SHAPE OSCILLATIONS OF GAS BUBBLES WITH NEWTONIAN INTERFACIAL RHEOLOGICAL PROPERTIES

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ABSTRACT

The oscillation frequency and damping rate for small-amplitude axisymmetric shape modes of a gas bubble in an ideal liquid are obtained, in the limit when the bubble interface possesses Newtonian interfacial rheology with constant surface shear and dilatational viscosities. Such results permit the latter surface properties to be measured by analyzing experimental data on frequency shift and damping rate of specific shape modes of suspended bubbles in the presence of surfactants.

INTRODUCTION

Shape oscillations of bubbles and drops, freely-suspended in microgravity or acoustically-levitated on earth, have been suggested as a technique for measuring such surface rheological properties as dynamic surface tension and shear and dilatational interfacial viscosities. As a prerequisite to such non-contact surface rheometry, one needs to have expressions for both the oscillation frequency and the damping parameter of the particular shape modes excited in the experiments (typically the quadrupole mode), when surface rheological effects are present and significant. The shape modes of an acoustically levitated drop or bubble can be excited by modulating the frequency of the ultrasound which is being used for levitation, at a frequency which is close to the natural frequency of the desired shape mode [10, 11, 12]. Since the natural frequency of each shape mode is dependent upon properties of the interface [9, 13] (e.g., surface tension and surface rheological constants), such an experiment can be used to measure the interfacial properties [1, 2, 4, 5, 8, 15, 16]. In particular, when the drop or bubble oscillations take place in the presence of surfactants, the contaminated interface exhibits a viscous behavior, with surface shear and dilatational viscosities which are often difficult to measure accurately by other means [3]. Thus, observation of the forced and free oscillations of drops or bubbles can be quite useful as a technique for a non-contact measurement of the surface viscosities, provided that explicit expressions are available relating the oscillation frequency and damping constants of the shape modes to the interfacial properties. Some expressions of this type have already been found [9, 13], although under certain restrictive assumptions. The present contribution derives analytical expressions for the frequency and damping rates of axisymmetric shape modes of gas bubbles in ideal liquids, when the interface possesses constant Newtonian rheological properties.

Surface rheological effects arise in the presence of surfactants, which are long molecules with separated hydrophilic and hydrophobic segments [3, 7]. In the presence of an interface

between an aqueous and a non-aqueous phase, surfactants preferentially adsorb at that surface. In addition to modifying the surface tension at the interface, an adsorbed layer of surfactants at a fluid-fluid interface may possess its own rheological properties (e.g., viscosity or elasticity), distinct from those of the bulk phases on either side. Scriven [14] provided the tensorial form of the constitutive equation for a "Newtonian" surface fluid, although the concept of surface viscosity originated with Plateau and Boussinesq [3].

INTERFACIAL RHEOLOGY

The rheological behavior of a surfactant-laden interface can be characterized by specifying the surface stress tensor $\mathbf{\Pi}_s$ which for a Boussinesq-Scriven Newtonian surface layer [14] has the invariant form

$$\mathbf{\Pi}_s = \sigma \mathbf{I}_s + 2\mu_s [\mathbf{E}_s - \frac{1}{2}\mathbf{I}_s (\mathbf{I}_s : \mathbf{E}_s)] + \kappa_s \mathbf{I}_s (\mathbf{I}_s : \mathbf{E}_s) , \tag{1}$$

in which

$$\mathbf{E}_s \equiv \frac{1}{2}[(\nabla_s \mathbf{u}) \cdot \mathbf{I}_s + \mathbf{I}_s \cdot (\nabla_s \mathbf{u})^\dagger] , \tag{2}$$

is the surface rate-of-strain tensor. Here, μ_s and κ_s are the shear and dilatational surface viscosities, σ is the surface tension, $\nabla_s \equiv \mathbf{I}_s \cdot \nabla$ is the surface gradient operator, $\mathbf{I}_s$ is the surface unit tensor which is related to the three-dimensional unit tensor $\mathbf{I}$ via $\mathbf{I}_s = \mathbf{I} - \hat{n}\hat{n}$ and $\mathbf{u}$ is the velocity vector at the interface. In addition, the superscript $\dagger$ designates the transpose of the tensor to which it is attached and $\hat{n}$ is the normal unit vector at the surface. The surface stress tensor appears in the dynamic boundary condition at a fluid/fluid interface in the form

$$\hat{n} \cdot (\mathbf{\Pi}_l - \mathbf{\Pi}_g) + \nabla_s \cdot \mathbf{\Pi}_s = 0 , \tag{3}$$

in which $\mathbf{\Pi}_l$ and $\mathbf{\Pi}_g$ are the respective stress tensors in the liquid and gas phases, and with the unit normal $\hat{n}$ taken to point from the gas to the liquid phase. Equation (3) represents an instantaneous balance of all forces acting on the interface, valid if the inertia of the interface is negligible. The dot products of (3) with $\hat{n}$ and with $\mathbf{I}_s$ result in the normal and tangential stress balance at the interface, respectively. In general, surface properties σ, μ_s and κ_s all depend on the local concentration of surfactants on the interface, which needs to be found by solving a surface transport equation. In this brief contribution, however, we focus on highly contaminated bubbles whose interfacial material properties have constant values, independent of surfactant concentration.

RESULTS FOR A NEARLY-SPHERICAL BUBBLE

As an illustrative example, consider the idealized problem of slight perturbations of an initially spherical bubble with equilibrium radius a_o and surface tension σ_o. Gravitational effects are neglected on the assumption that the Bond number, $\rho_l a_o^2 g / \sigma_o$, (with ρ_l the density of the external liquid and g the gravitational constant) is small. Thus, the equilibrium

pressures outside and inside the bubble are respectively given by p_o and $\hat{p}_o = p_o + 2\sigma_o/a_o$. The bubble is assumed to contain an ideal gas which has a uniform pressure determined by its instantaneous volume. The surrounding liquid of infinite expanse is treated as an incompressible *ideal* fluid with its velocity field deriving from a scalar potential. For this problem, it is convenient to work in a spherical coordinate system (r, θ, z), in which r and θ are the radial distance from the origin and the polar angle measured from the z-axis. Let ϵ be a small parameter measuring the magnitude of deformation. For axisymmetric surface deformations, the instantaneous shape of the bubble can be written in the form $r = a_o[1 + \epsilon f(\theta, t)]$, where $f(\theta, t)$ is the shape correction function.

For such slight perturbations from equilibrium shape, all quantities can be expanded in powers of the small parameter ϵ, as given in the following list:

Coordinate r of a surface point	a_o +	$\epsilon a_o f(\theta, t)$
Exterior velocity potential		$\epsilon \Phi(r, \theta, t)$
Normal interface velocity		$\epsilon U(\theta, t)$
Tangential interface velocity		$\epsilon V(\theta, t)$
Exterior pressure at the surface	p_o +	$\epsilon p(\theta, t)$
Interior pressure	$\hat{p}_o$ +	$\epsilon \hat{p}(t)$
Surface rate-of-strain		$\epsilon N(\theta, t)$
Surface rate-of-dilatation		$\epsilon M(\theta, t)$.

Here, the surface rates of dilatation and strain—corresponding to the trace of (2) and its remaining traceless part—can be related to the surface velocities given in the same table by

$$M(\theta, t) = \frac{1}{a_o}\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}[\sin(\theta)V] + 2U\right], \tag{4}$$

$$N(\theta, t) = \frac{1}{a_o}\left[\frac{\partial V}{\partial\theta} - \cot(\theta)V\right]. \tag{5}$$

The complete set of equations which describe the linearized dynamics of the bubble at $\mathcal{O}(\epsilon)$ can now be formulated as follows. Since the perturbation from the equilibrium spherical shape is assumed to be small, all surface boundary conditions can, to leading order, be imposed at the undisturbed position of the bubble surface, $r = a_o$. The velocity potential of the exterior liquid phase is a solution to

$$\nabla^2\Phi = 0 \qquad (r > a_o) \tag{6}$$

subject to boundary conditions

$$\Phi \to 0 \quad \text{as} \quad r \to \infty, \tag{7}$$

$$\partial\Phi/\partial r = a_o \, \partial f/\partial t = U(\theta, t) \quad \text{at} \quad r = a_o, \tag{8}$$

where (8) results from the kinematic condition at the surface. The normal stress condition, obtained by taking the dot product of (3) with $\hat{n}$, presently takes the form

$$\hat{p} - p = \frac{2}{a_o}(\kappa_{so}M) - \frac{\sigma_o}{a_o}[\frac{\partial^2 f}{\partial\theta^2} + \cot(\theta)\frac{\partial f}{\partial\theta} + 2f], \tag{9}$$

while the tangential stress condition, obtained by taking the dot product of (3) with $(\mathbf{I}-\hat{\mathbf{n}}\hat{\mathbf{n}})$, reduces to

$$0 = -\frac{\partial}{\partial\theta}(\kappa_{so}M + \mu_{so}N) - 2\mu_{so}\cot(\theta)N. \tag{10}$$

Here, the surface viscosities κ_{so} and μ_{so} are constants. The perturbation to the exterior pressure at the bubble surface is determined from the velocity potential by means of Bernoulli's equation for potential flow

$$p = -\rho_l \left.\frac{\partial\Phi}{\partial t}\right|_{r=a_o}, \tag{11}$$

with the higher order terms in ϵ omitted.

The set of equations given above, together with an equation-of-state which relates the uniform pressure inside the bubble to its instantaneous volume, fully characterize the linearized dynamics of the slightly perturbed surfactant-laden bubble. The solution to this set of equations can be obtained by modal expansion. Let the surface deformation $f(\theta,t)$ and the surface tangential velocity $V(\theta,t)$ have decompositions of the form

$$f(\theta,t) = \sum_{n=0}^{\infty} f_n(t)P_n(\cos\theta), \tag{12}$$

$$V(\theta,t) = \sum_{n=1}^{\infty} V_n(t)\frac{dP_n(\cos\theta)}{d\theta}, \tag{13}$$

where, $P_n(\cos\theta)$ represents the Legendre function of order n. The kinematic condition (8) allows a similar modal expansion to be obtained for the normal velocity $U(\theta,t)$ with coefficients given by $\dot{f}_n(t)$, and the solution to the exterior velocity potential, satisfying (6)–(8), can also be found easily, resulting in an expression for the exterior pressure at the surface, based on Bernoulli's relation. The pressure in the bubble interior is found to depend only upon the $n = 0$ term in the shape expansion to this order in ϵ. The so-called breathing (i.e. $n = 0$) mode of the bubble is thus the only mode that is affected by the pressure within the bubble, which provides the primary "restoring force" for bringing the bubble back to its equilibrium volume. Here we will concentrate on the shape modes ($n > 1$) for which the characteristic time is determined by surface tension. Hence, we adopt the equilibrium radius a_o as the length scale and define the time scale τ by

$$\tau \equiv (\rho_l a_o^3/\sigma_o)^{1/2}. \tag{14}$$

Variables t, and (U, V) are then rendered dimensionless using respective scales τ and a_o/τ and dimensionless surface viscosities are defined by

$$\kappa^* = \frac{\kappa_{so}}{\sigma_o\tau}, \quad \mu^* = \frac{\mu_{so}}{\sigma_o\tau}. \tag{15}$$

Substitution of the modal expansion into the the normal and tangential stress conditions (9) and (10) produces the following coupled equations for the evolution of the n-th mode:

$$\frac{1}{n+1}\ddot{f}_n + 4\kappa^*\dot{f}_n + (n-1)(n+2)f_n = 2\kappa^*n(n+1)V_n, \tag{16}$$

$$2\kappa^* \dot{f_n} = [\kappa^* n(n+1) + \mu^*(n-1)(n+2)] V_n . \tag{17}$$

Here, overdot represents differentiation with respect to dimensionless time and f_n and V_n are also dimensionless. If exponential behavior of the form $e^{\lambda_n t}$ is assumed in each of the modal coefficients, the linear system (16)–(17) produces an eigenvalue problem for λ_n which determines the frequency and damping rate of the n-th shape mode.

Interestingly, for any mode of the bubble, if the surface shear viscosity μ^* is set to zero, the equation for the n-th shape mode reduces to

$$\ddot{f_n} + (n-1)(n+1)(n+2) f_n = 0 . \tag{18}$$

Thus, in the absence of surface shear viscosity, the linearized shape oscillations are the same as those for a clean bubble. In that case, the dimensionless frequency of oscillations is found from (18) to be

$$(\omega_n^*)^2 = (n-1)(n+1)(n+2) , \tag{19}$$

in agreement with known results [6]. For the quadrupole $(n=2)$ mode, the eigenvalues λ_2 are easily found to be

$$\lambda_2^{\pm} = -\frac{12\kappa^* \mu^*}{3\kappa^* + 2\mu^*} \pm i\sqrt{12 - (\frac{12\kappa^* \mu^*}{3\kappa^* + 2\mu^*})^2} . \tag{20}$$

The complex conjugate pair of eigenvalues (20) characterize the damped oscillation of the quadrupole shape mode, as modified by constant surface shear and dilatational viscosities. If either of these vanishes, the oscillation reduces to that dictated by the Lamb formula (19). In the limit when one of the surface viscosity coefficients is much smaller than the other, (20) shows that it is the *smaller* of the two viscosities which contributes the most to damping and frequency modification.

OUTLOOK

Although idealized, the above calculation can be used, in conjunction with existing estimates of surface viscosity coefficients, to show that surface rheological effects can exert a strong influence on the frequency-shift and damping of the oscillations. To make quantitative comparisons against experimental results (e.g., see [2]), however, one must also include in the analysis the effects of viscous boundary layers in the bulk fluids [11], as well as the influence of surface and bulk transport of surfactants and their sorptive exchange, the role of Marangoni stresses, and possible nonlinear modal interactions when the amplitude of oscillations is large. Such issues are currently under investigation and will be addressed in forthcoming contributions.

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