

Terminal Velocity and Mobile Surface Species in Rising Microbubbles

Ofer Manor[†] and Derek Y. C. Chan^{*†‡}

[†]Particulate Fluids Processing Centre, Department of Mathematics and Statistics, The University of Melbourne, Parkville, Victoria 3010, Australia, and [‡]Department of Mathematics, National University of Singapore, 117543 Singapore

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The terminal velocity of rising microbubbles is a sensitive function of the bubble size and the surface concentration of mobile insoluble surfactants at the gas/liquid interface due to the Marangoni effect. With a model that allows for surface convection and diffusion, we delineate the regimes when the terminal velocity varies between the fully mobile (Hadamard–Rybczynski) and the fully immobile (Stokes) behavior at low Reynolds numbers. Results are presented in a universal form to facilitate conversion from bubble rise terminal velocity to trace amounts of surface contaminants.

There has been a recent resurgence in interest in the hydrodynamic properties of rising microbubbles in water with diameters below about 100 μm under conditions of extreme cleanliness.^{1–3} When the bubble gas/liquid interface is free of impurities, it is expected to be fully mobile and will not support hydrodynamic shear stress tangential to the surface. Under Stokes flow, the drag force on such a bubble of radius R with velocity U in a fluid of dynamic viscosity μ is expected to be given by the Hadamard–Rybczynski (HR) formula: $F_{\text{HR}} = -4\pi\mu RU$. In contrast, the drag force on a solid sphere with the no-slip or fully immobile boundary condition is given by the Stokes formula: $F_{\text{St}} = -6\pi\mu RU$. Recent measurements of terminal velocities of rising microbubbles under buoyancy force show that the HR result applies in ultrapure water (Milli-Q water cleaned by sparging with nitrogen). The addition of different salts at high concentrations (≥ 0.5 M) where some ion pairs would prevent coalescence in bubble swarms while others will not reveals no deviations from the HR result as long as the solution is cleaned by sparging with nitrogen for at least 1 h.⁴ However, trace amounts (10^{-7} M) of added surfactants³ or exposure of the system to the atmosphere^{1,2} will cause deviations from the HR results toward the Stokes result. On the other hand, atomic force microscope measurements of dynamic forces between ultrasonically generated microbubbles moving relative to a mica plate show that, in Milli-Q water, the measured forces are consistent with a bubble surface that contains trace amounts of insoluble mobile species at a concentration that lowers the gas/liquid interfacial tension by only 0.1 mN/m.⁵ The addition of well-roasted NaCl to a concentration of 10^{-3} M is sufficient to change the gas/liquid interface to a no-slip hydrodynamic boundary that would be consistent with the Stokes formula.

In this Letter, we wish to quantify the effects on the terminal velocity of microbubbles rising under buoyancy force due to the

presence of low concentrations of insoluble surface-active species that are confined to the gas/liquid interface but otherwise are free to diffuse along the interface. Surface-active species may be assumed to be insoluble when the time scales of desorption and adsorption are slow compared to the time of the experiment. Detailed measurements and analysis of the effects of the rate of adsorption and desorption of different surfactants have been considered by Ferri and Stebe.⁶ The aim here is to provide a way to use terminal velocity measurements as a method of determining the surface concentration of insoluble surface-active species. Such species, present at surface concentration Γ , will lower the interfacial tension of the clean gas/liquid interface from σ_0 to $\sigma = \sigma_0 - \pi_s$, by an amount equal to the surface pressure π_s . At low concentrations, the surface pressure is related to the surface concentration by the ideal gas equation:⁷ $\pi_s = \Gamma kT$. For a rising bubble, the surface concentrations will be nonuniform around the bubble surface due to convection effects and will therefore generate a surface tension gradient that opposes the hydrodynamic tangential stress. Therefore, the fluid flow problem around the bubble and the convection–diffusion problem of the mobile surface-active species along the surface need to be solved together. At steady state, the solution of the two coupled problems will determine the terminal velocity, the distribution of surface species, and the surface velocity at the bubble gas/liquid interface.

For microbubbles, where Stokes flow applies, the coupling of the hydrodynamic flow with surface convection and diffusion results in a nonlinear problem that requires numerical solution. To calculate the terminal velocity of a spherical bubble of radius R rising under a buoyancy force $\mathbf{F}_{\text{buoy}} = (4\pi/3)\rho g R^3 \hat{z}$ (gravitational acceleration g) in a Newtonian fluid of density ρ , we consider a spherical stationary bubble centered at the origin with the fluid moving past it with velocity $-U\hat{z}$ at infinity. In this axisymmetric problem, the fluid velocity has a radial component $v_r(r, \theta)$ and an angular component $v_\theta(r, \theta)$, where the polar angle θ is measured from the upstream pole of the bubble. On the bubble surface $r = R$, the impenetrable condition $v_r(R, \theta) = 0$ holds while the

*Corresponding author. E-mail: D.Chan@unimelb.edu.au.

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hydrodynamic tangential stress $\tau_{r\theta}$ is balanced by the surface tension gradient:⁸

$$\tau_{r\theta} \equiv \mu \left(\frac{1}{r} \frac{\partial v_r}{\partial \theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} \right) = \frac{1}{R} \frac{d\sigma}{d\theta} \quad \text{at } r = R \quad (1)$$

Under Stokes flow, the terminal velocity is⁹

$$U = U_{\text{HR}} + \frac{1}{4\mu} \int_0^\pi \sin^2 \theta \frac{d\sigma}{d\theta} d\theta \quad (2)$$

where $U_{\text{HR}} = (\rho g R^2 / 3\mu)$ is the Hadamard–Rybczynski terminal velocity for a bubble with a fully mobile surface with the zero shear stress: $\tau_{r\theta} = 0$, boundary condition. Since $(d\sigma/d\theta) < 0$, the terminal velocity will be less than U_{HR} in the presence of surfactants that generate a surface tension gradient.

In general, the concentration $\Gamma(\theta, t)$ of insoluble and mobile surface species at the bubble surface is distributed according to the surface convection–diffusion equation:

$$\frac{\partial \Gamma}{\partial t} + \frac{1}{R \sin \theta} \frac{\partial}{\partial \theta} [\sin \theta u(\theta) \Gamma] = \frac{D}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial \Gamma}{\partial \theta} \right] \quad (3)$$

where D is the diffusion coefficient of the surface species. The term $u(\theta) \equiv v_\theta(r = R, \theta)$ is the surface velocity given by⁹

$$u(\theta) = \frac{1}{2} U \sin \theta + \frac{1}{2\mu} \sum_{n=2}^{\infty} \frac{n(n-1) C_n^{-1/2}(\cos \theta)}{\sin \theta} \int_0^\pi C_n^{-1/2}(\cos \theta) \frac{d\sigma}{d\theta} d\theta \quad (4)$$

where $C_n^{-1/2}(\cos \theta)$ is the Gegenbauer polynomial of order n and degree $(-1/2)$.

We assume the ideal surface equation of state holds between the surface pressure and the surface concentration: $\pi_s = \Gamma k T$. The steady state solution of eq 3 is required to determine the terminal velocity in terms of the gradient of the surface tension $\sigma(\theta) \equiv \sigma_0 - \pi_s(\theta)$ in eq 2. With the boundary conditions $(\partial \Gamma / \partial \theta) = 0$ at $\theta = 0$ and π , eqs 3 and 4 can be solved using the method of lines.¹⁰ With the bubble starting from rest with a convenient initial distribution $\Gamma(\theta, 0)$, we then allow the equations to evolve toward the steady-state concentration distribution and the terminal velocity, under the constraint $\int_0^\pi \Gamma \sin \theta d\theta = 2\Gamma_0$, where Γ_0 is the average concentration of surface impurities. The terminal velocity U is reached after a period of 5 times the characteristic time $t_c = R / U_{\text{HR}}$. Nevertheless, in order to ensure the existence of steady bubble rise, the results presented in the figures correspond to a rise period of $15t_c$. The curves in the figures were calculated with 200 spatial nodes on the surface of the bubble, and 20 terms are used in the summation in eq 4.

This model differs from previous studies^{9,11–17} in that we have concentrated on the effects of insoluble mobile surface active

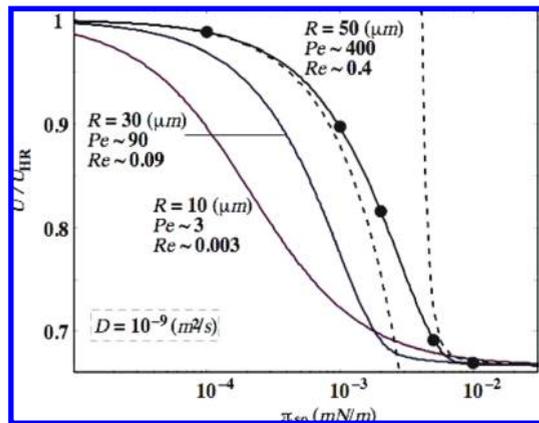


Figure 1. Terminal velocity U scaled by the Hadamard–Rybczynski value $U_{\text{HR}} = (\rho g R^2 / 3\mu)$ as a function of the average surface pressure $\pi_{\text{so}} = \Gamma_0 k T$ with a diffusion constant $D = 1.0 \times 10^{-9} \text{ m}^2/\text{s}$ at various bubble radii (—). Also shown are the limiting forms for low (eq 5) and high (eq 6) concentrations of surfactants (---) for $R = 50 \mu\text{m}$. The Peclet number is $Pe = U_{\text{HR}} R / D = (\rho g R^3) / (3\mu D)$, and the Reynolds number is $Re = \rho U_{\text{HR}} R / \mu = \rho^2 g R^3 / 3\mu^2$.

species at the gas/liquid interface rather than the problem of diffusion of such species from the bulk and their subsequent adsorption/desorption to/from the gas/liquid interface. In addition, the steady-state distribution of the surface-active species is determined consistently with the surface flow conditions and is not a predefined solid cap of a given size in the downstream part of the bubble.

The characteristic velocity of the system is the Hadamard–Rybczynski terminal velocity $U_{\text{HR}} = (\rho g R^2 / 3\mu)$, and a measure of the effects of convection to diffusion of the system is the Peclet number $Pe = U_{\text{HR}} R / D = (\rho g R^3) / (3\mu D)$. For microbubbles with radii below about $60 \mu\text{m}$, the Reynolds number $Re = \rho U_{\text{HR}} R / \mu = (\rho^2 g R^3) / (3\mu^2)$ is less than 1 and the present Stokes flow model is appropriate. For such small bubbles, deformations are negligible because the magnitude of the Laplace pressure is much larger than the normal viscous stress ($2\sigma/R \gg \mu U_{\text{HR}} / R$). Results for the bubble terminal velocity, surface velocity distribution, and surface distribution of the mobile surfactants spanning a range of physical parameters are presented in Figures 1–3. The behavior of the system can be summarized in a universal plot of the scaled terminal velocity (U/U_{HR}) against the scaled average surfactant concentration or surface pressure ($\Gamma_0 k T / \rho g R^2 = (\pi_{\text{so}} / \rho g R^2)$) at various Peclet numbers Pe (Figure 4).

In Figure 1, we show the terminal velocity U , scaled by the Hadamard–Rybczynski terminal velocity U_{HR} as this ratio varies between the fully mobile interface of the Hadamard–Rybczynski limit $U/U_{\text{HR}} = 1$, and the immobile interface (“no-slip”) of the Stokes limit: $U/U_{\text{HR}} = 2/3$ as the average surface pressure π_{so} changes. The diffusion constant is taken to be $D = 1.0 \times 10^{-9} \text{ m}^2/\text{s}$ for bubble radii 10, 30, and $50 \mu\text{m}$. In this range of bubble size, the Hadamard–Rybczynski regime corresponds to a very low average surface pressure $\pi_{\text{so}} \leq 10^{-2} \text{ mN/m}$, which equates to about one surfactant molecule per 40 nm^2 . Also given in Figure 1 are two asymptotic results valid in the limit of low or high surface concentration of mobile surfactants for a $50 \mu\text{m}$ radius bubble. In the limit of low surface concentration of surfactants

$$U/U_{\text{HR}} \approx 1 - 3(\coth(Pe/2) - 2/Pe) \left(\pi_{\text{so}} / \rho g R^2 \right) \quad (5)$$

This is the first order correction to the Hadamard–Rybczynski terminal velocity and is derived by calculating the steady-state

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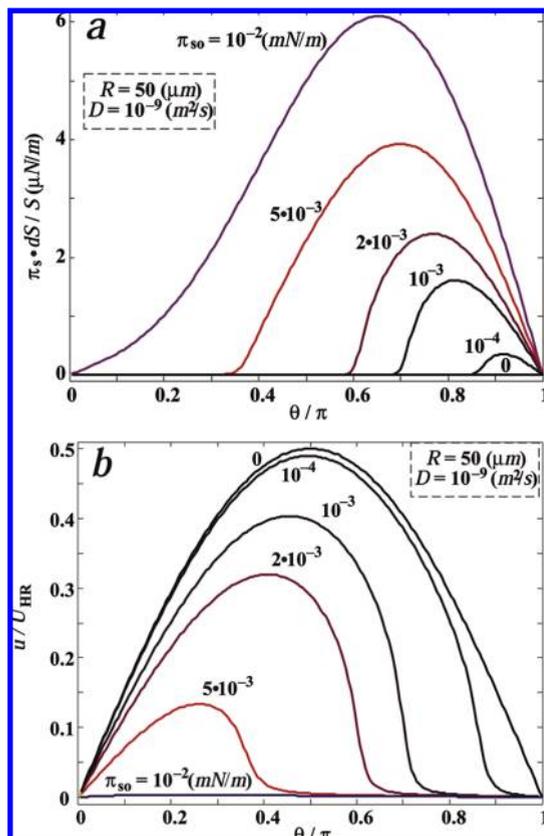


Figure 2. (a) Amount of the species adsorbed to a certain bubble surface segment $dS(\theta)$ with respect to the entire bubble surface S presented in terms of the surface pressure as $\pi_s(\theta) dS(\theta)/S = \pi_s(\theta) \sin \theta/2$ and (b) scaled surface velocity $u(\theta)/U_{HR}$ as a function of the polar angle θ for various average surface pressure π_{so} .

distribution of surface-active species in eq 3 assuming the fully mobile surface velocity $u(\theta) = (1/2)U \sin \theta$. The result was then substituted into eq 2 to estimate the correction term to the Hadamard–Rybczynski result. We also give the result for the terminal velocity in the limit of high surface concentration of surfactants

$$U/U_{HR} \approx 2/3 + (1/Pe)(2\rho g R^2/3\pi_s) + 3/(2Pe) \sum_{n=1}^{\infty} (3\pi_{so}/\rho g R^2)^{-2n-1} \int_0^{\pi} \sin^3 \theta \cos^{2n} \theta d\theta \quad (6)$$

This is a first correction to the Stokes terminal velocity (that assumes a “no-slip”, immobile interface) due to a small surface velocity that results from surfactant diffusion (via the steady eq 3) that perturbs the distribution of surface tension which is required to fully immobilize the interface.⁹

For the case of a bubble of radius $R = 50 \mu\text{m}$ and diffusion constant $D = 1.0 \times 10^{-9} \text{m}^2/\text{s}$, we show the variations of surfactant concentration (Figure 2a) and surface velocity with angular position (Figure 2b) on the bubble surface corresponding to different average surfactant concentrations indicated by the solid dots in Figure 1. This allows us to see the connection between the value of the terminal velocity, the surface distribution of surfactants, and the surface velocity. The amount of the species located within a certain bubble surface segment $dS(\theta)$ with respect to the entire bubble surface S is presented in terms of the surface pressure as $\pi_s(\theta) dS(\theta)/S$ in view of the ideal gas law that is assumed to relate surface pressure to surface

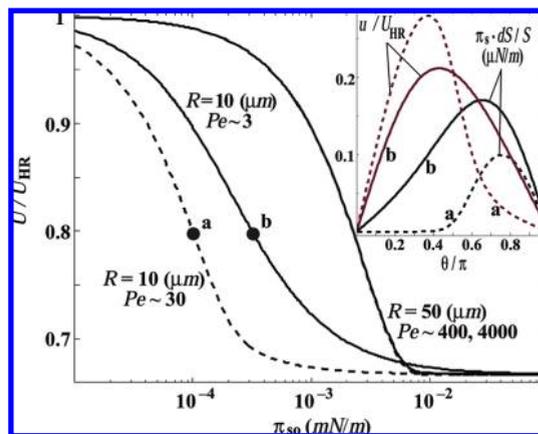


Figure 3. Variations of the terminal velocity U scaled by the Hadamard–Rybczynski value $U_{HR} = (\rho g R^2/3\mu)$ with the average surface pressure $\pi_{so} = \Gamma_0 k T$ for different bubble radii R and different Peclet numbers $Pe = U_{HR} R/D$, for diffusion coefficients $D = 10^{-9}$ (—) and 10^{-10} (---) m^2/s . Inset: For a bubble of radius $R = 10 \mu\text{m}$, angular variations of the surface velocity $u(\theta)$ and the surface angular distribution of adsorbed species presented in terms of the surface pressure as $\pi_s(\theta) dS(\theta)/S = \pi_s(\theta) \sin \theta/2$ for diffusion coefficient $D = 10^{-9} \text{m}^2/\text{s}$, average surface pressure $\pi_{so} = 3.0 \times 10^{-4} \text{mN/m}$ (—) (labeled a), and for diffusion coefficient $D = 10^{-10} \text{m}^2/\text{s}$, average surface pressure $\pi_{so} = 1.0 \times 10^{-4} \text{mN/m}$ (---) (labeled b).

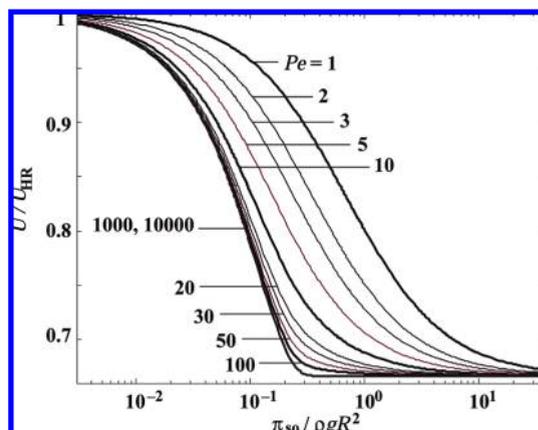


Figure 4. Terminal velocity U scaled by the Hadamard–Rybczynski value $U_{HR} = (\rho g R^2/3\mu)$ as a function of the average surface pressure π_{so} scaled by the quantity $\rho g R^2$. The Peclet number is $Pe = U_{HR} R/D = (\rho g R^3)/(3\mu D)$.

concentrations. On comparing parts a and b of Figure 2, it is clear that the surface species are mobile at angular positions where their concentration is low. We can also see the natural development of a stagnant cap of surfactants at the downstream portion of the bubble as the average surface concentration increases. Unlike other models,^{14,15} the size of this stagnant cap is not an assumed quantity but rather emerges naturally as a consequence of the model. For cases where a well-developed stagnant cap of surfactants can be identified, for example, for average surface pressures π_{so} between 1×10^{-4} and 10^{-2}mN/m in Figure 2a, the terminal velocities predicted from such models¹⁵ are in very good agreement from the computed terminal velocities shown in Figure 1.

Variations of the diffusion coefficient D within the practical range of $1.0 \times 10^{-10} - 1.0 \times 10^{-9} \text{m}^2/\text{s}$ is only significant for small microbubbles ($Pe = 30$ to 3), where the effects of molecular diffusion are not dominated by convection along the surface

(Figure 3). As an example, we see that the two points labeled (a) and (b) in Figure 3 have the same terminal velocity. However, for different diffusion constants or Peclet numbers, this terminal velocity is the result of different combinations of surface velocity u and surface distribution of surfactants as shown in the inset of Figure 3.

The general relation between the terminal velocity and the average surface concentration of surfactants, expressed as the average surface pressure π_{so} , can be completely summarized in Figure 4, with the velocity scaled by the Hadamard–Rybczynski value $U_{HR} = (\rho g R^2 / 3\mu)$, the surface pressure scaled by $(\rho g R^2)$, and the diffusion coefficient specified by the Peclet number $Pe = U_{HR} R / D = (\rho g R^3) / (3\mu D)$. This figure summarizes the predictions of our model for all practical parameter values and can be readily used to estimate the amount of surface contamination based on the measured bubble terminal velocity.

In this Letter, we have proposed a model to quantify the effects of small quantities of insoluble surface-active species adsorbed to the gas/liquid interface of microbubbles in which the adsorbed species can diffuse along the interface. As these microbubbles rise under buoyancy forces, a nonuniform steady-state distribution of

surface-active species along the interface is created by the balance of convection and diffusion effect.^{8,18} This gives rise to the Marangoni effect whereby the resulting surface tension gradient can arrest interfacial flow that would otherwise occur at an ideal, tangentially mobile gas/liquid interface that cannot support any shear stress. Even at very low surfactant concentrations, this effect can cause the terminal velocity of the rising bubble to lie between the fully mobile Hadamard–Rybczynski result and the immobile, no-slip Stokes result for which the bubble behaves hydrodynamically like a solid particle. In between these two limits, a natural consequence of the model is the formation of an apparent immobile surfactant cap of varying sizes at the downstream part of the rising bubble. The main result of the model, summarized in dimensionless form in Figure 4, provides a ready-made method to use terminal velocity measurements as a way to determine the concentration of trace amounts of surfactants or impurities at the gas/liquid interface. Approximate analytic results for the terminal velocity in the limit of low (eq 5) and high (eq 6) surfactant concentrations are also given.

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