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Shape oscillations of drops in the presence of surfactants

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The shape oscillations of drops in another fluid with or without surfactants has been analysed by normal mode expansions. The effects of surfactants are accommodated by considering the Gibbs elasticity, associated with the redistribution of surfactants, and a Boussinesq surface fluid with two surface viscosities. A general transcendental equation for the complex frequency of the free oscillations is derived. Explicit dispersion relations are given for fluids of small bulk viscosities and an interface of small, moderate, and large interfacial properties by a perturbation method. We have found that the oscillation always damps out faster for an interface exhibiting interfacial properties other than the interfacial tension, and the Gibbs elasticity is the most important parameter that alters the free-oscillation frequency and the damping constant. Moreover, the energy dissipation for an extensible interface can be much higher than that of an inextensible interface owing to the strong vorticity generated in the boundary layers.

1. Introduction

The dynamic response of a fluid drop has often been discussed in one form or another because of its significance in a great variety of applications, such as nuclear physics, meteorology, and chemical engineering. Rayleigh (1879, 1902) first studied the small-amplitude oscillations of an inviscid fluid drop held together by interfacial tension and identified the free oscillation frequencies. He also established the amount of charge allowed for stable oscillations of a charged liquid drop (Rayleigh 1882), which was later used as a model for nuclear fission (Cohen & Swiatecki 1962; Nix 1972). The rate of damping of the oscillations due to bulk viscosities of the fluids was investigated by Lamb (1932), Reid (1960), Miller & Scriven (1968) and Prosperetti (1977, 1980). Among them, Miller & Scriven (1968) analysed a more general case, in which not only the viscosities of the drop in an infinite outer fluid but also rheologic properties, besides the usual interfacial tension, manifest on the interface were considered. They, however, only gave expressions for the free-oscillation frequency and damping constant for the cases of a free and an inextensible interface.

In this paper we present a theoretical analysis of a fluid drop oscillating in another fluid with and without surfactants, a problem encountered frequently in emulsions and foams. The aim is to establish the effects of surface properties of arbitrary magnitude and of the rate of diffusion of surfactants on the oscillations of drops, and to lay the basis for probing the interfacial properties by investigating the oscillations of drops with an acoustic levitation technique (Lu & Apfel 1990). The study can also supplement Miller & Scriven's for an interface with small or moderate interfacial properties, since our case reduces to theirs when the surfactants are insoluble in both fluids and only condense onto the interface.

Our analysis parallels that of Miller & Scriven except that the surface elasticity is associated with the redistribution of surfactants while the drop is oscillating. A normal mode expansion and a perturbation method are used to find the free-oscillation frequency and damping constant of the drop for the cases of zero, small, moderate and large interfacial properties. We show that the change of the frequency and damping constant is more marked for an extensible than an inextensible interface, and the amplitude of the oscillation damps out faster when the interface exhibits rheological properties, owing to the generation of strong vorticities in the boundary layers. (Such an observation follows directly from the work of Landau & Liftshitz (1959), who showed that the decay of oscillations in an oscillating boundary layer is proportional to $(\omega\nu)^{\frac{1}{2}}$. Miller & Scriven (1968) retrieved the same result for oscillating drops, thus confirming that the mechanism of viscous dissipation in a boundary layer is of fundamental importance in this problem.)

2. Statement of the problem

We consider the small-amplitude oscillations of a drop immersed in an unbounded fluid. The outer fluid may contain surfactants, but the concentration is sufficiently low that the bulk properties of the outer fluid are unchanged. Therefore, the governing equations of the bulk motion are the same as those for the pure fluids. The presence of the surfactants, however, alters the interfacial properties. For example, the interfacial tension may be reduced, and the interface may become viscoelastic. In our analysis, the surface fluid is assumed to be of the Boussinesq type (Boussinesq 1913), so that the surface viscous force is a linear function of the surface strain with two proportional constants of surface shear and dilatational viscosities. Gibbs elasticity (surface dilatational elasticity) due to the sensitive dependence of the interfacial tension on the concentration of surfactants is also considered. Furthermore the interfacial tension gradient – caused by local expansion and compression of the interface as the drop oscillates, finite diffusion rates of surfactants and manifestation of the Gibbs elasticity – is analysed. These effects of surfactants result in additional resistance to the interfacial deformation and eventually change the characteristics of the oscillations.

3. Governing equations

We consider an incompressible fluid drop of radius R surrounded by another infinite incompressible fluid with surfactants, whose equilibrium concentration C_0 determines the equilibrium interfacial tension γ_0. The gravitational force is either balanced by other forces such as the acoustic radiation force, or negligible since the capillary constant $(2\gamma_0/\Delta\rho g)^{\frac{1}{2}}$ ($\Delta\rho$ is the difference in fluid densities and g the local acceleration due to gravity) is much larger than the radius of the drop. Therefore, in the absence of net body forces, the Navier–Stokes equation is

$$\frac{\partial \boldsymbol{v}^*}{\partial t^*} + (\boldsymbol{v}^* \cdot \boldsymbol{\nabla}^*)\, \boldsymbol{v}^* = -\boldsymbol{\nabla}^* p^* + \nu \nabla^{*2} \boldsymbol{v}^*, \tag{1}$$

where $\boldsymbol{v}^*$ is the velocity field, p^* the pressure field, and ν the kinematic viscosity. Note that all quantities, where applicable, carry subscripts i and o for the droplet and continuous phase respectively.

The viscosities of the fluids are assumed to be small, as in most practical cases. The free-oscillation frequency of the drop is, thus, close to the Lamb frequency ω^* (Lamb 1932),

$$\omega^{*2} = \frac{\gamma_0 L(L-1)(L+1)(L+2)}{[L\rho_o + (L+1)\rho_i]R^3},$$

where the integer L denotes the mode of oscillation. The Reynolds number for the oscillation, $x^2 \equiv R^2\omega^*/\nu$, is assumed to be sufficiently large that the penetration depth of the rotational flow is small compared with the radius of the drop. Additionally, only the nonlinear term in the Navier–Stokes equation can be neglected if the oscillation amplitude of the drop is much smaller than the radius (Landau & Lifshitz 1959).

Under these conditions, scales based on the linear theory for inviscid drops can be used to define the dimensionless velocity, $\boldsymbol{v} = \boldsymbol{v}^*/R\omega^*$, pressure, $p = p^*/\rho R^2\omega^{*2}$, time $t = \omega^* t^*$, and position, $\boldsymbol{r} = \boldsymbol{r}^*/R$. In terms of these variables, the condition of incompressibility and the linearized Navier–Stokes equation become

$$\boldsymbol{\nabla}\cdot\boldsymbol{v} = 0, \tag{2}$$

and

$$x^2\frac{\partial \boldsymbol{v}}{\partial t} = -x^2\boldsymbol{\nabla}p + \nabla^2\boldsymbol{v}. \tag{3}$$

If the time-dependent part $\mathrm{e}^{-\alpha^2 t}$ ($\alpha^2 \equiv \omega/\omega^*$ is the complex dimensionless frequency with the real and imaginary part being the damping constant and oscillation frequency respectively) in $\boldsymbol{v}$ and p is factored out, (2) and (3) can be solved readily by using normal mode expansions (Chandrasekhar 1961). In spherical coordinates (with the origin located at the centre of the drop) the solutions are

$$p_i(\boldsymbol{r}) = q_i r^L Y_{LM}(\Omega)\,\mathrm{e}^{-\alpha^2 t}, \tag{4a}$$

$$p_o(\boldsymbol{r}) = q_o r^{-L-1} Y_{LM}(\Omega)\,\mathrm{e}^{-\alpha^2 t}, \tag{4b}$$

$$\boldsymbol{v} = (\boldsymbol{v}_T + \boldsymbol{v}_S)\,\mathrm{e}^{-\alpha^2 t}, \tag{5a}$$

$$\boldsymbol{v}_T = -T(r)\,\boldsymbol{e}_r \times \boldsymbol{\nabla}_s Y_{LM}(\Omega), \tag{5b}$$

$$\boldsymbol{v}_S = \boldsymbol{e}_r\frac{L(L+1)}{r^2}S(r)\,Y_{LM}(\Omega) + \frac{\mathrm{d}S(r)}{\mathrm{d}r}\boldsymbol{\nabla}_s Y_{LM}(\Omega); \tag{5c}$$

$$T_i(r) = b_i\, r j_L(\alpha x_i r), \tag{5d}$$

$$T_o(r) = b_o\, r h_L^{(1)}(\alpha x_o r), \tag{5e}$$

$$S_i(r) = a_i\, r j_L(\alpha x_i r) + \frac{q_i r^{L+1}}{\alpha^2(L+1)}, \tag{5f}$$

$$S_o(r) = a_o\, r h_L^{(1)}(\alpha x_o r) - \frac{q_o r^{-L}}{\alpha^2 L}. \tag{5g}$$

Here

$$\boldsymbol{\nabla}_s \equiv \boldsymbol{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \boldsymbol{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi},$$

$Y_{LM}(\Omega)$ are the spherical harmonics with Ω denoting coordinates $\theta, \phi, j_L(r)$ the spherical Bessel function of order L and $h_L^{(1)}(r)$ the spherical Hankel function of the first kind of order L. The subscripts, L, M, are integers ($L \geqslant 0$, $-L \leqslant M \leqslant L$) representing the modes of the oscillation. Modes of the same L but different M are degenerate.

4. Boundary conditions

When the drop is undergoing shape oscillations with amplitude $Re_{LM}, \epsilon_{LM} \ll 1$, its surface profile is described by a dimensionless shape function,

$$F(\theta,\phi) = r - (1 + \epsilon_{LM}\, Y_{LM}(\Omega)\, \mathrm{e}^{-\alpha^2 t}) = 0. \tag{6}$$

The boundary conditions evaluated at $F = 0$ include the kinematic conditions, $\mathrm{d}F/\mathrm{d}t = 0$, the continuity of the velocities, and the total stress balance. By using the velocity and pressure field derived above, the kinematic condition – the interface remains in contact with the neighbouring fluids during the course of the oscillations – gives that

$$L(L+1)\left[a_\mathrm{i} j_L(\alpha x_\mathrm{i}) + \frac{q_\mathrm{i}}{\alpha^2(L+1)}\right] + \alpha^2 \epsilon_{LM} = 0. \tag{7}$$

By the continuity of velocities we get

$$a_\mathrm{i} j_L(\alpha x_\mathrm{i}) + \frac{q_\mathrm{i}}{\alpha^2(L+1)} - a_\mathrm{o} h_L^{(1)}(\alpha x_\mathrm{o}) + \frac{q_\mathrm{o}}{\alpha^2 L} = 0, \tag{8}$$

$$a_\mathrm{i}[(L-1) j_L(\alpha x_\mathrm{i}) - \alpha x_\mathrm{i} j_{L+1}(\alpha x_\mathrm{i})] + \frac{(L-1)\, q_\mathrm{i}}{(L+1)\,\alpha^2} - a_\mathrm{o}[(L-1)\, h_L^{(1)}(\alpha x_\mathrm{o}) - \alpha x_\mathrm{o}\, h_{L+1}^{(1)}(\alpha x_\mathrm{o})] - \frac{(L+2)\, q_\mathrm{o}}{L\alpha^2} = 0, \tag{9}$$

$$b_\mathrm{i} j_L(\alpha x_\mathrm{i}) - b_\mathrm{o} h_L^{(1)}(\alpha x_\mathrm{o}) = 0. \tag{10}$$

Finally, the condition of the total stress balance should be satisfied. The total stress acting on the spherical interface consists of four parts: pressure stress $\boldsymbol{F}^*_\mathrm{p}$, bulk viscous stress $\boldsymbol{F}^*_\mathrm{bv}$, surface viscous stress $\boldsymbol{F}^*_\mathrm{sv}$, and tension stress $\boldsymbol{F}^*_\mathrm{ten}$. The pressure stress is

$$\boldsymbol{F}^*_\mathrm{p} = \boldsymbol{e}_r R^2 \omega^{*2} \langle \rho p \rangle_\mathrm{io}, \tag{11a}$$

where $\langle \rho p \rangle_\mathrm{io} \equiv \rho_\mathrm{i} p_\mathrm{i} - \rho_\mathrm{o} p_\mathrm{o}$. The bulk viscous stress is associated with the bulk shear viscosities of the fluids and is

$$\frac{1}{\omega^*}\boldsymbol{F}^*_\mathrm{bv} = \boldsymbol{e}_r \left\langle -2\eta \frac{\partial v_r}{\partial r} \right\rangle_\mathrm{io} - \left\langle \eta \boldsymbol{\nabla}_\mathrm{s} v_r + \eta \left(\frac{\partial}{\partial r} - 1\right) \boldsymbol{v}_\mathrm{s} \right\rangle_\mathrm{io}. \tag{11b}$$

Similarly, the surface viscous stress is associated with the surface shear viscosity (η_s) and surface dilatational viscosity (ξ_s) introduced by surfactants, and takes the form (Scriven 1960; Bupara 1964)

$$\frac{1}{\omega^*}\boldsymbol{F}_\mathrm{sv} = -\boldsymbol{e}_r \frac{2\xi_\mathrm{s}}{R}[\boldsymbol{\nabla}_\mathrm{s}\cdot \boldsymbol{v}_\mathrm{s} + 2v_r] + \frac{\xi_\mathrm{s}+\eta_\mathrm{s}}{R}\boldsymbol{\nabla}_\mathrm{s}(\boldsymbol{\nabla}_\mathrm{s}\cdot \boldsymbol{v}_\mathrm{s}) + \frac{2\eta_\mathrm{s} \boldsymbol{v}_\mathrm{s}}{R} + \frac{2\xi_\mathrm{s}}{R}\boldsymbol{\nabla}_\mathrm{s} v_r + \frac{\eta_\mathrm{s}}{R}\boldsymbol{e}_r \times \boldsymbol{\nabla}_\mathrm{s}(\boldsymbol{e}_r \cdot \boldsymbol{\nabla}_\mathrm{s} \times \boldsymbol{v}_\mathrm{s}). \tag{11c}$$

The tension stress has two terms: one due to the effect of curvature, and the other to the non-uniformity of the interfacial tension. It is

$$R\boldsymbol{F}^*_\mathrm{ten} = \gamma_0[-2(1+\gamma) H \boldsymbol{e}_r + \boldsymbol{\nabla}_\mathrm{s}\gamma], \tag{11d}$$

where γ is the dimensionless fluctuating interfacial tension and H is the dimensionless mean curvature of the interface.

The variation of the interfacial tension along the interface as the drop oscillates can be determined by assuming local equilibrium, with the interfacial tension and surface adsorption correlated by their equilibrium relationships (Levich 1962). We have assumed that the surfactants are only soluble in the outer fluid and that their distribution is governed by convection and diffusion. Under these conditions, the continuity equations for the fluctuating bulk surfactant concentration C and surface surfactant concentration Γ, non-dimensionalized by their dimensional equilibrium counterparts, are

$$y^2\frac{\partial C}{\partial t}+\nabla\cdot(Cv)=\nabla^2 C, \tag{12}$$

$$z^2\frac{\partial \Gamma}{\partial t}+z^2\left[\nabla\cdot v+\frac{2v_r}{r}\right]_{\mathrm{s}}=\nabla_{\mathrm{s}}^2\Gamma+\frac{RDC_0}{D_{\mathrm{s}}\Gamma_0}\left[\frac{\partial C}{\partial n}\right]_{\mathrm{s}}. \tag{13}$$

Here C_0 and Γ_0 are the equilibrium bulk and surface concentration of surfactants respectively, D and D_{s} are the bulk and surface diffusion constants of surfactants respectively, n the outward normal to the interface, $y^2\equiv R^2\omega^*/D$ the bulk Péclet number, and $z^2\equiv R^2\omega^*/D$ the surface Péclet number. To derive (13) we have used the Reynolds transport theorem on a curved surface (Lu 1988), and the term $D(\partial C/\partial n)_{\mathrm{s}}$ is the surfactant flux from the outer fluid to the interface. In general, D and D_{s} are of the order of 10^{-5} cm^2/s. Thus, y^2 and z^2 are of order 10^5 for oil drops of millimeter size and moderate interfacial tension (around 30 dyn/cm), which is much larger than the Reynolds number, x^2, of the order 10^2.

If the change of the bulk concentration is small and the interface is in equilibrium with the bulk fluids, the fluctuating interfacial tension can be expanded in terms of the fluctuating surface concentration, and the fluctuating surface concentration can be expanded in terms of the fluctuating bulk concentration. Hence,

$$\gamma\approx\left(\frac{\partial\gamma}{\partial\Gamma}\right)_0\Gamma=\frac{E\Gamma}{\gamma_0}, \tag{14}$$

and

$$\Gamma\approx\left(\frac{\partial\Gamma}{\partial C_{\mathrm{s}}}\right)_0 C_{\mathrm{s}}=\frac{\Lambda C_{\mathrm{s}}}{\Gamma_0}. \tag{15}$$

Here

$$E\equiv-\gamma_0\left(\frac{\partial\gamma}{\partial\Gamma}\right)_0,$$

and

$$\Lambda\equiv\Gamma_0\left(\frac{\partial\Gamma}{\partial C_{\mathrm{s}}}\right)_0.$$

Both E, usually termed Gibbs elasticity, and Λ are determined by the properties, and concentrations of surfactants, properties of the bulk fluids, and the local physical conditions. Note that variables with the subscript s should be evaluated at the interface, and variables with the subscript 0 denote quantities at equilibrium.

Again by using normal mode expansions, the solution of the linearized equation (12) can be found readily:

$$C=C_{LM}\;h_L^{(1)}(\alpha yr)\,Y_{LM}(\Omega)\,\mathrm{e}^{-\alpha^2 t}.$$

By using the known velocity field and (15), C_{LM} is determined by satisfying (13):

$$C_{LM}=\frac{-L(L+1)\,z^2\left[a_{\mathrm{i}}[(1-L)\,j_L(\alpha x_1)+\alpha x j_{L+1}(\alpha x_1)]+\dfrac{(1-L)\,q_1}{(1+L)\,\alpha^2}\right]}{\dfrac{\Lambda}{\Gamma_0}[\alpha^2 z^2-L(L+1)]\,h_L^{(1)}(\alpha y)+\dfrac{RDC_0}{D_{\mathrm{s}}\Gamma_0}[Lh_L^{(1)}(\alpha y)-\alpha y h_{L+1}^{(1)}(\alpha y)]}.$$

From (14) and (15), and the known surfactant distribution, the interfacial tension is then found as

$$\begin{aligned}\gamma^* &= \gamma_0+\gamma_0\left(\frac{\partial\gamma}{\partial\Gamma}\right)_0\left(\frac{\partial\Gamma}{\partial C_{\mathrm{s}}}\right)_0 C_{\mathrm{s}}\\ &= \gamma_0-\frac{E}{G\alpha^2}\left[\nabla\cdot\boldsymbol{v}+\frac{2v_r}{r}\right]_{\mathrm{s}},\end{aligned} \tag{16}$$

where

$$G = 1-\frac{L(L+1)}{\alpha^2 z^2}+\frac{LRC_0}{\alpha^2y^2A}-\frac{RC_0H_L(\alpha y)}{\alpha yA},$$

$$H_L(\alpha y) \equiv h^{(1)}_{L+1}(\alpha y)/h^{(1)}_L(\alpha y).$$

The factor $\nabla\cdot\boldsymbol{v}+(2v_r/r)_{\mathrm{s}}$ in (16) in fact represents the rate of local expansion of the interface. The interfacial tension thus changes with the local expansion and compression of the interface as the drop oscillates. The other two parameters that determine the change of the interfacial tension are the Gibbs elasticity and G, which is controlled by the diffusion rates both in the bulk fluids and on the interface and the amount of adsorption. In general, the adsorption number RC_0/A in G is much larger than one, so that the surface diffusion process is less important than the bulk diffusion process. Furthermore, higher diffusion rates lead to faster redistribution of surfactants and thus to a more uniform interfacial tension on the interface.

Stress balance demands that

$$\boldsymbol{F}^*_{\mathrm{p}}+\boldsymbol{F}^*_{\mathrm{bv}}+\boldsymbol{F}^*_{\mathrm{sv}}+\boldsymbol{F}^*_{\mathrm{ten}} = 0,$$

which gives

$$\begin{aligned}&\frac{-\Upsilon\epsilon_{LM}}{L(L+1)}+q_{\mathrm{i}}\left\{1-\frac{2L(L-1)}{\alpha^2}\left[\frac{1-\beta_{\mathrm{d}}}{x_{\mathrm{i}}^2}+\frac{\Upsilon\beta G}{L(L^2-1)(L+2)\alpha^2}\right]\right\}\\ &\quad -a_{\mathrm{i}}\,2L(L+1)\left[\frac{1-\beta_{\mathrm{d}}}{x_{\mathrm{i}}^2}+\frac{\Upsilon\beta G}{L(L^2-1)(L+2)\alpha^2}\right][(L-1)\,j_L(\alpha x_{\mathrm{i}})-\alpha x_{\mathrm{i}}j_{L+1}(\alpha x_{\mathrm{i}})]\\ &\quad -q_{\mathrm{o}}\hat{\rho}\left[1-\frac{2(L+1)(L+2)}{\alpha^2x_{\mathrm{o}}^2}\right]+a_{\mathrm{o}}\frac{2\hat{\rho}L(L+1)}{x_{\mathrm{o}}^2}[(L-1)\,h^{(1)}_L(\alpha x_{\mathrm{o}})\\ &\qquad\qquad -\alpha x_{\mathrm{o}}\,h^{(1)}_{L+1}(\alpha x_{\mathrm{o}})\,] = 0,\end{aligned} \tag{17}$$

$$\begin{aligned}&\frac{q_{\mathrm{i}}}{\alpha^2}\left[2(1-L)+\frac{\Upsilon\beta Gx_{\mathrm{i}}^2}{(L+1)(L+2)\alpha^2}-L(L-1)\,\beta_{\mathrm{d}}-(L-1)(L+2)\,\beta_{\mathrm{s}}\right]-\frac{2\hat{\eta}(L+2)\,q_{\mathrm{o}}}{\alpha^2}\\ &\quad -a_{\mathrm{i}}\left[2(L^2-1)-\alpha^2x_{\mathrm{i}}^2-\frac{\Upsilon\beta Gx_{\mathrm{i}}^2}{(L+2)\,\alpha^2}+L(L^2-1)\,\beta_{\mathrm{d}}+(L+2)(L^2-1)\,\beta_{\mathrm{s}}\right]j_L(\alpha x_{\mathrm{i}})\\ &\quad -a_{\mathrm{i}}\left[[2-L(L+1)\,\beta_{\mathrm{d}}-(L+2)(L-1)\,\beta_{\mathrm{s}}]\alpha x_i+\frac{\Upsilon\beta Gx_{\mathrm{i}}^3}{(L-1)(L+2)\,\alpha}\right]j_{L+1}(\alpha x_{\mathrm{i}})\\ &\qquad +a_{\mathrm{o}}\,\hat{\eta}[[2(L^2-2)-\alpha^2x_{\mathrm{o}}^2]\,h^{(1)}_L(\alpha x_0)+2\alpha x_{\mathrm{o}}\,h^{(1)}_{L+1}(\alpha x_{\mathrm{o}})] = 0,\end{aligned} \tag{18}$$

$$\begin{aligned}&b_{\mathrm{i}}[[(L-1)+(L+2)(L-1)\,\beta_{\mathrm{s}}]\,j_L(\alpha x_{\mathrm{i}})-\alpha x_{\mathrm{i}}j_{L+1}(\alpha x_{\mathrm{i}})]-\hat{\eta}b_{\mathrm{o}}[(L-1)\,h^{(1)}_L(\alpha x_{\mathrm{o}})\\ &\qquad -\alpha x_{\mathrm{o}}\,h^{(1)}_{L+1}(\alpha x_{\mathrm{o}})] = 0.\end{aligned} \tag{19}$$

Here $\hat{\rho}\equiv\rho_{\mathrm{o}}/\rho_{\mathrm{i}}$ is the density ratio, $\Upsilon\equiv L\hat{\rho}+L+1$ the reduced density ratio, $\hat{\eta}\equiv\eta_{\mathrm{o}}/\eta_{\mathrm{i}}$ the bulk shear viscosity ratio, $\beta_{\mathrm{s}} = \eta_{\mathrm{s}}/\eta_{\mathrm{i}}R$ the surface shear viscosity number, $\beta_{\mathrm{d}}\equiv\xi_{\mathrm{s}}/\eta_{\mathrm{i}}R$ the surface dilatational viscosity number, and $\beta\equiv E/\gamma_0$ the surface dilatational elasticity number.

5. Transcendental equation

Matching the boundary conditions results in seven homogeneous equations, (7)–(10), and (17)–(19), in seven unknown coefficients, ϵ_{LM}, a_i, q_i, a_o, q_o, b_i, and b_o. Hence non-trivial solutions for the seven unknowns exist only when the determinant of the coefficients is zero. This constraint leads to a transcendental equation for the dimensionless complex frequency α^2. Since b_i and b_o and the other five unknowns appear in two sets of equations independently, there are two transcendental equations corresponding to two different types of motions. The transcendental equation derived from (10) and (19) is

$$\begin{vmatrix} j_L(\alpha x_\mathrm{i}) & (L-1)[1+(L+2)\,\beta_\mathrm{s}]j_L(\alpha x_\mathrm{i})-\alpha x_\mathrm{i} j_{L+1}(\alpha x_\mathrm{i}) \\ h_L^{(1)}(\alpha x_\mathrm{o}) & \hat{\eta}[(L-1)\,h_L^{(1)}(\alpha x_\mathrm{o})-\alpha x_\mathrm{o} h_{L+1}^{(1)}(\alpha x_\mathrm{o})] \end{vmatrix} = 0. \tag{20}$$

This equation does not involve any interfacial properties except the surface shear viscosity. Furthermore, it can be found that the associated motion always decays without oscillations and is purely rotational with no radial motion of the fluid on the interface or in the bulks (Lu 1988). Therefore, this type of motion will not be considered here.

The transcendental equation obtained by setting the determinant of the other five coefficients to zero is

$$\begin{vmatrix} b_{11}\, b_{12}\, b_{13} \\ b_{21}\, b_{22}\, b_{23} \\ b_{31}\, b_{32}\, b_{33} \end{vmatrix} + A \begin{vmatrix} c_{11}\, c_{12}\, c_{13} \\ c_{21}\, c_{22}\, c_{23} \\ c_{31}\, c_{32}\, c_{33} \end{vmatrix} + B \begin{vmatrix} d_{11}\, d_{12}\, d_{13} \\ d_{21}\, d_{22}\, d_{23} \\ d_{31}\, d_{32}\, d_{33} \end{vmatrix} + 4ABJ_L(\alpha x_\mathrm{i})\left[\frac{-(2L+1)}{\alpha x_0}+H_L(\alpha x_\mathrm{o})\right] = 0, \tag{21}$$

where $$A = \frac{L(L+1)\,\beta_\mathrm{d}}{\alpha^2 x_\mathrm{i}^2} - \frac{\Upsilon \beta G}{(L-1)(L+2)\,\alpha^4}, \quad B = \frac{(L-1)(L+2)\,\beta_\mathrm{s}}{\alpha^2 x_\mathrm{i}^2},$$

$$b_{11} = c_{11} = d_{11} = -J_L(\alpha x_\mathrm{i}), \quad b_{12} = c_{12} = d_{12} = 2L+1,$$

$$b_{13} = c_{13} = d_{13} = \frac{-(2L+1)}{\alpha x_0} + H_L(\alpha x_\mathrm{o}), \quad b_{21} = d_{21} = \frac{-(L+1)}{\alpha x_\mathrm{i}} + \frac{2L(L+1)\,J_L(\alpha x_\mathrm{i})}{\alpha^2 x_\mathrm{i}^2},$$

$$b_{22} = d_{22} = \Upsilon(1+\alpha^{-4}) - \frac{2\hat{\eta}L(L+1)(L+2)}{\alpha^2 x_\mathrm{i}^2} - \frac{2L(L^2-1)}{\alpha^2 x_\mathrm{i}^2},$$

$$b_{23} = d_{23} = \frac{-L\hat{\rho}}{\alpha x_\mathrm{o}} + \frac{2L(L+1)\,\hat{\eta}}{\alpha^2 x_\mathrm{i}^2}\left[\frac{(2L+1)}{\alpha x_\mathrm{o}} - H_L(\alpha x_\mathrm{o})\right],$$

$$b_{31} = \frac{1}{\alpha x_\mathrm{i}} - \frac{2J_L(\alpha x_\mathrm{i})}{\alpha^2 x_\mathrm{i}^2}, \quad b_{32} = \frac{2[1-L^2+\hat{\eta}L(L+2)]}{\alpha^2 x_\mathrm{i}^2},$$

$$b_{33} = \frac{-2\hat{\eta}(2L+1)}{\alpha^3 x_\mathrm{i}^2\, x_0} - \frac{\hat{\eta} x_\mathrm{o}}{\alpha x_\mathrm{i}^2} + \frac{2\hat{\eta} H_L(\alpha x_\mathrm{o})}{\alpha^2 x_\mathrm{i}^2}, \quad c_{21} = \frac{-(L-1)}{\alpha x_\mathrm{i}} + \frac{2(L-1)(L+2)\,J_L(\alpha x_\mathrm{i})}{\alpha^2 x_\mathrm{i}^2},$$

$$c_{22} = \Upsilon(1+\alpha^{-4}) - \frac{2(L+2)(L^2-1)}{\alpha^2 x_\mathrm{i}^2} - \frac{2\hat{\eta}L(L-1)(L+2)}{\alpha^2 x_\mathrm{i}^2},$$

$$c_{23} = \frac{-\hat{\rho}(L+2)}{\alpha x_\mathrm{o}} + \frac{2\hat{\eta}(L-1)(L+2)(2L+1)}{\alpha^3 x_\mathrm{i}^2\, x_\mathrm{o}} - \frac{2\hat{\eta}(L-1)(L+2)\,H_L(\alpha x_\mathrm{o})}{\alpha^2 x_\mathrm{i}^2},$$

$$c_{31} = d_{31} = J_L(\alpha x_\mathrm{i}) \quad c_{32} = 1-L, \quad c_{33} = d_{33} = 0, \quad d_{32} = -(L+1),$$

$$J_L(\alpha x_\mathrm{i}) \equiv j_{L+1}(\alpha x_\mathrm{i})/j_L(\alpha x_\mathrm{i}),$$

and
$$H_L(\alpha x_o) \equiv h^{(1)}_{L+1}(\alpha x_o)/h^{(1)}_L(\alpha x_o).$$

Equation (21) is so complicated that a general analytic solution is impossible to obtain. Nevertheless, by employing proper expansions, approximate solutions can be derived for several limiting cases.

6. Limiting cases

For a system with small viscosities and large Reynolds number, α, $J_L(\alpha x_i)$, $H_L(\alpha x_o)$, and G can be expanded as (Lu 1988)

$$\alpha^{-n} \approx i_s^{-n}[1-\tfrac{1}{2}n\epsilon^{(1)}+\tfrac{1}{4}n(\tfrac{1}{2}n+1)\,\epsilon^{(1)\,2}-\tfrac{1}{2}n\epsilon^{(2)}+\ldots], \tag{22}$$

$$J_L(\alpha x_i) \approx i+\frac{(L+1)}{i_s x_i}-\frac{(L+1)\,\epsilon^{(1)}}{2i_s x_i}+\ldots, \tag{23}$$

$$H_L(\alpha x_o) \approx -i+\frac{(L+1)}{i_s x_0}-\frac{(L+1)\,\epsilon^{(1)}}{2i_s x_o}+\ldots, \tag{24}$$

and
$$G \approx 1+i_s\lambda(1+\tfrac{1}{2}\epsilon^{(1)})-i\lambda L/y+\ldots. \tag{25}$$

Here $\epsilon^{(n)}$ is of the order $1/x^n$, $i_s \equiv (1+i)/\sqrt{2}$, and λ is the surface diffusion–adsorption number,

$$\lambda \equiv (C_0/\mathit{\Lambda})\,(D/w^*)^{\frac{1}{2}}.$$

The approximate solutions for ϵ can be found by making appropriate perturbation expansions of the transcendental equation and by equating terms of the same order. Since the transcendental equation depends on many non-dimensional parameters – such as the density ratio, viscosity ratio, surface dilatational elasticity number, and surface dilatational viscosity number, the approximate solutions are meaningful only when their orders of magnitude are specified. For simplicity we assume that the ratios of the densities and viscosities, $\hat{\rho}$ and $\hat{\eta}$, are of order 1. Results for other surface parameters of different orders are then discussed separately.

Examination of (21) shows that the surface shear viscosity number β_s and the surface dilatational viscosity number β_d always appear with a factor of order $1/x_i^2$. The surface dilatational elasticity number, however, appears with a factor of order 1. Hence, the ratios, β_d/β and β_s/β, must be of order x^2 to offset the differences. Furthermore, λ is assumed to be of order 1, so the effects due to the diffusion and adsorption of surfactants can be easily examined. For the cases studied below, except Case 1, these conditions are retained.

Case 1: $\beta = \beta_d = \beta_s = \lambda = 0$; i.e. Gibbs elasticity, surface dilatational viscosity, surface shear viscosity, and surface diffusion–adsorption numbers are zero.

Here the system contains no surfactants or contaminants. For fluids of small viscosities, we find that, to order $1/x^2$, the complex angular velocity is

$$\omega \approx i\omega^*(1+\epsilon^{(1)}+\epsilon^{(2)}+\ldots), \tag{26}$$

where
$$\epsilon^{(1)} = -\frac{i_s(2L+1)^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}{2\Upsilon x_i[1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}}]} = \frac{-(1+i)\,(2L+1)^2(\rho_i\,\eta_i\,\rho_o\,\eta_o)^{\frac{1}{2}}}{2\sqrt{2R\omega^{*\frac{1}{2}}}[L\rho_o+(L+1)\,\rho_i][(\rho_i\,\eta_i)^{\frac{1}{2}}+(\rho_o\,\eta_o)^{\frac{1}{2}}]}, \tag{27a}$$

and
$$\epsilon^{(2)} = \epsilon^{(1)\,2}-\frac{i(2L+1)\,[2(L^2-1)+(L+2)\,\hat{\eta}-(L-1)\,\hat{\rho}\hat{\eta}+2L(L+2)\,\hat{\rho}\hat{\eta}^2]}{2\Upsilon x_i^2[1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}}]^2}. \tag{27b}$$

The first-order term, due to the energy dissipated in the boundary layers through rotational motion (Landau & Lifshitz 1959), is identical to Miller & Scriven's, which

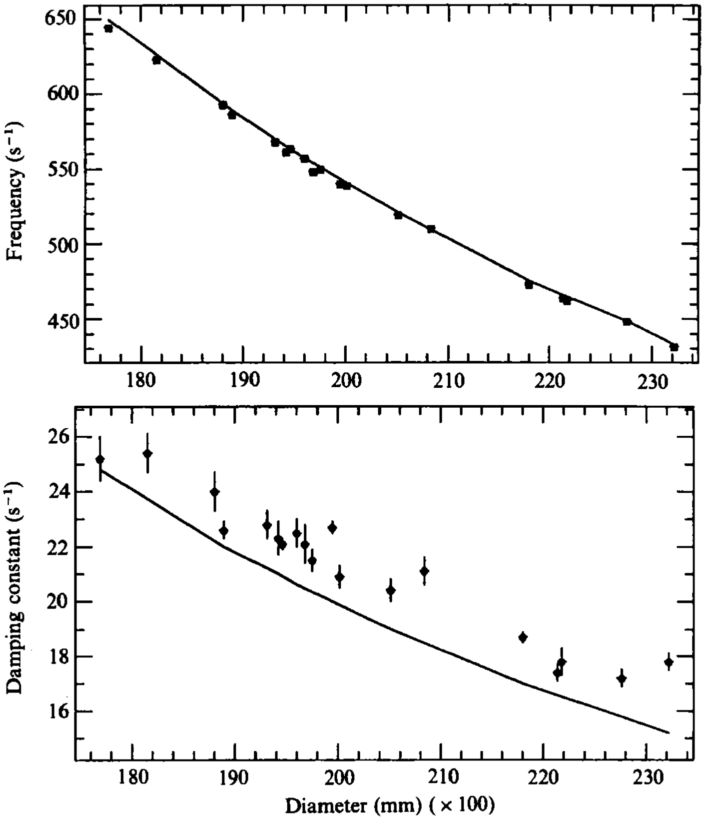

FIGURE 1. Frequency and damping constant versus diameter for hexane drops in pure water at 24 ± 2 °C. The solid curves are the theoretical predictions based on (27). Symbols are experimental results from Lu & Apfel (1990).

exists only when neither of the densities of the fluids is negligible. The second-order term is the same as Marston's (1980) confirming that Miller & Scriven had a missing term $\epsilon^{(1)2}$.

As depicted in figure 1, experimental results obtained by using an acoustic method (Lu & Apfel 1990) are in good agreement with the theoretical predictions shown here, thus supporting the validity of the hydrodynamic analysis.

Case 2: Surface dilatational elasticity number is of order $1/x^2$, surface dilatational and shear viscosity numbers order 1, and surface diffusion–adsorption number, at most, of order 1.

This case corresponds to a system exhibiting small surface dilatational, shear viscosities, and Gibbs elasticity, which give an additional second-order term, $\epsilon^{(2)\prime}$, besides the terms in Case 1. The new term of the complex frequency is thus

$$\mathrm{i}\omega^*\epsilon^{(2)\prime} = \frac{1}{2\Upsilon}\left[\frac{\mathrm{i}\Upsilon E\omega^*}{(L-1)(L+2)\gamma_0(1+\mathrm{i_s}\lambda)}+\frac{L(L+1)\xi_s}{R^3}\right]\left[\frac{(L-1)-(L+2)(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}{1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}\right]^2 + \frac{(L-1)(L+2)\eta_s}{2\Upsilon R^3}\left[\frac{(L+1)-L(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}{1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}\right]^2. \quad (28)$$

If the diffusion–adsorption number is much smaller than 1, so that effects of the surfactant diffusion are negligible, the Gibbs elasticity and the surface viscosities affect the characteristic frequency and the energy dissipation rate of the system, respectively. The damping constant increases with the surface viscosities, as expected. The increase of the characteristic frequency with the Gibbs elasticity is due to the higher effective interfacial tension (averaged over the interface) assumed by the drop as it oscillates (cf. (16)). Hsu's simplified model (Hsu & Apfel 1987) for calculating the additional effects introduced by the surface dilatational viscosity is adequate only in this case.

If the diffusion–adsorption number is small but not negligible, both the characteristic frequency and the energy dissipation rate are affected by the Gibbs elasticity as well as the surface viscosities. The effects can be seen by using the approximation, $1/(1+\mathrm{i_s}\,\lambda) \approx 1-\mathrm{i_s}\,\lambda$, such that (28) is transformed into

$$\mathrm{i}\omega^*\epsilon^{(2)\prime} = \frac{1}{2\Upsilon}\left[\frac{\mathrm{i}\Upsilon E\omega^*(1-(1+\mathrm{i})\,\lambda/\sqrt{2})}{(L-1)(L+2)\,\gamma_0}+\frac{L(L+1)\,\xi_\mathrm{s}}{R^3}\right]\left[\frac{(L-1)-(L+2)\,(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}{1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}\right]^2$$
$$+\frac{(L-1)(L+2)\,\eta_\mathrm{s}}{2\Upsilon R^3}\left[\frac{(L+1)-L(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}{1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}\right]^2. \tag{29}$$

Since the diffusion of the surfactants smooths out the interfacial tension gradient, the oscillation frequency is slightly reduced. The damping constant, however, is slightly increased owing to the phase difference between the redistribution of surfactants and the oscillation of the drop.

Comparing the rate of energy dissipation due to surface dilatational viscosity with that due to surface shear viscosity gives

$$\frac{\text{shear decay constant}}{\text{dilatational decay constant}} = \frac{(L-1)(L+2)[(L+1)-L(\hat{\rho}\hat{\eta})^{\frac{1}{2}}]^2}{L(L+1)[(L-1)-(L+2)(\hat{\rho}\hat{\eta})^{\frac{1}{2}}]^2}.$$

This ratio increases towards 1 as L increases if the product of the density ratio and viscosity ratio is of order 1, suggesting that the shear and dilatational motions of a flat interface are equally important; the shear motion is less important than the dilatational motion on a curved interface. For quadrupole oscillations ($L = 2$) of a hexane drop (at 25 °C, density = 0.6548 g/cm^3, viscosity = 0.294 cP) in water the energy dissipation caused by the shear motion on the interface is about 2%.

Case 3: Surface dilatational elasticity number and surface dilatational viscosity number are much larger than other non-dimensional parameters.

In this case the Gibbs elasticity and the surface dilatational viscosity are so large that motion in the boundary layers is changed drastically. Therefore, the first-order solution is no longer the same as the previous ones. It becomes

$$\epsilon^{(1)} = \frac{-\mathrm{i_s}[(L-1)^2+(L+2)^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}}]}{2\Upsilon x_\mathrm{i}}, \tag{30}$$

which is the same as Miller & Scriven's (1968) result. $\epsilon^{(1)}$, however, does not depend on the surface parameters β and β_d, since the interface is inextensible; the local expansion of the interface is impossible to the first order. Yet the surface parameters will come into play only when there is a local variation of the interfacial area.

Comparing (30) with (27*a*) shows that

$$\frac{\text{inextensible interface decay constant}}{\text{free interface decay constant}} \approx \frac{[1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}}][(L-1)^2+(L+2)^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}}]}{(2L+1)^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}}},$$

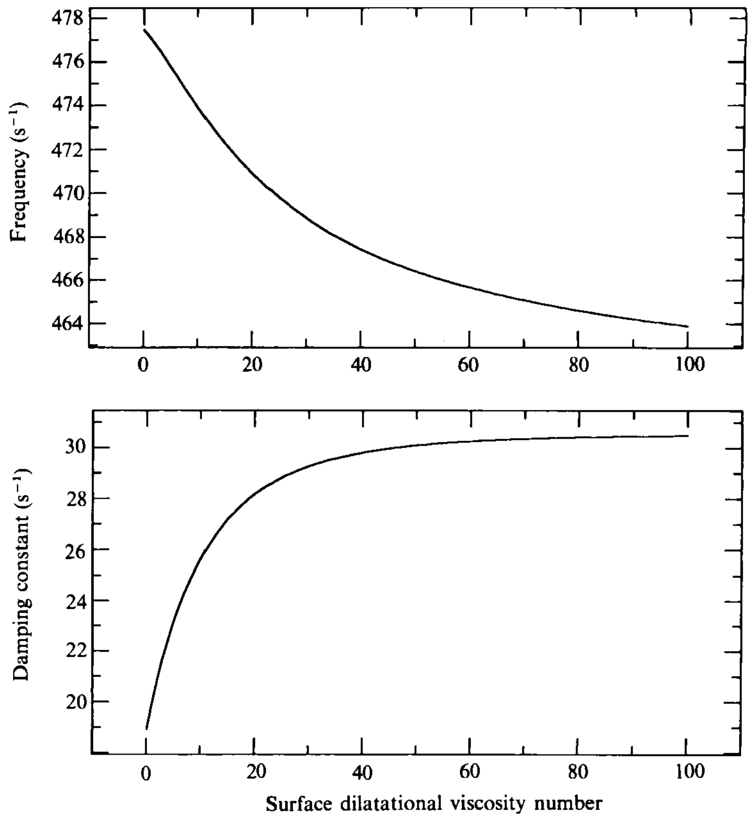

FIGURE 2. Free quadrupole oscillation frequency and damping constant versus surface dilatational viscosity number. The calculations are for a hexane drop of a radius 0.1 cm in an aqueous solution with an equilibrium interfacial tension of 40 dyn/cm, against hexane. The Gibbs elasticity and surface shear viscosity are zero.

which is always greater than one. For the quadrupole oscillations of a hexane drop in water, the ratio is about two.

Case 4: Surface shear viscosity number is much larger than other non-dimensional parameters.

The interface cannot sustain any shear motion to the first order. The correction to the complex frequency is

$$\epsilon^{(1)} = \frac{-\mathrm{i}_s[(L+1)^2+L^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}}]}{2\Upsilon x_\mathrm{i}}. \tag{31}$$

Comparing the result with (27*a*) yields

$$\frac{\text{no shear interface decay constant}}{\text{free interface decay constant}} \approx \frac{[1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}}][(L+1)^2+L^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}}]}{(2L+1)^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}.$$

The ratio is still greater than 1 but not significantly different from it. For the quadrupole oscillations of a hexane drop in water, the ratio is about 1. This again shows that there is not much shear motion on the spherical hexane–water interface even though the interface is free.

Case 5: Surface dilatational elasticity number is of order $1/x$, surface dilatational and shear viscosity numbers are of order x, and the surface diffusion–adsorption number is 1.

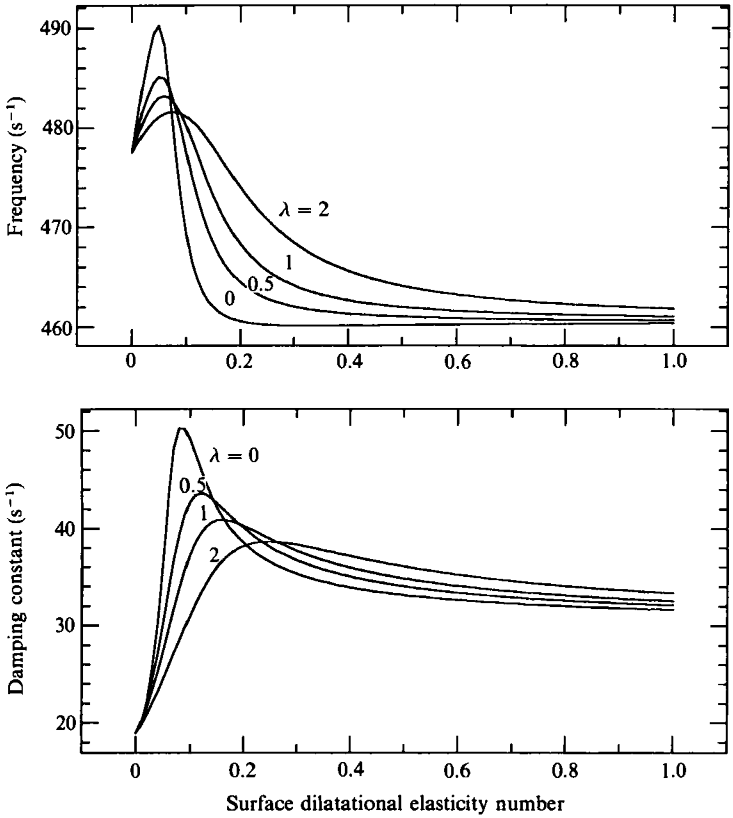

FIGURE 3. Free quadrupole oscillation frequency and damping constant versus surface dilatational elasticity number for different surface diffusion–adsorption numbers. The calculations are for a hexane drop of a radius 0.1 cm in an aqueous solution with an equilibrium interfacial tension, 40 dyn/cm, against hexane. The surface dilatational and shear viscosities are zero.

Here the Gibbs elasticity and the dilatational viscosity are moderate. The first-order correction to the complex frequency is

$$\epsilon^{(1)} = \frac{\dfrac{-\mathrm{i}_s(2L+1)^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}{2\Upsilon x_i^2} + A_d\,\epsilon_d + A_s\,\epsilon_s + \dfrac{4\mathrm{i}\mathrm{i}_s A_d A_s}{2\Upsilon}}{\dfrac{1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}{x_i} + \mathrm{i}\mathrm{i}_s(A_d + A_s)}, \tag{32a}$$

where
$$\epsilon_d = \frac{(L+2)^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}} + (L-1)^2}{2\Upsilon x_1}, \quad \epsilon_s = \frac{L^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}} + (L+1)^2}{2\Upsilon x_1},$$

$$A_d = \frac{\Upsilon\beta}{(L-1)(L+2)(1+\mathrm{i}_s\lambda)} - \frac{\mathrm{i}L(L+1)\,\beta_d}{x_1^2}, \quad A_s = \frac{-\mathrm{i}(L-1)(L+2)\,\beta_s}{x_1^2}.$$

Again the first-order term is due to the energy dissipation in the boundary layers. The boundary layer, however, is always present for an interface with elasticities and viscosities, even when the density of one of the fluids is negligible. The second-order result is

$$\epsilon^{(2)} = \frac{\mathrm{i}\mathrm{i}_s[f + f_s + f_d - 4\mathrm{i}_s A_d A_s(L(\hat{\eta}/\hat{\rho})^{\frac{1}{2}} + (L+1))]}{2\Upsilon\left[\dfrac{1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}}}{x_i} + \mathrm{i}\mathrm{i}_s(A_d + A_s)\right]}, \tag{32b}$$

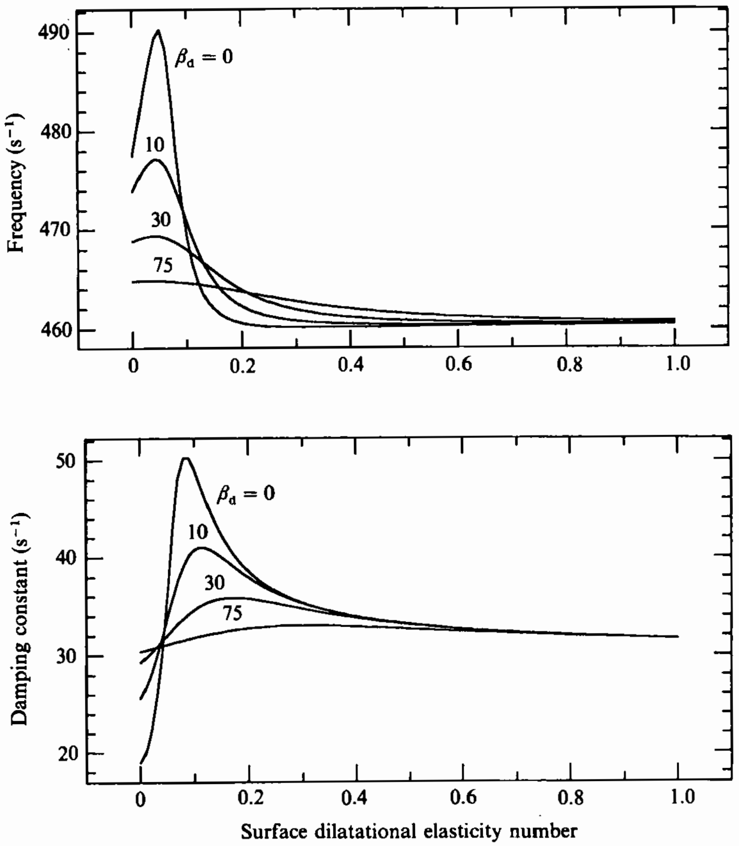

FIGURE 4. Free quadrupole oscillation frequency and damping constant versus surface dilatational elasticity number for different surface dilatational viscosity numbers. The calculations are for a hexane drop of a radius 0.1 cm in an aqueous solution with an equilibrium interfacial tension, 40 dyn/cm, against hexane. The surface shear viscosity and surface diffusion–adsorption number are zero.

where

$$f(x_i, \hat{\rho}, \hat{\eta}) = \frac{4\Upsilon}{x_i}(1+(\hat{\rho}\hat{\eta})^{\frac{1}{2}})\,\epsilon^{(1)\,2} - \frac{i2\Upsilon}{x_i^2}[(L+1)\,(\hat{\rho}\hat{\eta})^{\frac{1}{2}} + 2(1-\hat{\eta}) + L(\hat{\eta}/\hat{\rho})^{\frac{1}{2}}]\,\epsilon^{(1)}$$

$$-\frac{i(2L+1)^2}{x_i^2}(\hat{\rho}\hat{\eta}\epsilon^{(1)})^{\frac{1}{2}} + \frac{2i_s(2L+1)}{x_i^3}(\hat{\eta}-1)\,[(\hat{\rho}\hat{\eta}L)^{\frac{1}{2}}(L+2)+1-L^2],$$

$$f_d = A_d\left\{3\Upsilon\epsilon^{(1)\,2} + \frac{2i_s\,\Upsilon\epsilon^{(1)}}{x_i}[L(\hat{\eta}/\hat{\rho})^{\frac{1}{2}} + (L+1)] + \frac{i_s\,\epsilon^{(1)}}{2x_i}[(L+2)^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}} + (L-1)^2]\right.$$

$$\left.-\frac{i}{x_i^2}[4(L-1)\,(L+2)\,(1-\hat{\eta}) - (L+1)\,(L+2)^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}} - L(L-1)^2(\hat{\eta}/\hat{\rho})^{\frac{1}{2}}]\right\}$$

$$+\left[\frac{2\Upsilon\beta}{(L-1)\,(L+2)\,(1+i_s\,\lambda)} - \frac{iL(L+1)\,\beta_d}{x_i^2}\right]\left[2\Upsilon\epsilon^{(1)} + \frac{i_s}{x_i}[(L+2)^2\,(\hat{\rho}\hat{\eta})^{\frac{1}{2}} + (L-1)^2]\right]\epsilon^{(1)},$$

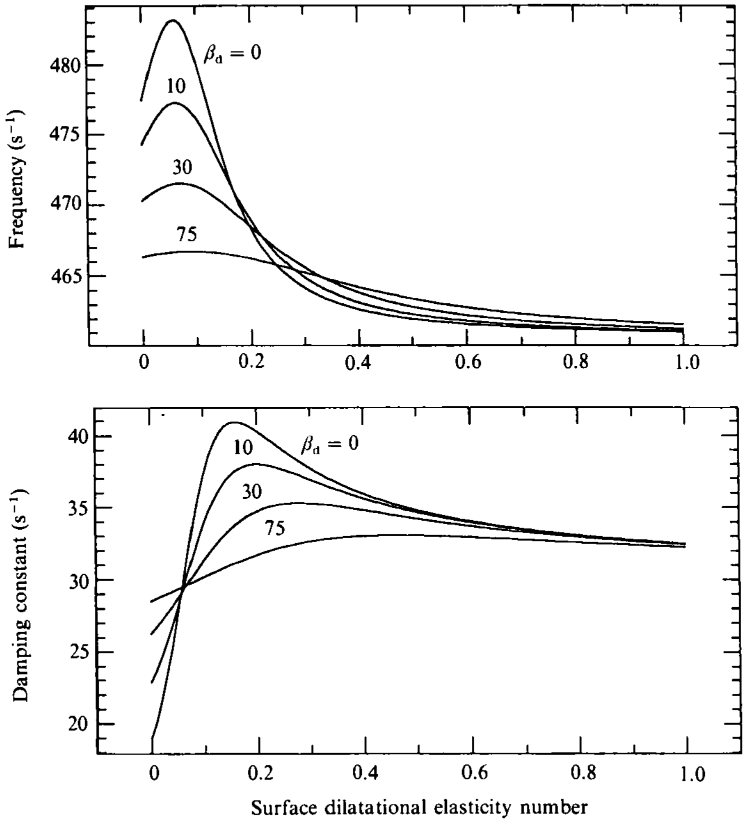

FIGURE 5. Free quadrupole oscillation frequency and damping constant versus surface dilatational elasticity number for different surface dilatational viscosity numbers. The calculations are for a hexane drop of a radius 0.1 cm in an aqueous solution with an equilibrium interfacial tension, 40 dyn/cm, against hexane. The surface shear viscosity is zero, and the surface diffusion–adsorption number is one.

and
$$f_s = A_s\left\{5\Upsilon\epsilon^{(1)2} + \frac{2\mathrm{i}_s\Upsilon\epsilon^{(1)}}{x_\mathrm{i}}[L(\hat{\eta}/\hat{\rho})^{\frac{1}{2}} + (L+1)] + \frac{3\mathrm{i}_s\epsilon^{(1)}}{2x_i}[(L+1)^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}} + L^2]\right.$$
$$\left. + \frac{\mathrm{i}}{x_\mathrm{i}^2}[4L(L+1)(1-\hat{\eta}) + (L+1)L^2(\hat{\rho}\hat{\eta})^{\frac{1}{2}} + L(L+1)^2(\hat{\eta}/\hat{\rho})^{\frac{1}{2}}]\right\}$$
$$-4\epsilon^{(1)}A_s\left[\frac{\Upsilon\beta}{(L-1)(L+2)(1+\mathrm{i}_s\lambda)} + A_\mathrm{d}\right].$$

Effects of the surface parameters are intertwined such that simple observations become formidable. To see the importance of each surface parameter, we plot the free oscillation frequency and damping constant against each surface parameter (see figures 2–6). The sample system chosen is a hexane drop in a dilute aqueous solution. The drop has a radius of 0.1 cm, and the equilibrium interfacial tension is 40 dyn/cm.

Figure 2 depicts the change of the frequency and damping constant with the surface dilatational viscosity number when the Gibbs elasticity and surface shear viscosity are zero. For such a system, the frequency decreases and the damping constant increases monotonically with the surface dilatational viscosity number. These changes of the characteristics of the system are similar to those due to the bulk viscosity.

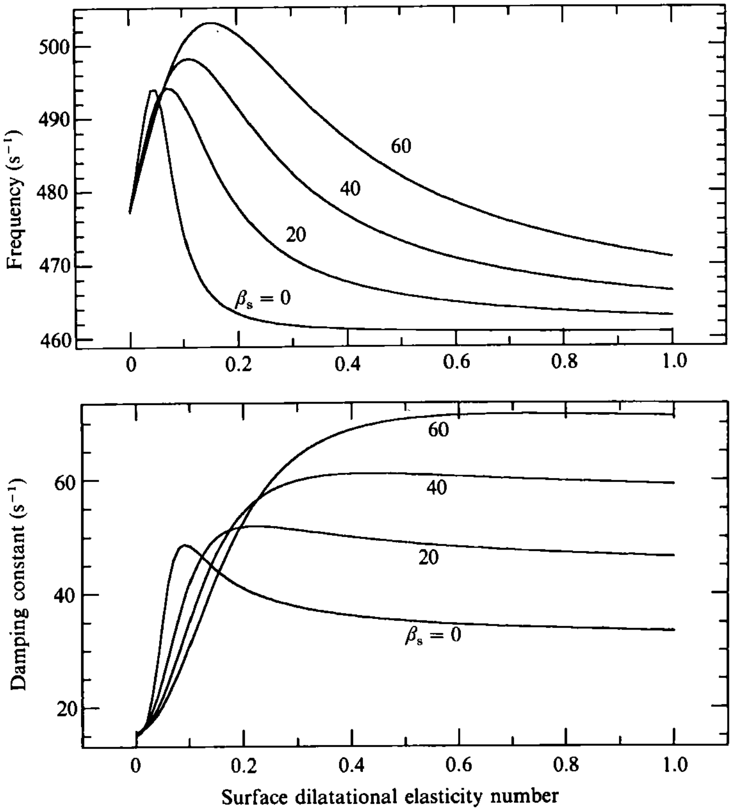

FIGURE 6. Free quadrupole oscillation frequency and damping constant versus surface dilatational elasticity number for different surface shear viscosity numbers. The calculations are for a hexane drop of a radius 0.1 cm in an aqueous solution with an equilibrium interfacial tension, 40 dyn/cm, against hexane. Both the surface dilatational viscosity and diffusion–adsorption number are zero.

In figure 3 we show the variation of the frequency and damping constant with the surface dilatational elasticity number assuming that the surface viscosities are zero. Both the frequency and damping constant have maxima. Similar effects have also been found for a planar air–liquid surface by Mann & Hansen (1963) and Tempel & Riet (1965). The frequency can be higher or lower than the case with zero Gibbs elasticity, depending on the magnitude of the Gibbs elasticity. The damping constant, however, is always higher than that for zero Gibbs elasticity. This is probably due to the increased vorticity generated in the boundary layers caused by the additional shear stress, the interfacial tension gradient. The maxima, on the other hand, may result from the phase difference between the tangential component of the bulk viscous stress on the interface and the interfacial tension gradient (cf. (11)). Furthermore, increasing the surface diffusion–adsorption number, which leads to more rapid redistribution of surfactants and thus smaller interfacial tension gradient, has a similar effect to decreasing the effective Gibbs elasticity of the system.

When both the Gibbs elasticity and the surface dilatational viscosity are present at the interface, but the surface shear viscosity is still zero, the dependence of the frequency and the damping constant on the surface parameters is shown in figures 4 and 5. The general trend of the variation of the frequency and damping constant with the surface elasticity number is the same for all surface viscosity numbers. The

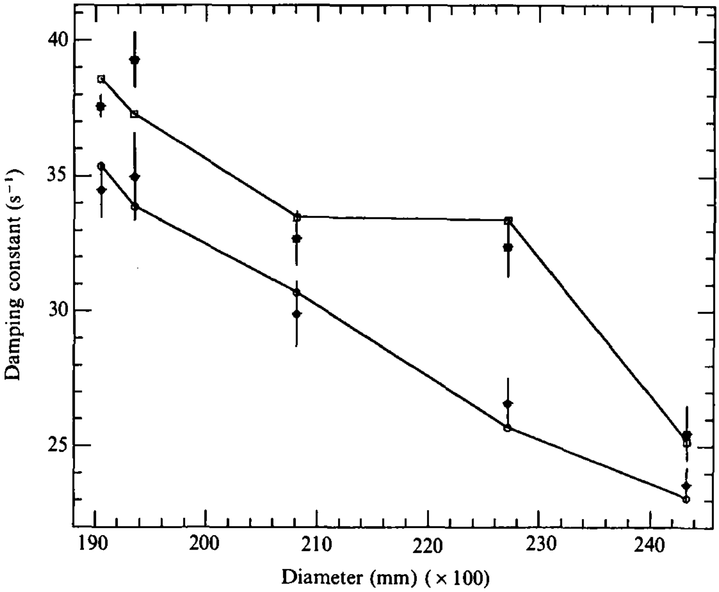

FIGURE 7. Damping constant versus diameter for hexane drops in 0.396 mM (5.2% CMC) SDS aqueous solution at 25 °C. The open symbols connected by line represent calculated results and the filled symbols the measured ones. The squares and circles denote data taken within five minutes and one hour after the drop is introduced into the solution, respectively.

trend of the variation of the frequency and damping constant with the surface viscosity is, however, completely reversed after the crossing region. This behaviour is because the stresses caused by the Gibbs elasticity and the surface dilatational viscosity are out of phase (cf. (11)).

If the interface does not exhibit any dilatational property, both the damping constant and frequency change very slowly with the surface shear viscosity since little shear motion exists on the spherical interface. Nonetheless, when both the dilatational and shear properties are present at the interface, the effects of the surface shear viscosity are no longer negligible owing to coupling, unique in a non-planar interface, between Gibbs elasticity and surface shear viscosity. As shown in figure 6, the surface shear viscosity increases the damping constant and frequency significantly. It is not clear, however, whether the unusually large effects are spurious owing to the approximate nature of (32). If the effects are real, the measured damping constant and frequency can be used to detect the presence of surface shear viscosity.

7. Experimental results

The interfacial tension, Gibbs elasticity, and surface viscosities can be controlled experimentally by choosing appropriate materials and the concentration of surfactants. Nevertheless, it is difficult to change these interfacial parameters independently. For example, if the surfactant concentration is increased, all interfacial parameters are changed simultaneously. The conditions for the different limiting cases discussed above, therefore, cannot be easily achieved experimentally. Recently, Lu & Apfel (1990) have measured the free quadrupole oscillation frequency and damping constant for hexane drops in SDS aqueous solutions of different

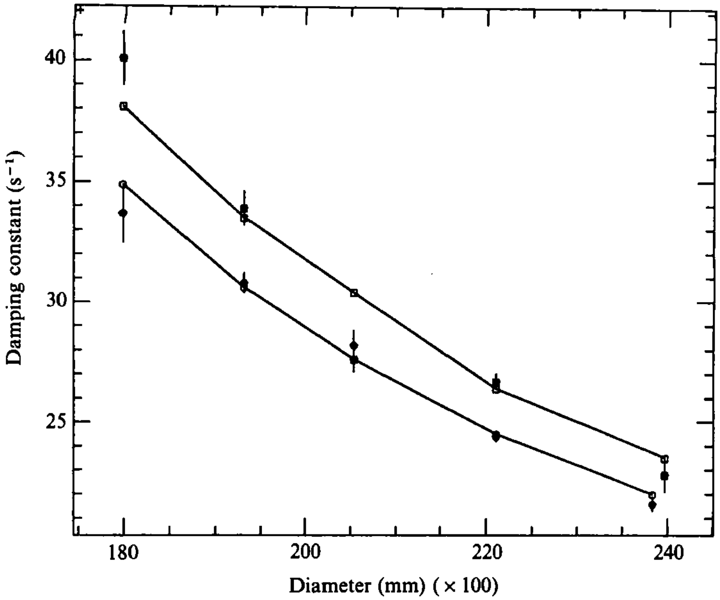

FIGURE 8. Damping constant versus diameter for hexane drops in 0.839 mM (11% CMC) SDS aqueous solution at 25 °C. The open symbols connected by line represent calculated results and the filled symbols the measured ones. The squares and circles denote data taken within five minutes and one hour after the drop is introduced into the solution, respectively.

concentrations. To reduce the complexities of the problem and make comparisons between the theoretical and experimental results possible, they assume that the effects of surface viscosities are negligible, and the surfactants adsorbed on the interface behave according to the perfect gas law, which are generally true for a dilute surfactant solution (Adamson 1982; Reichl 1980; Ting, Wasan & Migano 1985). By using (32) (since the dilatational elasticity number ranges between zero and one) and the measured frequency, the equilibrium interfacial tension is inferred and the damping constant is then calculated. The calculated and measured damping constants are shown in figures 7 and 8. Despite the apparent agreement between the theoretical and experimental results, further experimental work is required to fully test the theoretical predictions.

8. Conclusions

We have studied the effects of surface properties, such as Gibbs elasticity and surface dilatational and shear viscosities, introduced by surfactants on shape oscillations of a fluid drop in another fluid with and without surfactants. A general transcendental equation for the complex frequency has been obtained. Explicit results for cases of zero, small, intermediate, and large surface properties are reported. We have shown that the rate of energy dissipation is always higher for an interface exhibiting surface elasticity and viscosities because of stronger vorticity generated in the boundary layers. The effects of the interfacial properties become measurable if the surface viscosity number is of order 1 or the surface elasticity number is of the same order as the Reynolds number. When the surface dilatational viscosity or elasticity is so large that the interface is inextensible, or the surface shear viscosity is so large that the interface cannot sustain any shear deformation, the dispersion relations are extremely simple. The result of for no-shear interface, however, is not so different from that for a free interface, since the shear motion on a spherical interface is not important. For the case of moderate interfacial properties, we have shown that the Gibbs elasticity is the most important surface property and changes the damping constant significantly owing to stronger vorticity generated in the boundary layers caused by the interfacial tension gradient. Furthermore, at a certain surface elasticity number both the frequency and damping constant show maxima.

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