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Small amplitude shape oscillations of a spherical liquid drop with surface viscosity

D. V. LYUBIMOV[1], V. V. KONOVALOV[2], T. P. LYUBIMOVA[2]† AND I. EGRY[3]

[1]Theoretical Physics Department, Perm State University, Perm 614990, Russia
[2]Institute of Continuous Media Mechanics, Perm 614013, Russia
[3]Institut fuer Materialphysik im Weltraum, German Aerospace Center, DLR, 51170 Cologne, Germany

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The analysis of surface oscillations of liquid drops allows measurements of the surface tension and viscosity of the liquid. For small oscillations of spherical drops with a free surface, classical formulae by Rayleigh and Lamb relate these quantities to the frequency and damping of the oscillations. In many cases, however, the drop's surface is covered by a surface film, typically an oxide layer or a surfactant, exhibiting a rheological behaviour different from the bulk fluid. It is the purpose of this paper to investigate how such surface properties influence the oscillation spectrum of a spherical drop. For small bulk shear viscosity, the cases of small, finite and large surface viscosities are discussed, and the onset of aperiodic motion as a function of the surface parameters is also derived.

Key words: drops, capillary waves, multiphase flow

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1. Introduction

Oscillations of drops and bubbles have been a subject of hydrodynamics for more than 100 years. The first treatment is due to Rayleigh (1879) who considered a force-free, non-viscous and spherical liquid drop. The Rayleigh frequency, corresponding to the fivefold degenerate fundamental oscillation mode, is given by

$$\omega_R = \sqrt{\frac{8\gamma}{\rho R^3}}, \tag{1.1}$$

where γ is the surface tension, ρ is the density and R is the radius of the drop.

Later, Lamb (1881) generalised Rayleigh's treatment by considering viscous drops. While for small viscosity values the oscillation frequency remains essentially unchanged, the damping of the oscillations is given by Chandrasekhar (1959) and Reid (1960),

$$\lambda_L = \frac{5\nu}{R^2}, \tag{1.2}$$

where ν is the bulk shear viscosity.

In the applications discussed below, λ_L is of the order of $1\,\mathrm{s}^{-1}$, while ω_R is of the order of $50\,\mathrm{s}^{-1}$. Therefore, the ratio λ_L/ω_R is a small quantity, leading to the definition

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† Email address for correspondence: lyubimov@psu.ru

of a reciprocal Reynolds number δ,

$$\delta = \frac{\nu}{R^2}\sqrt{\frac{\rho R^3}{\gamma}}. \tag{1.3}$$

This parameter characterises the undisturbed system, and we will make use of the fact that $\delta \ll 1$ in the following.

Suryanarayana & Bayazitoglu (1991) have developed an improved method to consider the case of viscous drops for arbitrary δ ($1/\alpha^2$ in their terminology) and presented implicit solutions for both, frequency and damping of the oscillations. Depending on the parameters chosen, they find either two complex conjugate periodic or one aperiodic solution. The critical values of the parameter α^2 for the transition to the aperiodic solutions have been derived already by Chandrasekhar (1961). The value that corresponds to the fundamental oscillation mode is $\alpha^2_{crit} \approx 3.69$.

Apart from the academic interest in this classical case, there is also a practical interest in studying these oscillations. With the advent of containerless processing techniques, such as acoustic, aerodynamic, electromagnetic and electrostatic levitation, the frequency spectrum of levitated liquid drops could be studied, and, initially, the Rayleigh frequency, (1.1) was used to determine the surface tension γ of the levitated sample. In these experiments, liquid metallic droplets of a few millimetre in diameter have been studied. Except for experiments under microgravity conditions (Egry, Lohöfer & Jacobs 1995), the levitation forces had to be included in the original treatment. For electromagnetic levitation, this was done by Cummings & Blackburn (1991), and their correction formula was later verified experimentally (Egry *et al.* 1993).

By the same token, also the viscosity was determined from the damping of the surface oscillations through (1.2) in a microgravity experiment (Egry *et al.* 1998). Although good agreement with existing data for a Pd–Si alloy was found, this experiment was later criticised for not taking the surface viscosity into account (Earnshaw 1998). In fact, later attempts to measure the bulk shear viscosity by the oscillating drop method yielded generally too high values for the viscosity, the error being sometimes more than 100 % (Mock 2004; Wunderlich 2008; Egry & Schick 2011). Such discrepancies may be either due to magnetohydrodynamic effects (Bardet 2006), not included in Lamb's treatment, or to the presence of a surface layer, e.g. a metal oxide, giving rise to a surface viscosity. Whereas the magnetohydrodynamic effects can be at least minimised by performing the experiment under microgravity, an oxide layer can be hardly avoided when dealing with highly reactive liquid metals, such as, e.g. aluminium. In addition, Earnshaw has argued that even clean liquid metal surfaces possess an intrinsic surface layer, due to a varying density profile of the conduction electrons close to the surface.

It is, therefore, the aim of the present paper to quantify the effect of a surface layer on the damped oscillations of a liquid drop. This problem has been addressed before for a liquid–liquid interface, i.e. when the liquid drop is immersed into another, host, liquid by Miller & Scriven (1968), Lu & Apfel (1991) as well as Sparling & Sedlak (1989), and for a liquid–gas interface by Tian, Holt & Apfel (1995). Whereas Miller's, Lu's and Apfel's works are analytical solutions for limiting cases, Sparling and Sedlak present a numerical solution in more general cases.

In this paper, we concentrate on the liquid–gas interface and extend previous works by deriving analytical expressions for small, finite and large surface viscosities. In particular, we show that finite surface viscosities can suppress surface oscillations, leading to aperiodic solutions, even in the case of small bulk shear viscosity.

We obtain our results through systematic perturbation theory in powers of the surface viscosity. This is in contrast to the method applied by Miller & Scriven (1968) who treated the surface as inextensible in their approximation. Simular theories were built by Lu & Apfel (1991) for the liquid–liquid interface and Tian *et al.* (1995) for the liquid–gas interface. Their approaches to construct the perturbation theory weren't sufficiently systematic in our opinion. The former tended to reduce the analysis to the case of inextensible or having no shear interface. The latter didn't specify directly the conditions when simplified expressions for the corrections can be given. We try to avoid both these shortages in our theory.

In the next chapter, we will state the problem in mathematical terms by introducing the surface viscosity tensor into the stress balance equation of the surface. Then, we will derive the dispersion relation for the complex eigenfrequency and discuss in particular the case when the bulk shear viscosity is small and the surface viscosity dominates. Finally, we will make some concluding remarks.

2. Statement of the problem. Equations and boundary conditions

2.1. *Equations. Perturbation modes*

Consider a spherical equilibrium drop of a liquid with a surfactant adsorbed in the surface layer, performing small-amplitude free capillary oscillations.

The liquid is assumed viscous and incompressible. The velocity field $\boldsymbol{u}$ is described by the linearized Navier–Stokes equation,

$$\frac{\partial \boldsymbol{u}}{\partial t} = -\frac{1}{\rho}\nabla p + \nu \Delta \boldsymbol{u} \tag{2.1}$$

and the continuity equation

$$\nabla \boldsymbol{u} = 0. \tag{2.2}$$

The origin of the spherical coordinates $\{r, \vartheta, \phi\}$ is located in the centre of the drop.

In spherical coordinates, (2.2) allows us to distinguish between two types of perturbations: meridional perturbation with the following velocity components (see, for example, Chandrasekhar 1961):

$$u_r = \frac{l(l+1)}{r^2} T(r) Y_l^m(\vartheta, \phi) \exp(\mathrm{i}\Omega_l t) + \text{c.c.}, \tag{2.3}$$

$$u_\vartheta = \frac{1}{r}\frac{\mathrm{d}T}{\mathrm{d}r}\frac{\partial}{\partial \vartheta} Y_l^m(\vartheta, \phi) \exp(\mathrm{i}\Omega_l t) + \text{c.c.}, \tag{2.4}$$

$$u_\phi = \frac{1}{r\sin\vartheta}\frac{\mathrm{d}T}{\mathrm{d}r}\frac{\partial}{\partial \phi} Y_l^m(\vartheta, \phi) \exp(\mathrm{i}\Omega_l t) + \text{c.c.}; \tag{2.5}$$

and azimuthal perturbation with the following velocity components:

$$u_r = 0, \tag{2.6}$$

$$u_\vartheta = \frac{S(r)}{r\sin\vartheta}\frac{\partial}{\partial \phi} Y_l^m(\vartheta, \phi) \exp(\mathrm{i}\Omega_l t) + \text{c.c.}, \tag{2.7}$$

$$u_\phi = -\frac{S(r)}{r}\frac{\partial}{\partial \vartheta} Y_l^m(\vartheta, \phi) \exp(\mathrm{i}\Omega_l t) + \text{c.c.}. \tag{2.8}$$

Here $Y_l^m(\vartheta, \phi)$ is a spherical harmonic, $T(r)$ and $S(r)$ are functions of the radial coordinate r, Ω_l is the natural frequency of the l-th free oscillation mode of the drop and *c.c.* means complex conjugate.

As stated previously (Prosperetti 1980), only perturbations of the meridional type are related to oscillations of the drop shape. Perturbations of the azimuthal type are related to shear waves when different layers of the liquid rotate about their centres. Since there is no restoring force for this kind of motion, it is natural to expect that these modes will be aperiodically damped. It will be shown below that small perturbations of the azimuthal type do not cause redistribution of the surfactant in the film. The perturbations are aperiodically damped by viscous dissipation in the liquid and in the surfactant film. In what follows, our primary concern is with the perturbations of the meridional type.

The pressure perturbation, created by the fluid flow corresponding to (2.1) and (2.2), satisfies the Laplace equation $\Delta p = 0$. The solution satisfying the boundedness condition at the drop centre is written as

$$p = \varPi r^l Y_l^m(\vartheta, \phi) \exp(\mathrm{i}\varOmega_l t) + \text{c.c.}. \tag{2.9}$$

The velocity fields defined by (2.3)–(2.5) satisfy identically the continuity equation (2.2).

Substituting (2.3)–(2.5) and (2.9) into (2.1), we obtain the equation for $T(r)$,

$$\frac{\mathrm{d}^2 T}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} T - \frac{\mathrm{i}\varOmega_l}{\nu} T = \frac{1}{l+1} \frac{\varPi}{\rho\nu} r^{l+1}. \tag{2.10}$$

The solution of this equation satisfying the boundedness condition at the drop centre is

$$T = \mathrm{A} r \frac{j_l(xr/R)}{j_l(x)} + \frac{\mathrm{i}}{l+1} \frac{\varPi}{\rho\varOmega_l} r^{l+1}, \tag{2.11}$$

where $x = \sqrt{-\mathrm{i}\varOmega_l/\nu}R$ and $j_l(x)$ is the spherical Bessel function of the first kind of lth order.

Here A and $\varPi$, as well as $\varPhi$ and $\varLambda$ below, are perturbation amplitudes.

2.2. *Boundary conditions*

Now consider the boundary conditions on the free surface of the drop. The surface shape is given by the equation

$$f(r, \vartheta, \phi, t) = r - R - \varepsilon(\vartheta, \phi, t) = 0, \tag{2.12}$$

where $\varepsilon(\vartheta, \phi, t)$ describes a small deviation from the equilibrium position.

The free surface of the drop satisfies the kinematic condition,

$$\frac{\partial f}{\partial t} + \boldsymbol{u}\nabla f = 0. \tag{2.13}$$

At the drop surface, adsorption leads to the formation of a high-concentration surfactant layer, which has an equilibrium distribution of the surfactant. The disturbance of equilibrium initiates the processes of surfactant redistribution. The equation of mass conservation for the surfactant can be written as (Stone 1990)

$$\frac{\partial \varGamma}{\partial t} + \nabla^{(s)}(\varGamma \boldsymbol{u}^{(s)}) + \varGamma \mathrm{H} u_n = D_s \Delta^{(s)} \varGamma, \tag{2.14}$$

where $\varGamma$ is the space and time dependent surface concentration of a surfactant, D_s is the coefficient of the surface diffusion, u_n and $\boldsymbol{u}^{(s)}$ are the velocity components normal and tangential to the surface, $\nabla^{(s)}$ and $\Delta^{(s)}$ are the analogues to the gradient and Laplace operators with respect to the surface coordinates and H is the mean curvature.

In this study, no consideration is given to the processes of surfactant transfer between the liquid and its surface layer, namely bulk diffusion and adsorption. Such assumption is legitimate because in the limit of small bulk dissipation, both viscous and diffusion, the influence of these processes on the natural frequencies is apparently small, even smaller than the influence of viscous dissipation. For the same reason, we further neglect the surface diffusion of the surfactant and assume that $D_s = 0$.

The distribution of the surfactant in the film is given as

$$\varGamma = \varGamma_0 + \varGamma'(\vartheta, \phi, t), \tag{2.15}$$

where $\varGamma_0$ is the value of the surface concentration of a surfactant in equilibrium, $\varGamma'(\vartheta, \phi, t)$ is a small deviation of the surfactant concentration from the equilibrium value.

As $\nabla^{(s)}\boldsymbol{u}^{(s)} = 0$ and $u_n = 0$ for perturbations of the azimuthal type (2.6)–(2.8) and (2.14) conserve the surface concentration of a surfactant in equilibrium. Redistribution of the surfactant in the film due to convective transfer and compression–extension of the interface is absent and $\varGamma \equiv \varGamma_0$.

The condition of stress balance at the liquid surface under the assumption of negligible thickness of the surfactant film is given by (see, for example, Bratukhin 1994)

$$\varGamma \frac{\partial u_j}{\partial t} + \varGamma \left(\boldsymbol{u}^{(s)} \nabla^{(s)}\right) u_j = -p n_j + \sigma_{jk} n_k + \nabla_k^{(s)} \sigma_{jk}^{(s)} - \nabla_j^{(s)} \gamma + \gamma \mathrm{H} n_j. \tag{2.16}$$

This expression involves, in addition to the normal viscosity tensor σ_{jk}, the surface viscosity tensor $\sigma_{jk}^{(s)}$, for which the indices j and k can run through the values only along the coordinates of the plane tangential to the interface; γ is the surface tension, $\boldsymbol{n}$ is the unit vector normal to the surface. Inertia of the surfactant, defined by the left-hand side of (2.16), is inessential and is neglected in the following.

The surface viscosity tensor $\sigma_{jk}^{(s)}$ in (2.16) is derived from general mathematical considerations: linearity with respect to the derivatives of the velocity components tangential to the interface along the coordinates of the plane tangential to the interface, and invariance under surface rotation. This tensor was first introduced by Scriven (1960) and is written as

$$\sigma^{(s)} = (\eta_d - \eta_s)\left(\nabla^{(s)}\boldsymbol{u}^{(s)}\right) \cdot \boldsymbol{I}^{(s)} + \eta_s \left[\left(\nabla^{(s)}\boldsymbol{u}^{(s)}\right) \cdot \boldsymbol{I}^{(s)} + \boldsymbol{I}^{(s)} \cdot \left(\nabla^{(s)}\boldsymbol{u}^{(s)}\right)^{\mathrm{T}}\right]. \tag{2.17}$$

Here $\boldsymbol{I}^{(s)} = \boldsymbol{I} - (\boldsymbol{n}\boldsymbol{n})$ (where $\boldsymbol{I}$ is the unit tensor) is the surface tensor projecting any vector onto the interface, the tensor $(\nabla^{(s)}\boldsymbol{u}^{(s)})^{\mathrm{T}}$ is conjugate to the tensor $(\nabla^{(s)}\boldsymbol{u}^{(s)})$, η_s and η_d are the shear and dilation surface viscosities, respectively.

The boundary conditions, linearly approximated in perturbation amplitude, are applied to the undisturbed drop surface. Then, from (2.12)–(2.17), we obtain the relations fulfilled at $r = R$,

$$\frac{\partial \varepsilon}{\partial t} - u_r = 0, \tag{2.18}$$

$$\begin{aligned} -p + 2\rho\nu \frac{\partial u_r}{\partial r} + 2\eta_d \frac{1}{r^2}\left(\frac{\partial u_\vartheta}{\partial \vartheta} + u_\vartheta \mathrm{ctg}\vartheta + \frac{1}{\sin\vartheta}\frac{\partial u_\phi}{\partial \phi} + 2u_r\right) + \varGamma' \frac{\partial \gamma}{\partial \varGamma}\frac{2}{r} \\ - \gamma_0 \frac{1}{r^2}\left(2\varepsilon + \frac{\partial^2 \varepsilon}{\partial \vartheta^2} + \mathrm{ctg}\vartheta \frac{\partial \varepsilon}{\partial \vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2 \varepsilon}{\partial \phi^2}\right) = 0, \end{aligned} \tag{2.19}$$

$$\rho\nu\left(\frac{1}{r}\frac{\partial u_r}{\partial\vartheta}+\frac{\partial u_\vartheta}{\partial r}-\frac{u_\vartheta}{r}\right)-(\eta_s+\eta_d)\frac{1}{r^2}\frac{\partial}{\partial\vartheta}\left(\frac{\partial u_\vartheta}{\partial\vartheta}+u_\vartheta\mathrm{ctg}\vartheta+\frac{1}{\sin\vartheta}\frac{\partial u_\phi}{\partial\phi}\right)$$
$$-2\eta_s\frac{u_\vartheta}{r^2}-2\eta_d\frac{1}{r^2}\frac{\partial u_r}{\partial\vartheta}-\frac{\partial\gamma}{\partial\Gamma}\frac{1}{r}\frac{\partial\Gamma'}{\partial\vartheta}=0, \qquad (2.20)$$

$$\frac{\partial\Gamma'}{\partial t}+\Gamma_0\frac{1}{r}\left(\frac{\partial u_\vartheta}{\partial\vartheta}+u_\vartheta\mathrm{ctg}\vartheta+\frac{1}{\sin\vartheta}\frac{\partial u_\phi}{\partial\phi}\right)+2\Gamma_0\frac{u_r}{r}=0. \qquad (2.21)$$

Here γ_0 is the surface tension when the surfactant has its equilibrium distribution, not to be confused with the surface tension of the pure system, γ_{pure}, without surfactant. It can be calculated from the Langmuir adsorption isotherm by the (Szyszkowski 1908; Belton 1976) equation,

$$\gamma_0=\gamma_{pure}-\bar{R}T\Gamma_0\ln(1+Ka), \qquad (2.22)$$

where $\bar{R}$ is the gas constant, T is the absolute temperature, K is the adsorption coefficient and a is the activity of the surface active species.

It should also be noted that a variation in surface coverage, as defined in (2.15), leads, through the Belton equation, (2.22), to a variation of the surface tension along the surface. As is well known, this leads to Marangoni convection, which is neglected here as a second-order effect.

3. Results and discussion

3.1. *The dispersion relation for eigenfrequencies*

For perturbations of the meridional type, the deformation of the shape of the drop surface and the deviation of the surface concentration of a surfactant from its equilibrium value are, in linear approximation, given by

$$\varepsilon=\Phi Y_l^m(\vartheta,\phi)\exp(\mathrm{i}\Omega_l t)+\text{c.c.}, \qquad (3.1)$$

$$\Gamma'=\Lambda Y_l^m(\vartheta,\phi)\exp(\mathrm{i}\Omega_l t)+\text{c.c.}. \qquad (3.2)$$

Substituting (2.3)–(2.5), (2.9), (2.11), (3.1) and (3.2) into (2.18)–(2.21), we can derive an equation for the amplitudes of the perturbations (some obvious transformations have been done to remove the amplitude Λ from the consideration). It reads in dimensionless variables

$$l(l+1)\mathrm{A}+l\frac{\mathrm{i}}{\theta_l}\Pi-\mathrm{i}\theta_l\Phi=0, \qquad (3.3)$$

$$2l(l+1)H_2Q(x)\mathrm{A}+\left[2l(l-1)H_2\frac{\mathrm{i}}{\theta_l}-1\right]\Pi+(l-1)(l+2)\Phi=0, \qquad (3.4)$$

$$[\mathrm{i}\theta_l+MQ(x)+2(l-1)(l+2)H_1]\mathrm{A}+(M+2lH_2)\frac{\mathrm{i}}{\theta_l}\Pi=0. \qquad (3.5)$$

Here,

$$M=l(l+1)(H_1-H_2)-2H_1, \quad H_1=\delta+h_s, \quad H_2=\delta-h_d+k\frac{\mathrm{i}}{\theta_l}; \qquad (3.6)$$

$$Q(x)=l-1-\frac{xj_{l+1}(x)}{j_l(x)}. \qquad (3.7)$$

To reduce the problem to non-dimensional form, we have chosen the equilibrium radius of the drop R for the unit of length, and, for the unit of time the quantity $\tau = \sqrt{\rho R^3/\gamma_0}$, which is essentially the inverse of the Rayleigh frequency, (1.1). Then, the units of the perturbation amplitudes are expressed as follows: $[\mathrm{A}] = R^2\tau$, $[\Pi] = \rho/\tau^2 R^{l-2}$ and $[\Phi] = R$. Further, we use the same notation for the dimensionless amplitudes as for the dimensional ones. We have also introduced the following additional dimensionless parameters: $\theta_l = \Omega_l \tau$ is the natural frequency of the oscillations of the drop, $\delta = \nu\tau/R^2$ is the inverse Reynolds number, as defined in (1.3); $x = \sqrt{-\mathrm{i}\theta_l/\delta}$, $h_s = \eta_s \tau/R^3$ and $h_d = \eta_d \tau/R^3$ are the parameters of the shear and dilatation surface viscosities, respectively.

The dimensionless parameter $k = (\partial\gamma/\partial\Gamma)\Gamma_0/\gamma_0$ is the parameter of the surfactant effect on the surface tension. By definition, $k \leqslant 0$; it is related to the Gibbs elasticity E by $E = -k\gamma_0$, therefore, k is also the parameter of Gibbs elasticity. The Belton equation (2.22) gives

$$k = \frac{1}{1 - \dfrac{\gamma_{pure}}{\bar{R}\mathrm{T}\Gamma_0 \ln(1+\mathrm{K}a)}} = \frac{\gamma_0 - \gamma_{pure}}{\gamma_0}. \tag{3.8}$$

As can be seen, the absolute value of k increases when the surface tension decreases by the influence of surfactant.

The system (3.3)–(3.5), written for the amplitudes A, Π and Φ, has non-trivial solutions only when its determinant is equal to zero. From this condition, one obtains the frequencies as eigenvalues. The frequency mode with meridional number l exhibits an $2l+1$-fold degeneracy in the azimuthal number m.

3.2. *The limit of small bulk shear viscosity*

The limit of small bulk shear viscosity, commonly encountered in practice, is associated with the capillary number δ tending to zero. In this case, $Q(x)$ tends to its asymptotic value.

If $\mathrm{i}\theta_l$ is a negative real quantity, corresponding to aperiodic damping, we obtain the asymptotic estimate for $Q(x)$,

$$\lim_{x-l\to\infty} Q(x) \to l - 1 + x\,\mathrm{ctg}\left(x - l\frac{\pi}{2}\right), \tag{3.9}$$

which, obviously, is large for almost all combinations of parameters x and l.

If, on the other hand, $\mathrm{i}\theta_l$ is not a negative real quantity, we obtain for large negative values of the imaginary part of the argument,

$$\lim_{\mathrm{Im}\,x+l\to-\infty} Q(x) \to \mathrm{i}x. \tag{3.10}$$

We next define the principal part of the natural frequency of the free capillary oscillations of the drop, θ_{l0}, and a small correction to this part, θ_{l1}, caused by viscous dissipation in the liquid, and the influence of the surfactant film. Note that for certain cases discussed below the dissipation influence can occur already in the leading order.

3.2.1. *Weak dissipation case*

Now we consider the case of weak dissipation when its effect to the drop capillary oscillations is expressed by a small correction. Then the principal part of the natural frequency θ_{l0} is

$$\theta_{l0} = \sqrt{l(l-1)(l+2)}, \tag{3.11}$$

which corresponds to the Rayleigh frequency, for $l = 2$, (1.1).

General expression for the correction θ_{21} to the Rayleigh frequency has been given by Apfel and coworkers (Tian *et al.* 1995; Tian, Holt & Apfel 1997), allowing for different types of surfactant transfer between the liquid volume and the surface layer. Their correction can be rewritten in our terms, (neglecting the transport of the surfactant between the bulk of fluid and the surface layer and the diffusion of the surfactant in the layer) in the form,

$$\theta_{21} = \sqrt{2}\frac{12\beta_s \mathrm{i} - \left[1 + 16(8^{1/4}\sqrt{\mathrm{i}/\delta} - 3\mathrm{i})\beta_s\right] P}{1 + \left(8^{1/4}\sqrt{\mathrm{i}/\delta} - 3\mathrm{i}\right)(3P\mathrm{i} + 4\beta_s)}, \tag{3.12}$$

where

$$P = \frac{k}{4} + 2\beta_d \mathrm{i}, \quad \beta_s = (\delta + h_s)/\sqrt{8}, \quad \beta_d = (\delta - h_d)/\sqrt{8}. \tag{3.13}$$

This result has been obtained with the assumption that $\delta \ll 1$, and the correction, caused by viscous dissipation in the liquid and the influence of the surfactant film, is small with respect to the Rayleigh frequency.

The expression (3.12) can be reduced by removing some minor terms from its numerator and denominator without precision loss in the leading order. The reduced expression for the correction has the form,

$$\theta_{21} = \frac{5\delta\mathrm{i} + 6h_s\mathrm{i} - \left(\sqrt{2} + 8^{5/4}h_s\sqrt{\mathrm{i}/\delta}\right)q}{1 + 8^{1/4}\sqrt{\mathrm{i}/\delta}\left(3q\mathrm{i} + \sqrt{2}h_s\right)}, \tag{3.14}$$

where

$$q = \frac{k}{4} - \frac{h_d}{\sqrt{2}}\mathrm{i}. \tag{3.15}$$

Apparently, the general expression for θ_{l1} must have the same structure as the correction (3.14). The dilatation surface viscosity h_d and the Gibbs elasticity k must act together with the combination $(h_d - k\mathrm{i}/\theta_{l0})$ originating in the leading order from the combination H_2 in (3.4) and (3.5). It allows us to specify the conditions when simplified expressions for the corrections can be given. Each factor (the bulk shear viscosity, the surface viscosities and the Gibbs elasticity) has a separate contribution to these expressions presented below for arbitrary l.

If $h_s \ll 1$, $h_d \sim 1$ or $|k|/\theta_{l0} \sim 1$, the imaginary part of the correction θ_{l1} corresponding to the damping decrement is

$$\operatorname{Im}\theta_{l1} = \frac{1}{2\sqrt{2}}\frac{[l(l-1)(l+2)]^{1/4}(l-1)^2}{l+1}\sqrt{\delta} + \frac{2(l-1)(l+2)}{(l+1)}h_s, \tag{3.16}$$

and the real part of the correction corresponding to the frequency shift is

$$\operatorname{Re}\theta_{l1} = -\frac{1}{2\sqrt{2}}\frac{[l(l-1)(l+2)]^{1/4}(l-1)^2}{l+1}\sqrt{\delta}. \tag{3.17}$$

In the limit of vanishing h_s, the solutions (3.16) and (3.17) reduce to Miller–Scriven result (Miller & Scriven 1968) for a liquid drop of small bulk shear viscosity covered by an inextensible film. The inclusion of the shear surface viscosity leads to an increase of the imaginary part of the natural frequency but does not affect its real part. The dilatation surface viscosity, h_d, does not enter the leading correction to the natural frequency. Note, as mentioned by Tian *et al.* (1995), the dilatational surface viscosity is usually much larger than the shear surface viscosity ($\eta_d \gg \eta_s$) for a soluble surfactant (they can be compatible for insoluble surfactants).

Rewriting (3.16) for vanishing h_s and for $l=2$, we obtain, in physical quantities, the Miller–Scriven damping constant λ_{MS},

$$\lambda_{MS} = \frac{1}{6}\frac{\left(\dfrac{2\gamma R}{\rho}\right)^{1/4}\nu^{1/2}}{R^2}. \tag{3.18}$$

Equation (3.18) has been written in a form to resemble the classical result of Lamb, (1.2). Note the different dependencies on the material properties, namely surface tension, density and viscosity.

If $h_s \sim 1$, $h_d \ll 1$ and $|k|/\theta_{l0} \ll 1$, the corrections to the undamped periodic mode are given by

$$\operatorname{Im}\theta_{l1} = \frac{1}{2\sqrt{2}}[l(l-1)(l+2)]^{1/4}(l+1)\sqrt{\delta} + 2lh_d, \tag{3.19}$$

$$\operatorname{Re}\theta_{l1} = -\frac{1}{2\sqrt{2}}[l(l-1)(l+2)]^{1/4}(l+1)\sqrt{\delta} - 2\sqrt{\frac{l}{(l-1)(l+2)}}k. \tag{3.20}$$

Rewriting (3.19) for vanishing h_d and k and for $l=2$, we obtain, in physical quantities, some damping constant λ_1,

$$\lambda_1 = \frac{3}{2}\frac{\left(\dfrac{2\gamma R}{\rho}\right)^{1/4}\nu^{1/2}}{R^2}, \tag{3.21}$$

which is nine times higher than the Miller–Scriven damping constant (3.18).

If, h_s, h_d and $|k|/\theta_{l0}$ are small in comparison to $\sqrt{\delta}$ then the corrections to the eigenfrequency have the form,

$$\operatorname{Im}\theta_{l1} = \tfrac{1}{2}\left[2(2l+1)(l-1)\delta + (l^2-1)(l+2)h_s + l(l-1)^2h_d\right], \tag{3.22}$$

$$\operatorname{Re}\theta_{l1} = -\frac{1}{2}\sqrt{\frac{l(l-1)^3}{l+2}}k. \tag{3.23}$$

These equations are also a generalisation of Lamb's result, (1.2), but, in contrast to (3.16), they converge to the classical limit for $h_s \to 0$, $h_d \to 0$ and $k \to 0$.

Let us discuss (3.22) in some more detail. As can be seen, the different contributions to the imaginary part of the frequency by the bulk and surface viscosities scale differently with respect to l. Therefore, if one can measure the damping of the $l=2, 3, 4$ modes, one obtains three equations for the three unknowns δ, h_s and h_d, and all viscosities can be determined. On the other hand, if one considers (3.22) for $l=2$, one obtains, in physical quantities,

$$\operatorname{Im}\theta_{21} = \frac{5\tau}{R^2}\left(\nu + \frac{6\eta_s + \eta_d}{5R}\right), \tag{3.24}$$

which allows one to define an effective viscosity,

$$\nu_{eff} = \nu + \frac{6\eta_s + \eta_d}{5R}. \tag{3.25}$$

In this case, measurement of the damping constant for spheres of different radius R allows us to disentangle the contributions of the bulk and surface viscosities.

As can be seen from (3.16) and (3.19), the contribution to the damping rate due to bulk shear viscosity can be proportional to the square root of viscosity in the presence of a surfactant, whereas in its absence (1.2) is linear in the viscosity. Thus, the very presence of the surfactant film can increase the damping effect of bulk viscosity. Such increase in viscous dissipation has been reported before (Levich 1962; Miller & Scriven 1968; Tian *et al.* 1995). It is related to a change in the character of the boundary layer caused by a different boundary condition on the balance of the tangential stresses in the presence of a surfactant. The factor controlling such change for the fundamental oscillation mode, $l=2$, is the combination $(3q\mathrm{i}+\sqrt{2}h_s)$ from (3.14). The criterion for the transition to the linear damping rate is $|3q\mathrm{i}+\sqrt{2}h_s|\ll\sqrt{\delta}$. One can formulate the general criterion for arbitrary l as $h_s\ll\sqrt{\delta}$, $h_d\ll\sqrt{\delta}$ and $|k|/\theta_{l0}\ll\sqrt{\delta}$.

3.2.2. *Significant dissipation case*

Now we consider in detail the case when one or two of the surface viscosities is no longer a small quantity, which can cause significant dissipation already in the leading order. If $h_s\sim 1$ or $h_d\sim 1$, the leading order of the natural frequency is defined by

$$(a\theta_{l0}-1)\left[\theta_{l0}^2-l(l-1)(l+2)\right]+b\theta_{l0}^2+c\theta_{l0}=0, \tag{3.26}$$

where

$$a=\frac{l(l+1)(h_s+h_d)-2h_s}{l(l+1)k}\mathrm{i},\quad b=\frac{4(l-1)(l+2)}{(l+1)}\frac{h_sh_d}{k},\quad c=\frac{4(l-1)(l+2)h_s}{(l+1)}\mathrm{i}, \tag{3.27}$$

which reduces to a real cubic equation for $\mathrm{i}\theta_{l0}$.

As stated before, $k\leqslant 0$. In this case, for $h_s>0$ and $h_d>0$, the Hurwitz-criterion (Korn & Korn 1968) shows that all roots of (3.26) for $\mathrm{i}\theta_{l0}$ have negative real parts corresponding to damped oscillations.

Equation (3.26) for $\mathrm{i}\theta_{l0}$ has either one real and two complex conjugate roots or three real roots. This corresponds either to one aperiodic and one periodic mode, or three different aperiodic modes of drop oscillations (one aperiodic solution relates to the Gibbs elasticity (Tian *et al.* 1995) and vanishes for $k=0$ and there are one periodic or two aperiodic solutions in this case). The regions of the parameters h_s and h_d, where the above solutions exist, are shown in figure 1.

The real and imaginary parts of the solutions to (3.26), θ_{l0}, are shown for $l=2,3,4$ and $k=-1$ in figures 2 and 3, as functions of h_s and h_d, respectively. Note a slight effect of the meridional number l to the solution associated with the Gibbs elasticity (the lower curves in figures 2(a) and 3(a).

The transition to aperiodic solutions resulting from the action of the surface viscosities takes place at some curve connecting the shear and dilatational surface viscosities. It turns out that this transition is possible only in the presence of both viscosities and cannot occur if one of the surface viscosities is small (with the exception of the case of large negative values of the Gibbs elasticity to be discussed below).

From figures 1(a), 2(a) and 3(a), it can be seen that the onset of the overdamped regime is different for the surface viscosity as compared to the bulk shear viscosity (Prosperetti 1980). As the meridional number l increases, the region with aperiodic modes is reduced in contrast to the case of the bulk shear viscosity. But this is not accompanied by a decrease of the damping rate, which, of course, increases with increasing meridional number.

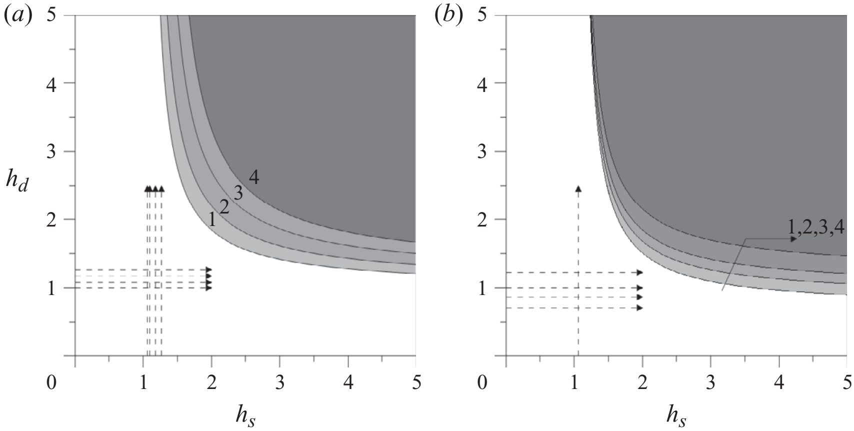

FIGURE 1. The regions of the parameters h_s and h_d for which, at small bulk shear viscosity, there exist either three aperiodic modes (shaded region) or one aperiodic and one periodic mode (unshaded region) of the solutions to (3.26). (a) $k=-1$. 1: $l=2$; 2: $l=3$; 3: $l=4$; 4: $l=5$. (b) $l=2$. 1: $k=0$; 2: $k=-0.5$; 3: $k=-1$; 4: $k=-2$. The arrowed dash lines present the asymptote locations to the shaded regions.

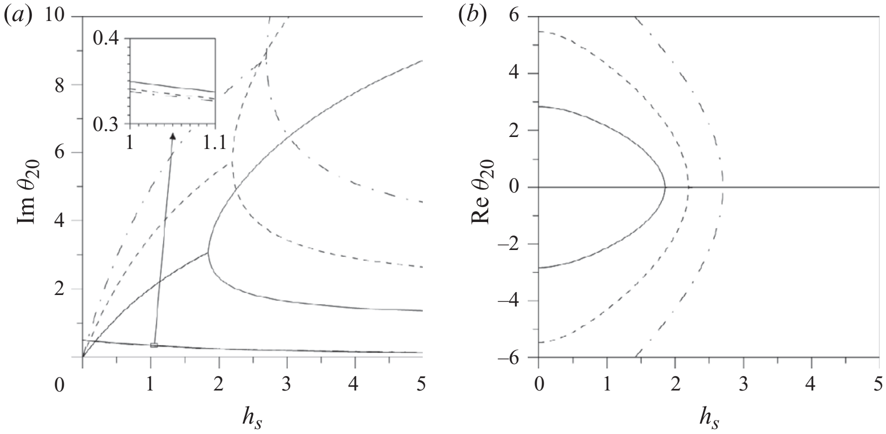

FIGURE 2. The imaginary (a) and real (b) parts of the solutions to (3.26) as function of the parameter h_s in the case of small bulk and finite surface viscosities. For the plot, $h_d=2$ and $k=-1$ were chosen. The solid, dash and dash-dotted line present the solution calculated for $l=2, 3, 4$, respectively.

As can be seen from figure 2, the decrement increases with the shear surface viscosity in general; upon further increase, the periodic decay is replaced by the aperiodic decay mode. This scenario, however, is not the only one possible. For large negative values of the Gibbs elasticity coefficient ($k<-8$), the damping rate decreases with increasing shear surface viscosity. In this special case, the transition to aperiodic damping occurs in other domains of the parameter space, different from those shown in figure 1, and is possible for arbitrary values of the dilatational surface viscosity. Under such circumstances, there is an alternation of modes with increasing shear surface viscosity: the periodic decay regime is first replaced by aperiodic decay, which then goes back to the regime of periodic decay. Note, however, that the realization of this particular case is hardly possible in practice, where the absolute value of k is

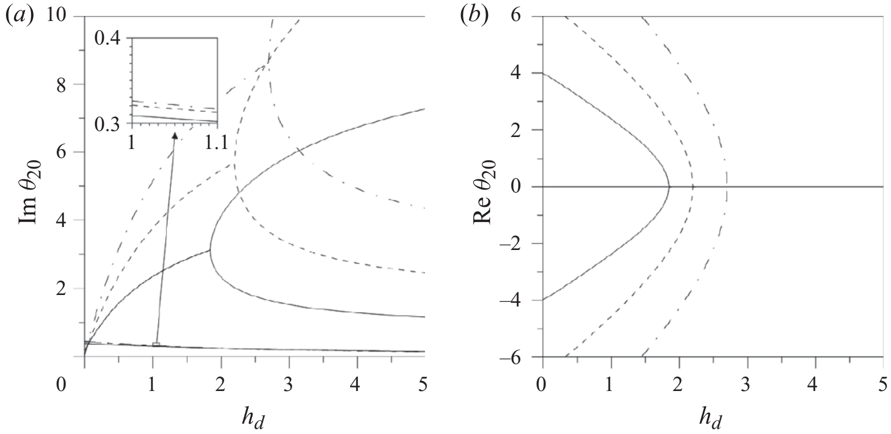

FIGURE 3. The imaginary (a) and real (b) parts of the solutions to (3.26) as function of the parameter h_d in the case of small bulk and finite surface viscosities. For the plot, $h_s = 2$ and $k = -1$ were chosen. The solid, dash and dash-dotted line present the solution calculated for $l = 2, 3, 4$, respectively.

usually of the order of unity. For this reason, in the present work, such case is not considered in detail.

3.2.3. *Special cases*

Here we consider some special cases of (3.26) when one of the parameters h_s, h_d and $|k|$ tends to infinity.

If $h_s \rightarrow \infty$, the solutions are given by

$$\theta_{l0}^2 - 4lh_d \mathrm{i}\theta_{l0} + 4lk - l(l-1)(l+2) = 0, \tag{3.28}$$

and one aperiodic mode is degenerate. Obviously, this is the mode related to the Gibbs elasticity. The transition between the aperiodic and periodic modes is defined by the threshold value of h_d,

$$h_{d\ thr} = \sqrt{\frac{(l-1)(l+2) - 4k}{4l}}. \tag{3.29}$$

If $h_d \rightarrow \infty$, the solutions are given by

$$\theta_{l0}^2 - \frac{4(l-1)(l+2)h_s}{(l+1)} \mathrm{i}\theta_{l0} - l(l-1)(l+2) = 0. \tag{3.30}$$

The aperiodic mode related to the Gibbs elasticity is degenerate and the transition between the case of one periodic mode and two aperiodic modes is defined by the threshold value of h_s,

$$h_{s\ thr} = \sqrt{\frac{l(l+1)^2}{4(l-1)(l+2)}}. \tag{3.31}$$

The threshold values (3.29) and (3.31) define the asymptotes for the boundaries of the system parameter regions with different mode types, as shown in figure 1.

If $k \rightarrow -\infty$, the solutions are given by (3.30), as for the case $h_d \rightarrow \infty$. In addition, a damped aperiodic mode related to the Gibbs elasticity exists,

$$\theta_{l0} = -\frac{l(l+1)k}{l(l+1)(h_s + h_d) - 2h_s} \mathrm{i}. \tag{3.32}$$

The transition to the parameter region, when only aperiodic modes exist, is defined by the threshold value (3.31). Note, the transition to aperiodic solutions can be carried out with an arbitrary dilatation viscosity. However, the threshold for the shear surface viscosity does not disappear in this case.

4. Conclusion

In the present work, the influence of a surfactant adsorbed in the surface layer of a liquid on free capillary oscillations of the spherical liquid drop has been considered in the limit of small bulk shear viscosity. In contrast to the previous works, we obtain our results through systematic perturbation theory in powers of the surface viscosity.

First the case of weak dissipation has been considered when the effect of the bulk shear viscosity, the shear and dilatation surface viscosities and the Gibbs elasticity to the drop capillary oscillations is expressed by a small correction. The conditions have been specified when simplified expressions for the correction can be given. Each factor (the bulk shear viscosity, the surface viscosities and the Gibbs elasticity) has a separate contribution to these expressions. The corresponding expressions are presented.

It is well known that the very presence of the surfactant film can increase the damping effect of bulk viscosity. The contribution to the damping rate due to bulk shear viscosity can be proportional to the square root of viscosity in the presence of a surfactant, whereas in its absence or insufficient is linear in the viscosity. In the present work, a criterion has been presented about value orders of the surface viscosities and the Gibbs elasticity to save the linear contribution to damping rate.

In the limit of finite surface viscosity, which can cause significant dissipation already in the leading order, an equation that determines the leading order of the oscillation frequencies has been obtained. The parameter space has areas where there are periodic and aperiodic solutions, or three different aperiodic solutions. Note that one of the aperiodic solutions exists whenever the Gibbs elasticity is different from zero (Tian *et al.* 1995).

In the case of the small or finite Gibbs elasticity, the transition to aperiodic solutions is determined by the combined action of the shear and dilatation surface viscosities and is impossible, if one of the surface viscosities is small.

A difference exists between the surface viscosity effect to a transition to an overdamped regime, where only aperiodic solutions exist, from the similar effect of the bulk shear viscosity. As the meridional number increases, as the region with aperiodic modes is reduced that is opposite to the effect of the bulk shear viscosity. But it is not accompanied by decreasing of the damping rate, which increases when the meridional number increases.

If the Gibbs elasticity has a large negative value, then the transition to aperiodic solutions can be carried out with an arbitrary dilatation viscosity, but the threshold for the shear surface viscosity does not disappear in this case.

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