

The Effects of Gold Nanoparticles on the Stability of Microbubbles

*Graciela Mohamedi¹, Mehrdad Azmin², Isabel Pastoriza-Santos³, Victoria Huang²,
Jorge Pérez-Juste³, Luis M. Liz-Marzán³, Mohan Edirisinghe², Eleanor Stride¹¹*

¹ Institute of Biomedical Engineering, Department of Engineering Science, University of Oxford, Old Road Campus, Headington, OX3 7DQ, UK

²Department of Mechanical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK

³Departamento de Química-Física, Universidade de Vigo, 36310, Vigo, Spain

RECEIVED DATE

TITLE RUNNING HEAD Gold nanoparticle coated microbubbles

¹ Corresponding author: Institute of Biomedical Engineering, Department of Engineering Science, University of Oxford, Old Road Campus, Headington, OX3 7DQ. Tel. +44(0)1865 617 747, Fax. +44(0)1865 617 728, email: eleanor.stride@eng.ox.ac.uk

Supporting Information: Derivation of equation (3)

Equation (3) is derived by considering a spherical gas bubble of radius $R(t)$ centred at $r = 0$ in a liquid of infinite volume. Fick's 1st law states that the rate of mass transfer (flux) per unit area, J , of a component of concentration C across a plane is proportional to the concentration gradient across that plane. This is expressed in spherical polar coordinates (r, θ, ϕ) as:

$$J = -D \frac{\partial C}{\partial r} \quad \text{A.1}$$

Where D is the diffusivity of the component in the surroundings.

Epstein and Plesset²¹ define the rate of change of gas concentration at the bubble surface as:

$$\left(\frac{\partial C}{\partial r} \right)_R = (C_i - C_{sat}(R)) \left[\frac{1}{R} + \frac{1}{(\pi D t)^{\frac{1}{2}}} \right] \quad \text{A.2}$$

Where C_i and $C_{sat}(R)$ are the initial concentration of the gas in the liquid and the dissolved gas saturation concentration at the bubble wall respectively. It is assumed that C_i , the temperature (T) and pressure (p) are constant throughout the liquid and that Henry's law applies at the gas/liquid interface. The mass flow rate through the boundary can then be written as:

$$\frac{dm}{dt} = S_A D \left(\frac{\partial C}{\partial r} \right)_R = 4\pi R^2 D (C_i - C_{sat}(R)) \left[\frac{1}{R} + \frac{1}{(\pi D t)^{\frac{1}{2}}} \right] \quad \text{A.3}$$

where S_A is the instantaneous surface area of the bubble. In order to find an equation for the rate of change of bubble radius, the right hand side of equation A.3 can be equated to the first derivative of the equation for the mass of a bubble, m , under constant interfacial tension, σ :

$$\frac{dm}{dt} = 4\pi R^2 \left(\frac{dR}{dt} \right) \left[\rho(\infty) + \frac{4M\sigma}{3BTR} \right] \quad \text{A.4}$$

where B is the universal gas constant, M is the molecular weight of the gas, ρ is the density of the gas in the bubble and the term (∞) denotes conditions in the bulk liquid (i.e. neglecting the additional pressure on the gas due to surface tension). Equating A.3 with A.4 yields equation (2) in the main text.

The effect of a surfactant coating is to reduce the interfacial tension as well as providing a barrier to mass transfer across the bubble wall. These effects become increasingly significant with increasing surface concentration of surfactant molecules (Γ). For an insoluble molecular monolayer²⁷, the interfacial tension $\sigma(R)$ can be written as:

$$\sigma(R) = \int -2\Gamma_0 \frac{\partial \sigma}{\partial \Gamma} \frac{R_0^2}{R^3} dR = \sigma_0 + \frac{K\Gamma_0^{x+1}}{x+1} \left(1 - \left(\frac{R_0}{R} \right)^{2(x+1)} \right) \quad \text{A.5}$$

where Γ_0 is the initial surfactant concentration on the bubble surface at which $\sigma = \sigma_0$, $R = R_0$, and K and x are constants characterising a given surfactant.

Similarly, the coefficient of diffusion in the presence of a surfactant coating will also be a function of surface concentration, which in turn is a function of bubble radius.

Using a similar treatment to that of Cable and Frade²³, ^{Error! Bookmark not defined.} $D(R)$ can be written as the exponential function:

$$D(R) = aD_0 \exp \left(b \left(1 - \left(\frac{R_0}{R} \right)^2 \right) \right) \quad \text{A.6}$$

Again a , b and D_0 characterise a given surfactant. When nanoparticles are adsorbed on to the interface of a dissolving microbubble, they affect its dissolution in two ways. First, they reduce the effective surface area available for the diffusion of gas

molecules through the interface. As the radius of the bubble decreases, the particles remain on the interface and therefore their fractional coverage of the surface area of the bubble increases. Thus the uncovered interfacial surface area can be written as:

$$S_A(R) = 4\pi R^2 \left(1 - f_{p0} \left(\frac{R_0}{R} \right)^2 \right) \quad A.7$$

where f_{p0} is the initial fractional coverage of particles on the bubble surface. Again equating terms for the rate of change of mass of the bubble but now including the terms described in equations A.5-7 yields equation (3) in the main text:

$$\frac{dR}{dt} = \frac{(C_i - C_{sat}(R))}{\rho(\infty) + \frac{2M}{3BT} \frac{2}{R} \left[\sigma_0 + \frac{K\Gamma_0^{x+1}}{x+1} \left[x \left(\frac{R_0}{R} \right)^{2(x+1)} + 1 \right] \right]} \left[\frac{D(R)}{R} + \sqrt{\frac{D(R)}{\pi t}} \right] \left[1 - f_{p0} \left(\frac{R_0}{R} \right)^2 \right]$$

It should be noted that for the case of a variable diffusivity, Equation A.2 now represents an approximation to the true boundary condition, but the additional terms in the series will be small (*c.f.* equation (6) of Epstein and Plesset).