bubble growth rates are enhanced dramatically by the presence of surfactants. However, direct comparison has not yet been possible, owing to the lack of the adsorption isotherm and interfacial resistance of the surfactant under consideration (Fyrillas 1995).

At a static interface at the boundary of a still liquid, it is well known that there is an equilibrium adsorption isotherm that relates the surface excess of surfactant to the bulk concentration of dissolved surfactant. In this paper, our primary goal is to develop a *dynamic* equilibrium adsorption isotherm for the surface excess of surfactant on a spherical bubble undergoing large-amplitude periodic volume oscillations. Using this relationship, we return to the problem of bubble growth by rectified diffusion treated in two recent papers (Fyrillas & Szeri 1994, 1995), and extend our previous theory. We determine growth rates of bubbles by rectified diffusion for fixed bulk concentration of surfactant assuming that the dynamic equilibrium adsorption isotherm developed herein holds.

2. Formulation

In this section we formulate the surfactant transport problem outside a spherical bubble undergoing radial oscillations (with radius $R(t)$). As described by Edwards *et al.* (1991) this requires a transport equation for the bulk

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

an evolution equation for the surface excess

$$\frac{d\rho^s(t)}{dt} + 2\frac{\dot{R}(t)}{R(t)}\rho^s(t) = \Phi(\rho^s(t), \rho(r = R(t), t)) \quad (2.2)$$

and a relation for non-equilibrium partitioning of a soluble surfactant between interface and bulk

$$D_s \frac{\partial \rho}{\partial r} (r = R(t), t) = \Phi(\rho^s(t), \rho(r = R(t), t)). \quad (2.3)$$

Thus, (2.3) is regarded as the boundary condition for the field equation (2.1); (2.2) is an auxiliary equation for the surface excess concentration of surfactant. Here Φ is

the kinetic rate expression

$$\Phi = k_i \exp \left[\frac{A}{2} \left(\frac{\rho^s}{\rho_\infty^s} \right)^2 \right] \left(\rho(r = R(t), t) (\rho_\infty^s - \rho^s) - \frac{\rho^s}{K_a} \exp \left[-A \frac{\rho^s}{\rho_\infty^s} \right] \right), \quad (2.4)$$

where k_i is the forward rate constant in the kinetic rate expression, K_a is the adsorption coefficient, D_s is the diffusivity of the surfactant in the liquid, ρ is the molar concentration of surfactant, ρ^s is the surface excess molar concentration of the surfactant and ρ_∞^s is the maximum realizable surface excess. The parameter A measures the degree of non-ideality of the interface: A is positive if there is an attractive interaction between the surfactant molecules and negative if there is a repulsive interaction.

To clarify the effect of A on the sorption process, we consider the adsorption and desorption terms separately in the kinetic rate expression (equation (2.4)) by multiplying through with the pre-factor $\exp[A/2 (\rho^s/\rho_\infty^s)^2]$. While adsorption is accelerated because the pre-factor is greater than one (for positive A), its combination with the exponential $\exp[-A (\rho^s/\rho_\infty^s)]$, in the desorption term, leads to a decrease in desorption. Hence the effect of (positive) A is to both increase adsorption and decrease desorption. The reverse is true when A is negative.

For initial and far-field conditions we shall assume that the bubble was created in a liquid with initial bulk surfactant concentration ρ_0 , i.e. we have

$$\rho(r \rightarrow \infty, t) = \rho(r, t = 0) = \rho_0$$

and

$$\rho^s(t = 0) = 0.$$

In these equations $R(t)$ may be obtained by integration of the equations of motion of the bubble. We return to this point in §4.

The problem may be non-dimensionalized with respect to the following natural scales. As a length scale we take a , the radius of the undisturbed bubble; the time scale is Ω_0^{-1} , which is the inverse of the natural frequency of radial oscillation of the bubble about the undisturbed state; the surface excess is non-dimensionalized using ρ_∞^s and the bulk concentration by ρ_∞^s/a . This leads to dimensionless parameters corresponding to (i) the Péclet number for the bulk surfactant transport problem

$$\mathcal{P}_s = \frac{a^2 \Omega_0}{D_s},$$

(ii) a parameter we identify as the affinity of surfactant for the interface versus solution in the bulk

$$A_f = \frac{\rho_\infty^s K_a}{a},$$

and (iii) a parameter related to the adsorption per cycle of bubble oscillation

$$k = \frac{k_i \rho_\infty^s}{\Omega_0 a}.$$

Based on the literature (Joos & Van Uffelen 1993; Borwankar & Wasan 1983), typical values for the constants k_i , K_a , ρ_∞^s and D_s are $10^7 \text{ cm}^3 \text{ gmol}^{-1} \text{ s}^{-1}$, $10^7 \text{ cm}^3 \text{ gmol}^{-1}$, $10^{-10} \text{ gmol cm}^{-2}$ and $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ respectively, which lead to the following values for the dimensionless parameters: $\mathcal{P}_s = 10^6$, $A_f = 1$ and $k = 10^{-7}$. In the case of diffusion-controlled adsorption the value of k_i , hence k , is assumed to be infinity (Borwankar & Wasan 1983).

We shall also define a new dimensionless surfactant bulk concentration

$$\Psi = \frac{a}{\rho_\infty^s}(\rho - \rho_0)$$

and surface excess

$$\Psi^s = \frac{\rho^s}{\rho_\infty^s}.$$

Finally, we point out a combination of parameters that will emerge later in our analysis:

$$A_f \Psi_0 = K_a \rho_0,$$

where $\Psi_0 = a\rho_0/\rho_\infty^s$ is the dimensionless surfactant bulk concentration everywhere initially and in the far field at all times.

Following the analysis of Plesset & Zwick (1952), we recast the problem in the dimensionless Lagrangian coordinate

$$\sigma \equiv \frac{1}{3a^3} (r^3 - R^3(t))$$

and in the nonlinear time

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

where τ is the dimensionless time defined as $\tau \equiv t\Omega_0$, and $x = R/a$ is the dimensionless bubble radius. The evolution equations (2.1) and (2.2) take the forms

$$\frac{\partial \Psi}{\partial \hat{\tau}} = \frac{1}{\mathcal{P}_s} \frac{\partial}{\partial \sigma} \left(\left(\frac{3\sigma}{x^3(\hat{\tau})} + 1 \right)^{4/3} \frac{\partial \Psi}{\partial \sigma} \right) \quad (2.5)$$

and

$$\frac{d(x^2(\hat{\tau})\Psi^s(\hat{\tau}))}{d\hat{\tau}} = \frac{1}{x^2(\hat{\tau})} \Phi(\Psi^s(\hat{\tau}), \Psi(\sigma = 0, \hat{\tau})) \quad (2.6)$$

respectively, with boundary and initial conditions for the field equation

$$\frac{x^2(\hat{\tau})}{\mathcal{P}_s} \frac{\partial \Psi(\sigma = 0, \hat{\tau})}{\partial \sigma} = \Phi, \quad (2.7)$$

$$\Psi(\sigma, \hat{\tau} = 0) = \Psi(\sigma \rightarrow \infty, \hat{\tau}) = \Psi^s(\hat{\tau} = 0) = 0.$$

Here Φ is the dimensionless kinetic expression (2.4):

$$\Phi = k \exp \left[\frac{A}{2} (\Psi^s)^2 \right] \left((1 - \Psi^s)(\Psi(\sigma = 0, \tau) + \Psi_0) - \frac{\Psi^s}{A_f} \exp[-A\Psi^s] \right).$$

The task, then, is to determine the surface excess of surfactant and the bulk concentration of dissolved surfactants as functions of time, and time and space, respectively. This requires solution of (2.5)–(2.7). In cases of practical interest, the bubble is small (which implies that Ω_0 is large) and the diffusivity of the surfactant in the liquid is small. Hence the important problems are characterized by large \mathcal{P}_s . Physically, this means that the rate at which surfactant molecules populate the interface is limited by their slow transport via convection-enhanced diffusion through the liquid to the interface. By comparison, adsorption is rapid. This limiting case is known as the diffusion-controlled limit.

It is natural, therefore, to investigate the limit $\mathcal{P}_s \rightarrow \infty$. Clearly (2.7) implies that

$\Phi = 0$. This information and (2.6) suggest that $(d/d\hat{t})(x^2(\hat{t})\Psi^s(\hat{t})) = 0$. However (2.5) implies $(d/d\hat{t})(\Psi) = 0$. These limiting equations are inconsistent, as they yield a solution for Ψ and Ψ^s that cannot possibly satisfy $\Phi = 0$.

The resolution of this paradox is the realization that the limit $\mathcal{P}_s \rightarrow \infty$ is singular for the field equation (2.5). Hence we must treat the problem at large but finite \mathcal{P}_s using singular perturbation theory. Physically, this means that no matter how large the Péclet number is, there will be diffusive transport. The diffusive transport is critical to obtaining the solution of the transport problem for nearly insoluble surfactants. Before beginning the analysis, it is worthwhile to point out that by ‘nearly insoluble’ we mean here and throughout the paper a surfactant for which desorption and diffusion over the length scale of the bubble occurs slowly relative to the time scale for bubble oscillations.

3. Analysis

As we have remarked, the surfactant transport problem is characterized by a large Péclet number. Similar problems were treated by Fyrrillas & Szeri (1994, 1995, hereinafter referred to as FSI and FSII, respectively) for the gas transport across the dynamic interface of an oscillating bubble.

In the gas transport problem, we carefully refrain from any specification of the nature of the bubble oscillation that drives the transport problem, other than to require that it be periodic. What emerges from the perturbation approach is essentially an understanding of how to average the equations and boundary condition over a period of the bubble oscillation so as to obtain equations of reduced complexity for the slow growth or dissolution of the bubble on a diffusive time scale.

In the present work, we shall follow this same general scheme, although the non-linear boundary condition and surface excess evolution equation present significant challenges. The goal of the analysis, therefore, is to develop an understanding of how to average the equations over a period of the bubble oscillation to obtain simplified equations for the slow diffusive transport of surfactants.

The plan of the analysis is as follows. The bulk problem (2.5) is treated by splitting into an oscillatory and a smooth problem and expanding each in powers of the small parameter $\mathcal{P}_s^{-1/2}$. By treating the surface excess concentration (Ψ_s) as an arbitrary but known function of time we obtain expressions for the bulk concentration on the interface $\Psi(\sigma = 0, \hat{t})$ to each order in $\mathcal{P}_s^{-1/2}$. The surface excess evolution equation (2.6) can then be expanded in a perturbation series for large $\mathcal{P}_s^{1/2}$ and solved using the method of multiple scales.

The bulk problem (2.5) can be brought to a form similar to the problem solved in FSII, by rearranging the boundary condition (2.7) into the following form:

$$\frac{G(\hat{t})}{\mathcal{P}_s} \frac{\partial \Psi(\sigma = 0, \hat{t})}{\partial \sigma} = \Psi(\sigma = 0, \hat{t}) - \Psi_e(\hat{t}) + (\Psi_{sp}^0 - \Psi_{sp}^0) + \frac{1}{\mathcal{P}_s^{1/2}}(\Psi_{sp}^1 - \Psi_{sp}^1) + \frac{1}{\mathcal{P}_s}(\Psi_{sp}^2 - \Psi_{sp}^2) + \frac{1}{\mathcal{P}_s^{3/2}}(\Psi_{sp}^3 - \Psi_{sp}^3),$$

where

$$G(\hat{t}) \equiv \hat{G}(x(\hat{t}), N(\hat{t})) = \frac{x^4 \exp[-AN^2/x^4]}{k(x^2 - N)}$$

and

$$\Psi_e(\hat{\tau}) \equiv \hat{\Psi}_e(x(\hat{\tau}), N(\hat{\tau})) = \frac{N \exp[-AN/x^2]}{A_f(x^2 - N)} - \Psi_0.$$

Note that we have added and subtracted a number of splitting constants Ψ_{sp}^i for later use. In these equations the surface excess concentration, $\Psi^s(\hat{\tau})$, is related to a new dimensionless dependent variable $N(\hat{\tau})$,

$$N(\hat{\tau}) = x^2(\hat{\tau})\Psi^s(\hat{\tau}) = \frac{4\pi a^2 x^2(\hat{\tau})\rho^s(\hat{\tau})}{4\pi a^2 \rho_\infty^s},$$

which is proportional to the (excess) number of surfactant molecules assigned to the interface; the constant of proportionality is the number of surfactant molecules assigned to the saturated interface of a still bubble of equilibrium radius.

Because the diffusion is limiting in this surfactant transport problem, the number of molecules assigned to the surface is very nearly constant over a period of the bubble oscillation. Hence, it will simplify matters considerably to work in terms of N for the surface excess rather than Ψ^s . The point is that N is nearly constant, whereas Ψ^s varies greatly over a period when the bubble oscillations are strongly nonlinear. We shall refer to N as the surface excess population to distinguish it from Ψ^s which has the interpretation of concentration.

3.1. The oscillatory problem in the bulk

As mentioned in FSI solution of the oscillatory problem is (by design) non-zero only in a boundary layer near the bubble and is characterized by the stretched spatial coordinate $s = \mathcal{P}_s^{1/2}\sigma$. The oscillatory problem is

$$\frac{\partial \Psi_{osc}}{\partial \hat{\tau}} = \frac{\partial}{\partial s} \left(\left(\frac{3s}{x^3(\hat{\tau})\mathcal{P}_s^{1/2}} + 1 \right)^{4/3} \frac{\partial \Psi_{osc}}{\partial s} \right),$$

with the boundary condition

$$\begin{aligned} & \frac{G(\hat{\tau})}{\mathcal{P}_s^{1/2}} \frac{\partial \Psi_{osc}(s=0, \hat{\tau})}{\partial s} \\ &= \Psi_{osc}(s=0, \hat{\tau}) - \Psi_e(\hat{\tau}) + \Psi_{sp}^0 + \frac{1}{\mathcal{P}_s^{1/2}} \Psi_{sp}^1 + \frac{1}{\mathcal{P}_s} \Psi_{sp}^2 + \frac{1}{\mathcal{P}_s^{3/2}} \Psi_{sp}^3. \end{aligned} \quad (3.1)$$

Next we expand Ψ_{osc} and N in successive powers in $\mathcal{P}_s^{-1/2}$. Consequently $\Psi_e(\hat{\tau})$ and $G(\hat{\tau})$ can be expanded in successive powers in $\mathcal{P}_s^{-1/2}$ provided the surface excess is sufficiently away from saturation (as discussed in the Appendix). The expansions for N , G and Ψ_e are worked out in the Appendix.

To zeroth order we obtain

$$\frac{\partial \Psi_{osc}^0}{\partial \hat{\tau}} = \frac{\partial^2 \Psi_{osc}^0}{\partial s^2}, \quad (3.2)$$

with the boundary condition

$$\Psi_{osc}^0(s=0, \hat{\tau}) = \Psi_e^0(\hat{\tau}) - \Psi_{sp}^0.$$

The condition that defines the splitting to zeroth order is that the average of the

boundary condition with respect to the time $\hat{\tau}$, defined as

$$\langle f(\sigma, \tau) \rangle_{\hat{\tau}} \equiv \frac{1}{\hat{\tau}(T)} \int_0^{\hat{\tau}(T)} f(\sigma, \hat{\tau}) d\hat{\tau} = \frac{1}{\int_0^T x^4(\tau) d\tau} \int_0^T f(\sigma, \tau) x^4(\tau) d\tau, \quad (3.3)$$

should be zero. Here T is the dimensionless bubble period. This condition ensures that the oscillatory problem at this order is non-zero only in a thin layer near the bubble surface. Stated differently, the splitting ensures that the boundary-layer solution of the oscillatory problem should match zero (FSII), which is the solution of the oscillatory problem outside the boundary layer. Hence the splitting constant is given by

$$\Psi_{sp}^0 = \langle \Psi_e^0(\hat{\tau}) \rangle_{\hat{\tau}},$$

where

$$\Psi_e^0(\hat{\tau}) = \frac{N^0 \exp[-AN^0/x^2(\hat{\tau})]}{A_f(x^2(\hat{\tau}) - N^0)} - \Psi_0. \quad (3.4)$$

Higher-order terms in the expansion satisfy the forced heat equation (equation (3.2)), while the lower-order terms in the expansion appear in the forcing and in the boundary conditions. To first and second order the boundary conditions are

$$\begin{aligned} \Psi_{osc}^1(s=0, \hat{\tau}) &= \Psi_e^1(\hat{\tau}) + G^0(\hat{\tau}) \frac{\partial \Psi_{osc}^0(s=0, \hat{\tau})}{\partial s} - \Psi_{sp}^1, \\ \Psi_{osc}^2(s=0, \hat{\tau}) &= \Psi_e^2(\hat{\tau}) + G^0(\hat{\tau}) \frac{\partial \Psi_{osc}^1(s=0, \hat{\tau})}{\partial s} + G^1(\hat{\tau}) \frac{\partial \Psi_{osc}^0(s=0, \hat{\tau})}{\partial s} - \Psi_{sp}^2. \end{aligned}$$

3.2. The smooth problem in the bulk

The smooth problem is characterized by slow convection-enhanced diffusion on the diffusive time scale. Therefore we introduce a second time scale $\lambda \equiv \hat{\tau}/\mathcal{P}_s$, which captures the slow diffusive behaviour explicitly.

The smooth problem is

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

with the boundary condition

$$\frac{G(\hat{\tau})}{\mathcal{P}_s} \frac{\partial \Psi_{sm}(\sigma=0, \hat{\tau}, \lambda)}{\partial \sigma} = \Psi_{sm}(\sigma=0, \hat{\tau}, \lambda) - \Psi_{sp}^0 - \frac{1}{\mathcal{P}_s^{1/2}} \Psi_{sp}^1 - \frac{1}{\mathcal{P}_s} \Psi_{sp}^2 - \frac{1}{\mathcal{P}_s^{3/2}} \Psi_{sp}^3. \quad (3.5)$$

As with the oscillatory problem we expand the smooth problem and its boundary condition in successive powers of $\mathcal{P}_s^{-1/2}$. To zeroth and first order the smooth problem admits a solution independent of $\hat{\tau}$. By eliminating secular behaviour in the second and third problems (as outlined in FSII) we get an additional equation for Ψ_{sm}^0 and Ψ_{sm}^1 :

$$\frac{\partial \Psi_{sm}^i}{\partial \lambda} = \frac{\partial}{\partial \sigma} \left(\left\langle \left(\frac{3\sigma}{x^3(\hat{\tau})} + 1 \right)^{4/3} \right\rangle_{\hat{\tau}} \frac{\partial \Psi_{sm}^i}{\partial \sigma} \right), \quad (3.6)$$

where $i = 0, 1$. The boundary condition at each order is

$$\begin{aligned}\Psi_{sm}^0(\sigma = 0, \lambda) &= \Psi_{sp}^0, \\ \Psi_{sm}^1(\sigma = 0, \lambda) &= \Psi_{sp}^1, \\ \Psi_{sm}^2(\sigma = 0, \hat{\tau}, \lambda) &= G^0(\hat{\tau}) \frac{\partial \Psi_{sm}^0(\sigma = 0, \hat{\tau}, \lambda)}{\partial \sigma} + \Psi_{sp}^2.\end{aligned}$$

3.3. Slow evolution of the surface excess

From equations (3.2), (3.6) and their associated boundary conditions, we can, in principle, obtain an expression for the bulk concentration on the surface ($\Psi(\sigma = 0, \hat{\tau}, \lambda)$). Now we turn to the surface excess problem. The differential equation governing the surface excess population is

$$\frac{dN}{d\hat{\tau}} = \frac{1}{G(\tau)} [\Psi(\sigma = 0, \hat{\tau}, \lambda) - \Psi_e(\tau)].$$

We substitute the formal expression for the bulk concentration on the bubble interface (obtained by summing the surface concentration of the smooth and oscillatory problems) derived in the previous sections, and use the expansions for G and Ψ_e (see Appendix) to obtain

$$\begin{aligned}\frac{dN}{d\hat{\tau}} &= \frac{1}{\mathcal{P}_s^{1/2}} \frac{\partial \Psi_{osc}^0(s = 0, N^0(\tau), \hat{\tau})}{\partial s} \\ &+ \frac{1}{\mathcal{P}_s} \left(\frac{\partial \Psi_{sm}^0(\sigma = 0, N^0(\tau), \lambda)}{\partial \sigma} + \frac{\partial \Psi_{osc}^1(s = 0, N^0(\hat{\tau}), N^1(\hat{\tau}), \hat{\tau})}{\partial s} \right).\end{aligned}$$

The problem is treated by the method of multiple scales by introducing, as in the previous section, the slow time scale $\lambda \equiv \hat{\tau}/\mathcal{P}_s$ to capture the slow diffusion-controlled adsorption. Next we expand N in powers of $\mathcal{P}_s^{-1/2}$:

$$N(\lambda, \hat{\tau}) = N^0(\lambda, \hat{\tau}) + \frac{1}{\mathcal{P}_s^{1/2}} N^1(\lambda, \hat{\tau}) + \frac{1}{\mathcal{P}_s} N^2(\lambda, \hat{\tau}) + \frac{1}{\mathcal{P}_s^{3/2}} N^3(\lambda, \hat{\tau}) + \dots$$

To zeroth order we have

$$\frac{\partial N^0(\lambda, \hat{\tau})}{\partial \hat{\tau}} = 0,$$

which admits a solution independent of $\hat{\tau}$, i.e. $N^0(\lambda, \hat{\tau}) = N^0(\lambda)$. However N^0 is further determined by eliminating secular behaviour in N^2 . The differential equation for N^2 is

$$\frac{\partial N^2}{\partial \hat{\tau}} = -\frac{dN^0}{d\lambda} + \frac{\partial \Psi_{osc}^1(s = 0, N^0(\lambda), N^1(\lambda, \hat{\tau}), \hat{\tau}, \lambda)}{\partial s} + \frac{\partial \Psi_{sm}^0(\sigma = 0, N^0(\lambda), \lambda)}{\partial \sigma}.$$

To eliminate secular behaviour we force N^2 to have zero $\hat{\tau}$ -average. Here we should point out that Ψ_{osc}^0 and Ψ_{osc}^1 depend indirectly on the long time λ through their respective boundary conditions, which depend on $N^0(\lambda)$. Furthermore the oscillatory problem reaches its asymptotic limit after a few bubble oscillations (see FSII) and does not contribute to any secular behaviour because by design it is periodic with respect to $\hat{\tau}$ with zero mean. These considerations lead to the following equation for N^0 :

$$\frac{dN^0}{d\lambda} = \frac{\partial \Psi_{sm}^0(\sigma = 0, N^0(\lambda), \lambda)}{\partial \sigma}, \quad (3.7)$$

where we have explicitly noted the dependence of Ψ_{sm}^0 on N^0 , with initial condition

$$N^0(\lambda = 0) = 0.$$

Of course, this equation is coupled to the smooth problem in the bulk (3.6),

$$\frac{\partial \Psi_{sm}^0}{\partial \lambda} = \frac{\partial}{\partial \sigma} \left(\left\langle \left(\frac{3\sigma}{x^3(\hat{\tau})} + 1 \right)^{4/3} \right\rangle_{\hat{\tau}} \frac{\partial \Psi_{sm}^0}{\partial \sigma} \right), \tag{3.8}$$

with boundary conditions

$$\Psi_{sm}^0(\sigma = 0, \lambda) = \langle \Psi_e^0(\hat{\tau}) \rangle_{\hat{\tau}} = \left\langle \frac{N^0}{A_f (x^2(\hat{\tau}) - N^0)} \exp \left[-\frac{AN^0}{x^2(\hat{\tau})} \right] \right\rangle_{\hat{\tau}} - \Psi_0, \tag{3.9}$$

$$\Psi_{sm}^0(\sigma \rightarrow \infty, \lambda) = 0,$$

and initial condition

$$\Psi_{sm}^0(\sigma, \lambda = 0) = 0.$$

In a sense, the goal of our analysis has been achieved. We have developed a self-consistent scheme for averaging the transport problem over the short time of a bubble oscillation, in order to develop simpler equations that yield the behaviour over the long, diffusive time scale. One might question, however, whether equations (3.7)–(3.9) are simpler than the original transport problem. In defense of this point we offer the observation that \mathcal{P}_s has disappeared from the system!

We shall not end here, however, as there is an easily obtained asymptotic solution that we believe will prove of practical utility. At the asymptotic steady state (indicated by an overbar) we do not expect any λ dependence, i.e. $\partial \bar{\Psi}_{sm}^0 / \partial \lambda = d\bar{N}^0 / d\lambda = 0$. This leads directly to the solutions to $\bar{\Psi}_{sm}^0 \equiv 0$, and \bar{N}^0 is a constant. The constant \bar{N}^0 satisfies the following nonlinear integral equation:

$$A_f \langle \Psi_e^0(\hat{\tau}) \rangle_{\hat{\tau}} = \left\langle \frac{\bar{N}^0}{(x^2(\hat{\tau}) - \bar{N}^0)} \exp \left[-\frac{A\bar{N}^0}{x^2(\hat{\tau})} \right] \right\rangle_{\hat{\tau}} - A_f \Psi_0 = 0. \tag{3.10}$$

Hence, the asymptotic limit of the surfactant transport problem is such that the smooth problem is identically zero. This deduction is justified because the smooth problem is the one responsible for any surfactant flux to the bubble interface. Asymptotically in time the excess amount of surfactant adjusts itself in such a way that there is no adsorption or desorption between the interface and the bulk. This is a condition analogous to the threshold condition of rectified diffusion; see Eller & Flynn (1965) and FSI. The condition (3.10) may be regarded as a dynamic equilibrium adsorption isotherm in much the same way as $\Phi = 0$ for a still bubble yields a static equilibrium adsorption isotherm. In both cases, the surface excess of surfactant is related to the far-field bulk concentration of dissolved surfactant, in a way that depends on the affinity of the surfactant for the interface relative to the bulk (A_f) and on the non-ideality parameter (A). However, the dynamic equilibrium adsorption isotherm also involves the periodic bubble oscillation and the average with respect to the nonlinear time $\hat{\tau}$.

If \bar{N}^0 is small because ρ_0 is small or the surfactant has only a weak affinity for the interface, the nonlinear integral equation (3.10) can be solved explicitly for small

values of $A_f \Psi_0$ to give

$$\bar{N}_l^0 = (A_f \Psi_0) \frac{\langle x^4(\tau) \rangle_\tau}{\langle x^2(\tau) \rangle_\tau} + (A_f \Psi_0)^2 (A - 1) \frac{\langle x^4(\tau) \rangle_\tau^2}{\langle x^2(\tau) \rangle_\tau^3} + O((A_f \Psi_0)^3), \quad (3.11)$$

where we have used (3.3) to express the averages in the original dimensionless time τ . Here $\langle \rangle_\tau$ is defined as the average over one bubble oscillation with respect to time τ .

Because the solution of the smooth problem is zero asymptotically in time, the bulk concentration is given by the oscillatory problem. Hence the bulk concentration on the interface is equal to $\bar{\Psi}_e^0$ (equation (3.4)) asymptotically in time:

$$\Psi^0(s = 0, \hat{\tau}) = \frac{N^0 \exp[-AN^0/x^2(\hat{\tau})]}{A_f (x^2(\hat{\tau}) - N^0)}. \quad (3.12)$$

Note that the splitting constant has vanished as a consequence of (3.10). Because (3.12) is periodic, one may readily obtain the asymptotic solution to the oscillatory concentration field to leading order by a Fourier series approach similar to that employed in FSI and FSII.

4. Results and discussion

In our analysis, we have obtained: (i) simplified equations for surfactant transport on the slow diffusive time scale, (ii) a straightforward asymptotic result that reduces to a single nonlinear integral equation that may be regarded as a dynamic equilibrium adsorption isotherm, and (iii) an explicit solution of the asymptotic surface excess population in the case where the far-field bulk concentration is small or the surfactant has only a weak affinity for the interface. In what follows, we shall explore the consequences of the dynamic equilibrium adsorption isotherm that we have developed. First, we examine surface excess populations on dynamic, compared to still bubbles. Next, we consider briefly the equation of state and the surface tension. Finally, we redress our previous calculations of bubble growth rates via rectified diffusion in the presence of insoluble surfactants (FSII), in the light of our new understanding of surfactant transport.

4.1. A still versus an oscillating bubble: equilibrium adsorption isotherms

As mentioned earlier, in the case of a still bubble one can obtain an integral equation for the evolution of $\Psi^s(\tau)$, as a simplification of an initial value problem. The asymptotic limit to this initial value problem, however, can be easily obtained by setting all time derivatives equal to zero in equations (2.5) and (2.6) and solving the resulting problem. One readily obtains a nonlinear algebraic equation for Ψ^s :

$$\frac{\Psi^s}{1 - \Psi^s} \exp[-A\Psi^s] = A_f \Psi_0. \quad (4.1)$$

This is the (static) equilibrium adsorption isotherm. For an ideal interface, *i.e.* $A=0$, we can solve explicitly for Ψ^s to obtain

$$\Psi^s = \frac{A_f \Psi_0}{1 + A_f \Psi_0}.$$

It is important to note that these results for the surface excess are the same in the case of a bubble or of a plane interface. The transient analysis for a plane interface was presented by Borwankar & Wasan (1983). The asymptotic limit as presented in their figures 3 and 4 agrees with the solution of (4.1).

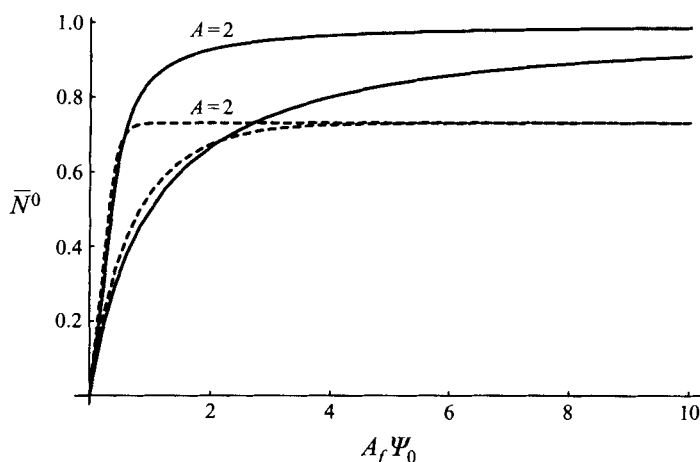


FIGURE 1. The dimensionless surface excess population of surfactant versus dimensionless far-field concentration for a bubble of radius $20\mu\text{m}$. The solid curves correspond to a still bubble and the dashed curves to an oscillating bubble forced by a pressure amplitude of 0.5 bar and frequency 26.6 KHz. The diffusivity of the gas in the liquid is $2.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and the interfacial tension is 73 dyn cm^{-1} .

Here we should point out that in the case of an oscillating bubble the asymptotic limit for the surface excess satisfies the equilibrium adsorption isotherm (4.1) in the average sense, as equation (3.10) may be recast in the more suggestive form

$$\left\langle \frac{\bar{\Psi}^s(\hat{\tau})}{1 - \bar{\Psi}^s(\hat{\tau})} \exp[-A\bar{\Psi}^s(\hat{\tau})] \right\rangle_{\hat{\tau}} = A_f \Psi_0.$$

Hence the nonlinear algebraic equation (4.1) becomes a nonlinear integral equation in the case of a periodic bubble oscillation. What is not intuitive about this very simple result is that the average should be taken with respect to the nonlinear time $\hat{\tau}$, rather than with respect to 'real' time τ .

To evaluate the expression for \bar{N}^0 , (3.10), we require a model for the bubble oscillation. We shall use the non-polytropic four-term Galerkin formulation of Kamath & Prosperetti (1989) (see FSI). This model allows for a spatially non-uniform temperature field inside the bubble and is more accurate near resonances than polytropic models. It consists of eight nonlinear ODEs which are integrated numerically using the software AUTO94 (see Doedel, Wang & Fairgrieve 1994).

The bubble model consists of an air bubble created in water and set into oscillation by a sinusoidal sound field. In figure 1 we show for comparison the asymptotic surface excess population of surfactant (\bar{N}^0) versus the dimensionless quantity $A_f \Psi_0$ for a still (solid curves) and an oscillating (dashed curves) bubble, and for an ideal ($A = 0$) and a non-ideal ($A = 2$) interface. For this calculation and in what follows, the bubble is of radius $20 \mu\text{m}$, the amplitude of the sound field is 0.5 bar, the driving frequency is 26.6 KHz and the interfacial tension is 73 dyn cm^{-1} . Other parameters are the same as in FSII. In this calculation we assumed that surfactants do not alter bubble dynamics through surface tension; we return to this point shortly.

If one examines figure 1 carefully it is clear that oscillations favour the presence of surfactants at small populations. Equation (3.11) reveals that the ratio between the fourth and second moments of the bubble oscillation is the controlling parameter to first order. If this ratio is greater than one the interface of an oscillating bubble would have a greater amount of surfactant than a still bubble, assuming both are immersed

in a liquid with the same far-field bulk concentration of dissolved surfactant. Because this ratio is greater than one for oscillations that linger at large x , the dashed curve always lies above the (companion) solid curve in figure 1. A second parameter that favours the presence of surfactants on the interface is positive values of the interaction parameter A , which measures the attraction between surfactant molecules (Borwankar & Wasan 1983).

The most important result is that while oscillations make the surface more 'attractive' to surfactant molecules at first, oscillations decrease the saturation limit of the interface. Analysis of equation (3.10) reveals that the dynamic saturation limit is controlled by the minimum bubble radius. The maximum amount of surfactant that can reside on the interface is that amount which renders the interface saturated at the minimum radius (x_{min}). Hence at saturation, \bar{N}^0 is equal to the square of the minimum bubble radius ($\bar{N}^0 = x_{min}^2$). The physical explanation is that any amount of surfactant that would yield a supersaturated interface has no time to diffuse to the bubble surface because desorption is instantaneous at such a condition while diffusion is rate-limited. One should be careful though, because, firstly, the present analysis is valid provided $x_{min}^2 - \bar{N}^0 \gg \mathcal{P}_s^{-1/2}$ as mentioned in the Appendix and, secondly, the validity of the kinetic rate expression is questionable very close to saturation owing to possible crystallization or collapse of the interface (Van Uffelen & Joos 1993).

4.2. Equation of state

Because, asymptotically in time, the interface complies with the Frumkin isotherm (equation (3.12)), the surface equation of state is (Edwards *et al.* 1991)

$$\pi \equiv \gamma_0 - \gamma \equiv -\frac{R_G T}{M} \rho_\infty^s \left(\ln \left[1 - \frac{\bar{N}^0}{x^2(\tau)} \right] + \frac{A}{2} \left(\frac{\bar{N}^0}{x^2(\tau)} \right)^2 \right), \quad (4.2)$$

where R_G is the universal gas constant, T is the temperature, π is the surface pressure and γ is the surface tension (where the subscript 0 corresponds to the surface tension of a clean interface). This equation is valid provided the solution is dilute enough that the behaviour is ideal and the mass concentration is proportional to the mole fraction (Gaines 1966).

We have used (4.2) as a modification of the interfacial surface tension due to the presence of surfactants in the liquid in order to compare dynamics of a clean bubble, i.e. $\bar{N}^0 = 0$, with a surfactant-covered bubble. No significant changes were observed in the bubble oscillation even for values of \bar{N}^0 very close to saturation. A comparison of the gas pressure term, $p_{Gi}(a/R(t))^{3n}$, and the surface tension term, $2\gamma/R(t)$, in the dynamical equation for bubble oscillations (e.g. the Rayleigh-Plesset equation), reveals that the former is two orders of magnitude larger than the latter for oscillations away from resonance (Prosperetti 1995, personal communication).

4.3. Bubble growth rates

Asymptotically in time, the present analysis of nearly insoluble surfactants suggests that they behave as though insoluble, although the number of surfactant molecules on the interface depends on the bubble oscillation. Hence the theory developed in FSII for bubble growth rates is not restricted to insoluble surfactants but applies also to the case of soluble surfactants at large \mathcal{P}_s . The difference is that for soluble surfactants the surface excess concentration is given by the following expression:

$$\bar{\rho}^s = \frac{\bar{N}^0 \rho_\infty^s}{x^2(\tau)},$$

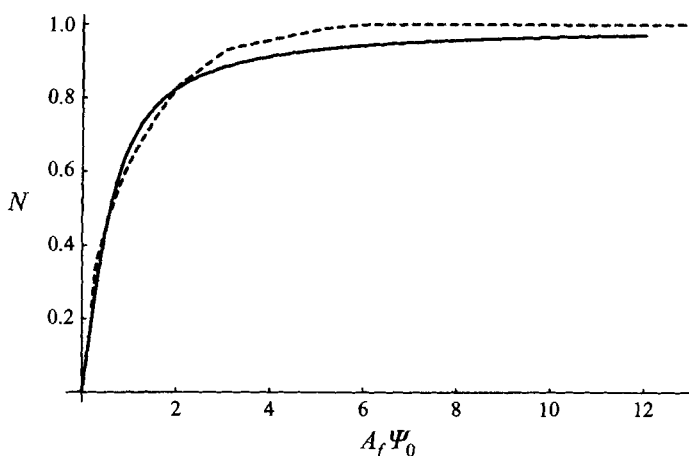


FIGURE 2. The adsorption isotherm for the surfactant dodecyl sodium sulphate ($C_{12}H_{25}SO_4Na$). The solid curve corresponds to Frumkin isotherm $\Psi^s / (1 - \Psi^s) \exp(-A \Psi^s) = A_f \Psi_0$, and the dashed curve to the experimental data of Caskey & Barlage (1971).

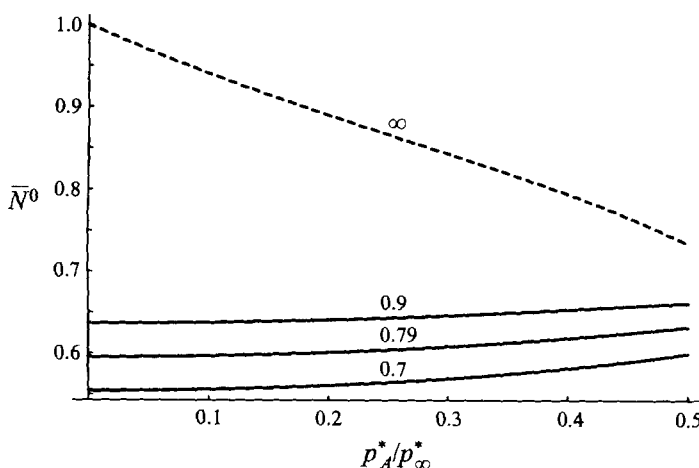


FIGURE 3. The dimensionless surface excess population of surfactant on an oscillating bubble versus the dimensionless pressure amplitude that forces the bubble dynamics. The solid curves correspond to dimensionless far-field concentrations ($A_f \Psi_0$) of 0.7, 0.79 and 0.9 (as shown) and the dashed curve to saturation conditions. The bubble is of equilibrium radius $20 \mu m$ as in figure 1.

and depends on a number of parameters (A, A_f, Ψ_0) and the bubble oscillation $x(\tau)$ as mentioned in §3.3. For truly insoluble surfactants the surface excess concentration depends only on the initial concentration.

Using experimental data from figures 4 and 5 of Caskey & Barlage (1971), we were able to obtain information on the static equilibrium adsorption isotherm for the three surfactants used in FSII, and to extend to the dynamic equilibrium adsorption isotherm (3.10). We concentrate on the surfactant dodecyl sodium sulphate ($C_{12}H_{25}SO_4Na$) because it best evinces the effect of solubility. As shown in figure 2, the Frumkin adsorption isotherm is an adequate characterization of the surfactant, with the following values for the constants: the adsorption coefficient $K_a = 1.49 \cdot 10^7 \text{ cm}^3 \text{ gmoles}^{-1}$, the surface excess saturation density $\rho_\infty^s = 4.87 \cdot 10^{-10} \text{ gmoles cm}^{-2}$,

and the non-ideality parameter $A = 1.05$. These parameters were obtained by curve-fitting.

In figure 3, we show the effect of bubble oscillations on the surface excess population, for a bubble of radius $20\ \mu\text{m}$. The conditions are the same as in figure 1. The solid curves correspond to three different dimensionless far-field concentrations, $K_a \rho_0 = 0.7, 0.79$ and 0.9 , which for the case of a still bubble correspond to a surface excess concentration of $2.7, 2.9$, and $3.1 \cdot 10^{-10}\ \text{gmoles cm}^{-2}$ respectively. The reason for choosing these values is to compare the present results, on soluble surfactants, with the results in FSII, on insoluble surfactants. Oscillations favour the presence of surfactants on the interface at these dilute conditions. Had the surfactant been insoluble, the solid lines in figure 3 would have been perfectly horizontal. The dashed curve shows the dimensionless amount of surfactant on the interface under saturation conditions and is equal to x_{min}^2 . As the dimensionless pressure amplitude increases, the minimum bubble radius decreases along with the maximum amount of surfactant that can reside on the interface.

Now we investigate the consequences of this enrichment of the surface by surfactants on rectified diffusion. Following the analysis in FSII, we assume an exponential dependence of interfacial resistance on surface concentration:

$$\tilde{R}_I(\tau) = \exp(\beta \bar{\rho}^s) = \exp\left(\frac{\alpha}{x^2(\tau)}\right), \quad (4.3)$$

where β is a constant depending on the surfactant and $\alpha = \beta \bar{N}^0 \rho_\infty^s$. In figure 4 we show plots of predicted bubble growth rates versus dimensionless pressure amplitude for a bubble of radius $20\ \mu\text{m}$ under the same conditions as for figure 1. We use the expression for growth rates obtained in FSII (equation (7.1)) along with (4.3) for the interfacial resistance, to compare the growth rates of a clean bubble (fine-dashed curve), to the growth rates of a bubble covered with the surfactant dodecyl sodium sulphate ($\beta = 0.36$). The long-dashed curves show the bubble growth rate under the assumption that the surfactant is insoluble (same as figure 5 in FSII), while the solid curves show the growth rate under the assumption that the surfactant is sparingly soluble and satisfies the dynamic equilibrium adsorption isotherm. Three different cases were considered for the three different bulk concentrations of figure 3. Because, for the conditions under consideration, oscillations favour the presence of surfactants on the interface (see figure 3), the effect of solubility is to enhance bubble growth rates (or inhibit bubble dissolution). Similar to insoluble surfactants, there is a critical bulk concentration for which soluble surfactants do not contribute to bubble growth rates. Higher bulk concentrations favour bubble growth rates while smaller concentrations inhibit bubble growth rates. For small oscillations the critical value of α is one (Fyrillas 1995), which corresponds to a dimensionless critical bulk concentration of 0.73 , for the surfactant under investigation.

For dilute solutions, the present theoretical results suggest that the assumption of the surfactant being soluble, instead of being insoluble, leads to higher bubble growth rates (or inhibits bubble dissolution).

5. Conclusions

We have employed the technique of *splitting* developed in our earlier papers (FSI and FSII), to find simplified equations for the surfactant transport problem associated with a spherical bubble undergoing arbitrarily large-amplitude periodic volume oscillations. These simplified equations are averaged over the period of the

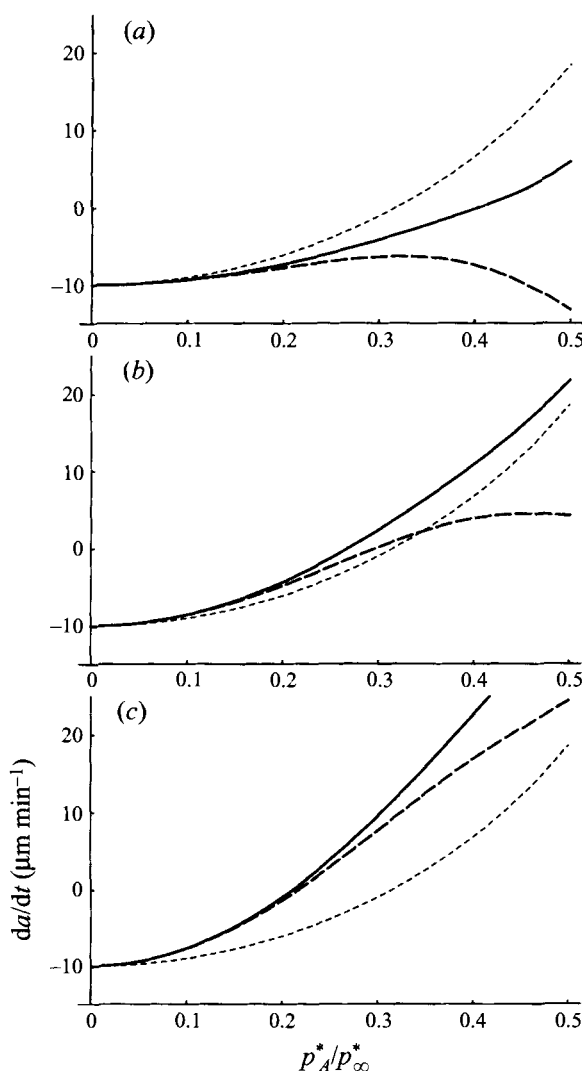


FIGURE 4. The rate of bubble growth in μm per minute versus dimensionless pressure amplitude p_A^*/p_∞^* . The bubble is of equilibrium radius $20\ \mu\text{m}$ as in figure 1. Each fine-dashed curve corresponds to a clean bubble and the other two to a surfactant-covered bubble, with surfactant dodecyl sodium sulphate ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$). Each long-dashed curve shows the bubble growth rate under the assumption that the surfactant is insoluble (same as figure 5 in FSII), while each solid curve shows the bubble growth rate under the assumption that the surfactant is sparingly soluble and satisfies the dynamic equilibrium adsorption isotherm (3.10). Three different cases were considered for three different dimensionless bulk concentrations ($K_a\rho_0$): (a) 0.7, (b) 0.79 and (c) 0.9.

oscillating bubble and clarify the surfactant dynamics over the long diffusive time scale. There is a straightforward asymptotic state for the surface excess population that reduces to the solution of a single nonlinear integral equation. This latter equation is interpreted as the dynamic equilibrium adsorption isotherm for the surfactant distribution.

The surfactant transport problem is governed by the convection–diffusion equation in spherical coordinates and an equation for the surface excess concentration, where the barrier to adsorption is based on a diffusion–kinetic model developed by

Borwankar & Wasan (1983). The problem was split into two parts. The oscillatory problem differs from zero only in a thin layer in the neighbourhood of the bubble surface and is not responsible for any net surfactant transport. The smooth problem is the one responsible for surfactant flux to or from the bubble interface and is identically zero asymptotically in time. It was found that the amount of surfactant adsorbed on the interface is controlled by the diffusion time scale, and asymptotically in time there is no adsorption or desorption. The surfactant behaves as though insoluble, and the amount of surfactant residing on the interface satisfies the corresponding adsorption isotherm in an average sense. For interfaces lightly populated by surfactant molecules, oscillations favour the adsorption process, and the surface excess population of surfactant on an oscillating bubble is higher than that on a still bubble. However, oscillations reduce the saturation limit of the interface which is controlled by the minimum bubble radius. The maximum surface excess population of surfactants on an oscillating bubble is that which renders the interface saturated at the minimum radius.

Using Gibbs' equation, an expression for the equation of state was developed which was used in the bubble dynamic model as a correction to the surface tension due to the presence of surfactants. Hence, associated with the addition of surfactants, there is a nonlinear dependence of surface tension on the bubble oscillation and the bulk concentration of surfactants. However, no significant changes were observed in the bubble oscillation at conditions away from resonance.

Based on experimental data of Caskey & Barlage (1972), an exponential dependence of interfacial resistance on surfactant surface concentration was assumed, of the form $R_f \propto \exp(\alpha/x^2(\tau))$ where $x(\tau)$ is the dimensionless bubble radius. The exponential coefficient α is related to the bulk concentration, through the adsorption isotherm. It was observed that for a fixed bubble oscillation, there is a critical bulk concentration, which determines the effect of the surfactant on the growth rate. For higher concentrations the bubble grows more quickly (or dissolves more slowly); for lower concentrations the bubble grows more slowly (or dissolves more quickly) as a consequence of the presence of surfactants. For dilute solutions, the present theoretical results suggest that the assumption of the surfactant being soluble, instead of being insoluble, leads to higher bubble growth rates (or inhibits bubble dissolution).

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Appendix. Expansions for N , G and Ψ_e

An expansion of N in successive powers of $\mathcal{P}_s^{-1/2}$, i.e.

$$N = N^0 + \frac{1}{\mathcal{P}_s^{1/2}} N^1 + O(\mathcal{P}_s^{-1}),$$

leads to the following expressions for G and Ψ_e to zeroth order:

$$G^0(\hat{\tau}) = \frac{x^4 \exp\left[-AN^{0^2}/x^4\right]}{k(x^2 - N^0)},$$

$$\Psi_e^0(\hat{\tau}) = \frac{N^0 \exp[-AN^0/x^2(\hat{\tau})]}{A_f(x^2(\hat{\tau}) - N^0)} - \Psi_0,$$

respectively. Higher-order terms may be developed, but are not required explicitly in the present analysis.

In §3, when treating the zeroth-order oscillatory and smooth problems (equations (3.2) and (3.6)), the term in the boundary conditions involving G^0 appears divided by $\mathcal{P}_s^{1/2}$ and \mathcal{P}_s respectively, and is thus moved to higher order. However, in some cases, a more careful treatment is required because the expression for G^0 has $(x^2 - N^0)$ in the denominator. This term, which is proportional to $(1 - \Psi^s)$, is very close to zero when the surface concentration is close to (dynamic) saturation, and can be omitted provided that

$$(x^2(\tau) - N^0(\lambda)) \gg \mathcal{P}_s^{-1/2}$$

This condition can be expressed more precisely using the asymptotic value of N^0 and the fact that the value of \bar{N}^0 is always less than the square of the minimum bubble radius (x_{min}^2):

$$x_{min}^2 - \bar{N}^0 \gg \mathcal{P}_s^{-1/2}.$$

For a given a bubble oscillation, use of figure 1 gives an idea of the maximum value of $A_f\Psi_0$ so that this condition is satisfied.

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