Drop Oscillations in Liquid-Liquid Systems

When the ratio of the drop radius to the distance separating any two drops *and* the relative importance of gravitational to surface forces are both small, the small amplitude oscillations of a drop of one viscous fluid immersed in another fluid are governed by the nonlinear dispersion relation derived by Miller and Scriven (1968). The dispersion relation has been solved numerically to determine the character of oscillations for arbitrary values of drop size, physical properties of the two fluids, and interfacial tension. The new theoretical results determine the range of validity of the low-viscosity approximation of Miller and Scriven, *and* are also shown to be essential for proper interpretation of many previously reported experimental results. New experimental measurements of natural frequencies of oscillation of water drops falling in 2-ethyl-1-hexanol, a system having properties characteristic of many others in solvent extraction, agree well with the theoretical predictions when drop radius is smaller than a critical size. The frequencies of oscillations of larger drops are better described by the dispersion relation due to Subramanyam (1969), which accounts for the relative motion of the two phases.

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Introduction

The oscillations of a drop of one fluid which is immersed in another fluid has attracted much attention for over a century (e.g., Rayleigh, 1879; Lamb, 1932; Chandrasekhar, 1959; Reid, 1960; Miller and Scriven, 1968; Tsamopoulos and Brown, 1983) because of its importance in areas as diverse as chemical technology, meteorology, and nuclear physics. Many mass transfer operations of chemical engineering, such as solvent extraction, involve small drops of one fluid immersed in another fluid. Moreover, there is renewed interest in and motivation for the study of drop oscillations because recent research has shown that, for example, mass and heat transfer to and from drops can be enhanced by the application of an electric field (Kaji et al., 1985; Wham and Byers, 1987; Scott and Wham, 1989).

Previous studies in our laboratory have involved the use of pulsed DC electric fields to induce oscillation of aqueous drops which are surrounded by a nonconducting continuous phase (Scott, 1987; Wham and Byers, 1987). In these studies, imposed drop oscillations were carried out to (1) achieve steady, moderate-amplitude oscillations which alter drop-continuous phase hydrodynamics and (2) cause high-amplitude oscillations which lead to drop break-up and/or emulsification.

Central to both of the aforementioned modes of operation is knowledge of the natural frequencies of oscillation of a drop. If the frequency of the transient electric field is swept over a range of frequencies while holding the field strength fixed, drop deformation is greatest when the frequency of the field equals the natural frequency. This natural frequency is the same as the frequency of free oscillations having an infinitesimally small amplitude (cf. Trinh et al., 1982). Accurate experimental measurement of the natural frequencies of oscillation over a range of drop sizes is not available and is a goal of this paper.

A drop of radius R is effectively isolated from its surroundings if the gravitational Bond number $B \equiv gR^2\Delta\rho/\gamma$ is sufficiently small (g is the acceleration of gravity, $\Delta\rho$ is the density difference between the drop and the surrounding fluid, and γ is the interfacial tension). An order of magnitude estimate of this critical drop size can be gotten from the value of the ratio $\beta_l R/U$ (cf. Subramanyam, 1969; Prosperetti, 1980): β_l is the frequency of oscillation, and U is the velocity of the drop center-of-mass relative to the surrounding fluid. Then, if $\beta_l R/U \gg 1$, the drop is isolated; if $\beta_l R/U \sim 1$, the relative motion between the two phases cannot be neglected; and if $\beta_l R/U \ll 1$, the drop does not oscillate. The last case describes the much-studied problem of flow past a slightly deformed drop and is not considered further in this paper.

β_l can be estimated from the lowest frequency of oscillation of an inviscid drop (e.g., Lamb, 1932; see also Eq. 4). U can be estimated from the well-known solution for the flow of an ambient fluid past a spherical fluid drop at low Reynolds number due to Hadamard and Rybczynski (see, e.g., Lamb, 1932).

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If $\beta_I R/U \gg 1$, it then follows that a drop of a viscous fluid immersed in another fluid is effectively isolated provided

$$R \ll \left\{ \frac{54\gamma}{2\rho_o + 3\rho_i} \left[\frac{\mu_o(2\mu_o + 3\mu_i)}{g\Delta\rho(\mu_o + \mu_i)} \right]^2 \right\}^{1/5}, \tag{1}$$

where μ is viscosity, ρ is density, and the subsripts i and o refer to the drop and the surrounding fluid, respectively. By way of example, for drops of water in 2-ethyl-1-hexanol (2EtOH), whose properties are listed in Table 1, $R \ll 0.17$ cm. This fluid pair has properties similar to those of many fluid pairs that are commonly used in solvent extraction.

Miller and Scriven (1968), hereafter referred to as Miller and Scriven, have made a thorough analysis of this situation and derived a nonlinear dispersion relation that governs the frequency and the rate of damping (or decay factor) of oscillations of small amplitude. The dispersion equation is expressed by the vanishing of the determinant of a 7 x 7 matrix, solutions to which have been known mainly in limiting cases (see Miller and Scriven). Miller and Scriven have obtained approximate solutions of the dispersion equation when the viscosities of both fluids are either "low" or "high." Marston (1980) and Prosperetti (1980) independently have shown that Miller and Scriven had omitted a term in the decay factor in their low-viscosity approximation (LVA). Moreover, Prosperetti (1980) has obtained numerical solutions of the dispersion relation for a drop undergoing second-harmonic oscillations. Numerical solutions for higher-order mode oscillations are not available; obtaining such solutions is another goal of this paper.

Using their LVA, Miller and Scriven have shown that for drops that are not too small, boundary layer flows on both sides of the interface become the dominant factor in the rate of viscous dissipation even when the viscosities of both fluids are low. Miller and Scriven's theoretical predictions are in much better agreement with experimental measurements than previous theoretical predictions based on the use of inviscid velocity profiles in approximating the damping rates (Valentine et al., 1965). However, Prosperetti (1980, p. 178) claimed that his theoretical predictions and those by the LVA of Miller and Scriven of decay factors experimentally measured by Valentine et al. (1965) differ by an order of magnitude. Unfortunately, his comparison (1980, p. 177) is not to the theoretical predictions of Miller and Scriven (1968, p. 430, Table 1) but to those of Valentine et al. (1965). Moreover, there is also a need to repeat the analyses of Miller and Scriven and others to determine if there is indeed a missing term in the decay factor in the LVA of Miller and Scriven.

Much experimental work has been done since Miller and Scriven to measure the frequencies of oscillation and decay factors of drops in immiscible liquid-liquid systems and compare the results to the predictions of the LVA of Miller and Scriven. Loshak and Byers (1973; see also Ramabhadran et al., 1976) have performed experiments with drops of various organics falling through an aqueous continuous phase. Though the drops in their experiments were not isolated, these authors have analyzed their data by means of the LVA of Miller and Scriven. They have reported good agreement between the measurements and calculations of the frequencies of oscillation. Good agreement, however, has not been found in the corresponding decay factors. More recently, Trinh et al. (1982) have reported results of very precise experiments with acoustically-levitated drops that are nearly neutrally buoyant in the surrounding liquid. Trinh et al. (1982) have observed very good agreement between their experimental measurements and theoretical predictions by the LVA of Prosperetti (1980) and Marston (1980), hereafter referred to as the LVA of P&M. However, Trinh et al. (1982) have also reported some discrepancies between the experimental measurements and the theoretical predictions, especially when the viscosities of the two phases were small but of different orders of magnitude.

Table 1. Physical Properties of Fluids in Experiments

Liquid Phase	Composition (wt. %)	Density at 20°C kg/m^3(g/cm^3)	Viscosity at 20°C kg/(m · s)(cp)
Aqueous	Water (99.9%)	1,000 (1.00)	0.001 (1.00)
Organic	2-Et-hexanol $\gamma = 0.0134$ N/m $\gamma = 13.4$ dyne/cm	830 (0.83)	0.008 (8.00)

The discrepancies between the experimental measurements and the theoretical predictions have been attributed by Loshak and Byers (1973), Trinh et al. (1982), and others to surface tension gradients and/or surface excess properties owing to the presence of contaminants or surfactants on the interface, variation of physical properties during the course of the experiments, nonlinear oscillations, etc. Thus, there is a need to understand the range of validity of the low-viscosity approximations to determine if and when these previously-listed effects play a role. This is done in this paper for the first time.

In many applications of practical importance, such as solvent extraction, there is relative mean motion between the drops (the dispersed phase) and the surrounding fluid (the continuous phase). In these situations, $\beta_I R/U \sim 1$. It is interesting to note that the only theoretical paper in this area appears to be the work of Subramanyam (1969), who has considered the oscillations of a drop of a viscous liquid moving in another viscous liquid at small Reynolds and Weber numbers. Subramanyam (1969) has shown that his predictions are in excellent agreement with measurements by Winnikow and Chao (1966) of frequencies of oscillation of drops falling in water. However, the agreement is fortuitous because his theory is valid for low Reynolds numbers, while the Reynolds numbers ranged between 138-971 in the experiments.

Theoretical Analysis of Drop Oscillations

Theories of drop oscillations

$\beta_I R/U \gg 1$: No Relative Motion between the Two Phases. The oscillation of a fluid drop immersed in another fluid is governed by the following dispersion equation (see Miller and Scriven, Eq. 24):

$$\det(\beta | \ell; R, \gamma, \rho_i, \rho_o, \mu_i, \mu_o) = \Delta = 0. \tag{2}$$

In Eq. 2, $\beta \equiv \beta_R + i\beta_I$ is the complex frequency, where i is the imaginary unit. The oscillations have a temporal variation $e^{-\beta t}$, where t is time, so that a positive β_R corresponds to a decay factor and a negative one to an amplification factor. The imaginary part β_I is the angular frequency of oscillation. $\ell(\geq 2)$ is the mode number: $\ell = 2$ corresponds to two-lobed or second-harmonic oscillations, $\ell = 3$ to three-lobed or third-harmonic oscillations, etc. Given ℓ, R, γ, ρ_i, ρ_o, μ_i, μ_o, values of β are sought, for which the determinant in Eq. 2 vanishes. The determinant presented by Miller and Scriven can be reduced to a 3 × 3 determinant

$$\Delta = \begin{vmatrix} \omega_i R Q^J & -(2\ell + 1) & C \\ \dfrac{2\mu_i\omega_i Q^J}{R} - \dfrac{\beta\rho_i}{\ell} & \dfrac{\beta\Gamma}{\ell(\ell+1)} - \dfrac{2}{R^2}[\mu_i(\ell - 1) + \mu_o(\ell + 2)] + \dfrac{\beta^{*2}\Gamma}{\beta\ell(\ell+1)} & \dfrac{2\mu_o C}{R^2} - \dfrac{\beta\rho_o}{\ell + 1} \\ \mu_i G & 2[\mu_i(\ell^2 - 1) - \mu_o\ell(\ell + 2)] & \mu_o F \end{vmatrix} = 0 \qquad (3)$$

where $\omega^2 \equiv \beta/\nu$ (where the kinematic viscosity, $\nu \equiv \mu/\rho$) and $\Gamma \equiv \rho_o\ell + \rho_i(\ell + 1)$. β^* is the frequency of oscillation for two inviscid fluids and is given by (Lamb, 1932)

$$\beta^* = \left[\frac{\gamma\ell(\ell + 1)(\ell - 1)(\ell + 2)}{R^3\Gamma}\right]^{1/2}. \qquad (4)$$

The functions C, F, and G are abbreviations for:

$$C \equiv 2\ell + 1 - \omega_o R Q^H, \qquad (5)$$

$$F \equiv 2(2\ell + 1) + \omega_o^2 R^2 - 2\omega_o R Q^H, \qquad (6)$$

$$G \equiv -\omega_i^2 R^2 + 2\omega_i R Q^J. \qquad (7)$$

The Qs are the ratios of Bessel functions of the first kind, J, and Hankel functions of the first kind, $H^{(1)}$, both of fractional order:

$$Q^J \equiv \frac{J_{\ell+3/2}(\omega_i R)}{J_{\ell+1/2}(\omega_i R)}, \quad Q^H \equiv \frac{H^{(1)}_{\ell+3/2}(\omega_o R)}{H^{(1)}_{\ell+1/2}(\omega_o R)}, \qquad (8)$$

It can be shown that the solution of Eq. 3 that is asymptotically valid when the viscosities of both fluids are "low," a result which was originally derived by Miller and Scriven from Eq. 2, is:

$$\beta = \frac{(2\ell + 1)^2(\beta^*\mu_i\mu_o\rho_i\rho_o)^{1/2}}{2\sqrt{2}R\Gamma[(\mu_i\rho_i)^{1/2} + (\mu_o\rho_o)^{1/2}]} - \frac{(2\ell + 1)^4\mu_i\mu_o\rho_i\rho_o}{4R^2\Gamma^2[(\mu_i\rho_i)^{1/2} + (\mu_o\rho_o)^{1/2}]^2}$$
$$+ \frac{(2\ell + 1)\{2(\ell^2 - 1)\mu_i^2\rho_i + 2\ell(\ell + 2)\mu_o^2\rho_o + \mu_i\mu_o[\rho_i(\ell + 2) - \rho_o(\ell - 1)]\}}{2R^2\Gamma[(\mu_i\rho_i)^{1/2} + (\mu_o\rho_o)^{1/2}]^2}$$
$$\pm i\left\{\beta^* - \frac{(2\ell + 1)^2(\beta^*\mu_i\mu_o\rho_i\rho_o)^{1/2}}{2\sqrt{2}R\Gamma[(\mu_i\rho_i)^{1/2} + (\mu_o\rho_o)^{1/2}]}\right\} \qquad (9)$$

Marston (1980) and Prosperetti (1980) have shown that Miller and Scriven have omitted the second term from the decay factor in Eq. 9, which is of the same order of magnitude as the third term in the decay factor. We have verified Marston and Prosperetti's claim using the symbolic manipulator MACSYMA. Incidentally, it has been found that there is no order viscosity correction to the angular frequency of oscillation, a point which has not been mentioned by previous investigators. Therefore, both the decay factor and the frequency are accurate to order viscosity to the three halves power.

Miller and Scriven have also shown that the solution of Eq. 1 that is asymptotically valid when the viscosities of both fluids are "high" is:

$$\beta = \frac{\beta^{*2}R^2(2\ell + 1)(\mu_i + \mu_o)\Gamma}{2\mu_i^2(\ell^2 - 1)(2\ell^2 + 4\ell + 3) + 2\mu_o^2\ell(\ell + 2)(2\ell^2 + 1) + 8\mu_o\mu_i\ell(\ell^2 - 1)(\ell + 2) + 3\mu_o\mu_i(2\ell + 1)^2} \qquad (10)$$

We have also verified Eq. 10, the high-viscosity approximation (HVA), by repeating Miller and Scriven's analysis. Note that the so-called least-damped or the slowly-decaying aperiodic mode given by Eq. 10 is independent of the densities of the two fluids.

$\beta_1 R/U \sim 1$: *Relative Motion between the Two Phases.* By allowing for relative motion between the drop and the surrounding fluid, Subramanyam (1969) has shown that the appropriate form of the dispersion relation for a drop undergoing second-harmonic oscillations is:

$$\frac{-40(\lambda + 1)}{\sigma'^2 We_i} + \frac{38\lambda^2 + 89\lambda + 48}{i\sigma'\lambda Re_i} + \frac{26\lambda + 29}{4} + \frac{16\lambda + 14}{K} = 0 \qquad (11)$$

In Eq. 11, $\lambda \equiv \mu_i/\mu_o$, $K \equiv \rho_i/\rho_o$; $Re_i \equiv UR/\nu_i$ is the Reynolds number and $We_i \equiv \rho_i R U^2/\gamma$ is the Weber number; and $\sigma' \equiv \sigma R/U$, where σ and σ' are dimensional and dimensionless frequencies and $\sigma \equiv i\beta$. Equation 11 is valid so long as both Re_i, $We_i \ll 1$.

Numerical solution of the dispersion relation of Miller and Scriven

The dispersion relation Eq. 3 was solved here by Newton's method in the complex plane. The calculation of solutions of Eq. 3 and presentation of the results are made efficient by introduction of dimensionless groups. The dimensionless complex frequency, $\bar{\beta}$, is a function of

$$\bar{\beta} = \beta\sqrt{\frac{\rho_i R^3}{\gamma}} = b + iw = F(\epsilon_i, \epsilon_o, K, B, We_i) \qquad (12)$$

where $\epsilon_i \equiv \nu_i \sqrt{\rho_i/\gamma R}$ and $\epsilon_o \equiv \nu_o \sqrt{\rho_o/\gamma R}$ are Ohnesorge numbers based on the properties of the droplet and continuous phases, respectively. For a truly isolated drop, $B = We_i = 0$ and the frequency is simply a function of the Ohnesorge numbers and the density ratio. In Eq. 12, $b = Re(\overline{\beta})$ is the dimensionless decay factor and $w = Im(\overline{\beta})$ is the dimensionless angular frequency of oscillation.

Experimental Methods and Procedures

Materials and apparatus

The fluids utilized in this study were mutually saturated distilled water and reagent-grade 2EtOH from Eastman Kodak. Table 1 contains a listing of the pertinent physical properties of the two saturated liquid phases.

Figure 1 is a schematic diagram of the experimental apparatus used in this study. The set-up is comprised of three subsystems: 1) the test cell, 2) the video analysis equipment, and 3) the voltage pulse generator.

The test cell is a 6.4-cm^2, 10.2-cm-tall glass container. A teflon plug was designed to fit snugly into the top of the cell and support the electrodes and droplet formation syringe. The 3.8 cm^2, 0.3 cm thick electrodes were constructed of stainless steel. Electrode spacing was varied from 1 to 2 cm, depending on droplet size. The "hot" electrode was connected to the voltage pulse generator by a 0.3-cm, stainless-steel rod which penetrated the teflon plug. Droplets were introduced into the system by using precision syringes. Droplets with volumes lying in the 1 to 8 μL range were made using a 2-μL capacity Gilmont micrometer syringe, while those below 1 μL in volume were made utilizing a SGE 1.0-μL syringe.

The video analysis system was comprised of a black and white TRITRONIX model DCSM-5600 shuttered video camera, light source, SUPER BRAIN model CM13L 13-in. monitor, SONY model VO-5800 video recorder, FOR.A model UTG-33 video timer, and a FOR.A model VPA-1000 video position analyzer. A BAUSCH & LOMB model EE225 32-mm macrolens was attached to a 4-in. barrel and used to form the image for the video camera. The resolution of the video position analyzer on the image displayed on the monitor translates to ± 7.1 μm for actual measurements.

The pulsed electric field was created by utilizing components of an automobile ignition system. A variable speed electric motor rotated a distributor that delivered six "ignitions" per revolution. A variable DC power supply (0-12 V) provided power to the primary windings of an automotive ignition coil. The "hot" side of the electrode system was connected to the high-voltage output of the secondary winding. Upon firing, the coil could deliver voltage spikes of up to 25 kV, dependent upon the primary coil voltage.

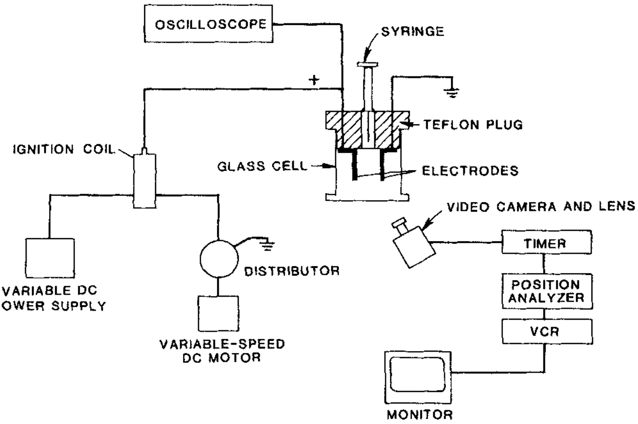

Figure 1. Experimental apparatus for droplet oscillation studies.

Procedures

The apparatus described above was used to investigate the amplitude of droplet oscillation in a pulsing electric field. For each of several droplet sizes, the amplitude of oscillation was recorded as a function of pulse frequency of the electric field. In each series of measurements, the peak field strength was maintained at a constant level. Typical procedure of the experiments involved obtaining a series of amplitude vs. pulse frequency measurements for a single droplet size. Before introduction of the droplet, the electric field pulse generator was activated and set to the desired frequency and field strength. The characteristics of the field at the hot electrode were checked by using an oscilloscope. Upon proper setting, the power supply to the primary coil was turned off. A single aqueous droplet of known volume was produced at the syringe tip and allowed to fall through the organic phase towards the electrode region. Before the droplet reached the electrode region, the pulse generator was activated.

The video camera was focused on a region which was approximately 1 cm down from the top of the electrodes. This placement allowed droplets to undergo a number of oscillations and therefore approach steady-state behavior before passing through the viewing zone. The events which occurred as droplets passed through the viewing zone were recorded on video tape and later replayed in order to allow measurement of the amplitude of the oscillations with the video position analyzer. At least three repeat measurements were carried out at each pulse frequency. Operation of the video camera was carried out without shuttering for droplets with "natural frequencies" below 60 Hz. In this mode, one video image (frame) is recorded every 1/60 s. For observations carried out at higher frequencies, multiple electronic scans could be taken to produce two to five images every 1/60 s (maximum effective speed of 300 frames/s). In addition to varying the framing speed the shutter speed of the camera can be adjusted from "open" to 1/10,000 s to freeze high-speed motion. Playback of the recorded tape was done in frame-by-frame fashion for data analysis. The droplet volumes studied ranged from 0.1 to 8.0 μL (0.025 to 0.124 cm radius, respectively).

Results

In this section, the term "exact" is used to denote the solution of Eq. 3 that was obtained numerically to distinguish it from various approximations such as the LVA or the HVA. In addition, both B and We_i are taken to be zero—no relative motion between the two phases, unless otherwise indicated.

Figure 2 shows the results of calculations for a drop of 1-cm radius undergoing second-harmonic oscillations ($\ell = 2$) in a continuous phase having the same viscosity. The results show that, when the viscosities of the two phases are equal, the low- and high-viscosity approximations are in excellent agreement with the exact solution, except over a narrow range of viscosities.

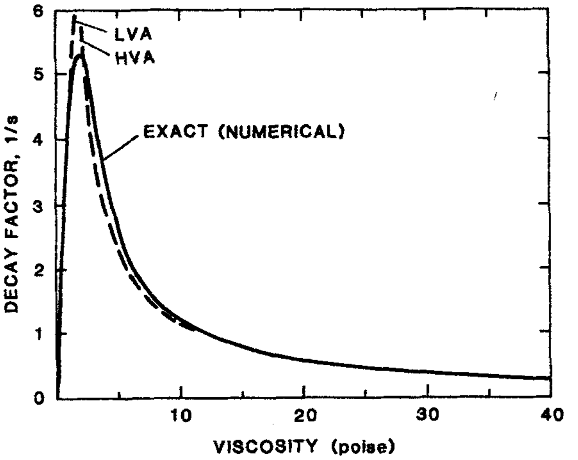

Figure 2. Exact and approximate solutions of Eq. 3 for a drop undergoing second-harmonic oscillations ($\ell = 2$): dimensional decay factor vs. viscosity ($\mu_i = \mu_o$).

$R = 1$ cm, $\gamma = 25$ dyne/cm, $\rho_o = \rho_i = 1$ g/cm^3.

Figures 3 and 4 show how the dimensionless angular frequency, $w = Im(\bar{\beta})$, varies with the Ohnesorge number for the drop phase as a function of the Ohnesorge number for the continuous phase for a drop undergoing second-harmonic oscillations ($\ell = 2$). These two figures make plain that the LVA is accurate so long as ϵ_i and ϵ_o (or μ_i and μ_o, if everything else is held fixed) are both small and are of the same order of magnitude. For $\epsilon_o = 0.1$, the error in the LVA is about 10% for $\epsilon_i \rightarrow 0$ but drops down to about 2% when $\epsilon_i = \epsilon_o = 0.1$. Figure 4 shows that the LVA is not accurate anywhere when $\epsilon_o = 0.5$ or 0.9. Figures 3 and 4 also show that Lamb's frequency for two inviscid fluids, which is the frequency predicted by the theory of Valentine et al. (1965), is valid only when ϵ_i and ϵ_o are both vanishingly small. Though this was pointed out 20 years ago by Miller and Scriven, use of the Lamb frequency in the context of liquid-liquid systems is still commonplace in the literature (see, e.g., Malalah et al., 1987).

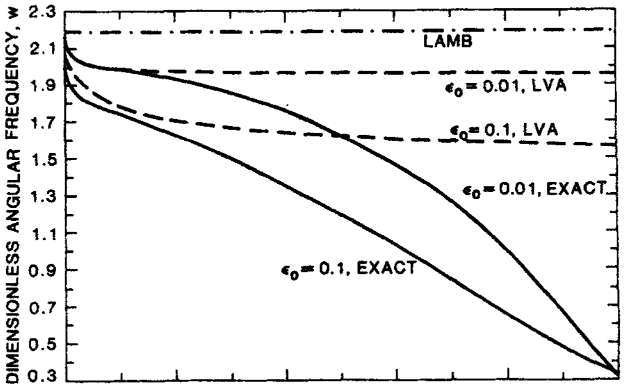

Figure 3. Exact and approximate solutions of Eq. 3 for a drop undergoing second-harmonic oscillations ($\ell = 2$): dimensionless angular frequency, w, vs. drop Ohnesorge number ϵ_i, as a function of the Ohnesorge number for the continuous phase, ϵ_o.

The straight line is Lamb's frequency, given by Eq. 4. In all cases shown, $\rho_o = \rho_i$.

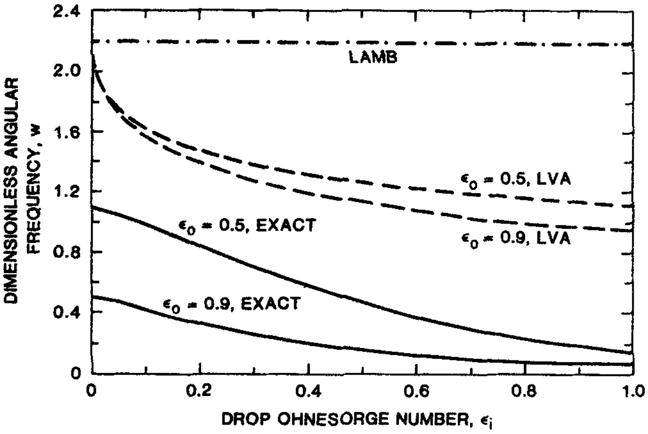

Figure 4. Exact and approximate solutions of Eq. 3 for a drop undergoing second-harmonic oscillations ($\ell = 2$): dimensionless angular frequency, w, vs. drop Ohnesorge number, ϵ_i, as a function of the Ohnesorge number for the continuous phase, ϵ_o.

The straight line is Lamb's frequency, given by Eq. 4. In all cases shown, $\rho_o = \rho_i$.

Figures 5 and 6 show how the dimensionless decay factor, $b = Re(\bar{\beta})$, varies with the Ohnesorge number for the drop phase as a function of the Ohnesorge number for the continuous phase for a drop undergoing second-harmonic oscillations ($\ell = 2$). These two figures demonstrate once more that the LVA is accurate so long as ϵ_i and ϵ_o (or μ_i and μ_o, if everything else is held fixed) are both small and are of the same order of magnitude. When ϵ_i, $\epsilon_o \rightarrow 0$ but $\epsilon_i \ll \epsilon_o$, the dimensionless decay factor is well approximated by (see Eq. 9):

$$b = \ell(\ell + 2)\epsilon_o \tag{13}$$

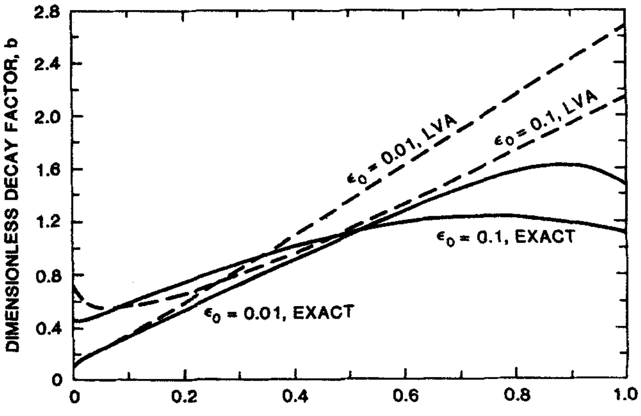

Figure 5. Exact and approximate solutions of Eq. 3 for a drop undergoing second-harmonic oscillations ($\ell = 2$): dimensionless decay factor, b, vs. drop Ohnesorge number, ϵ_i, as a function of the Ohnesorge number for the continuous phase, ϵ_o.

In all cases shown, $\rho_o = \rho_i$.

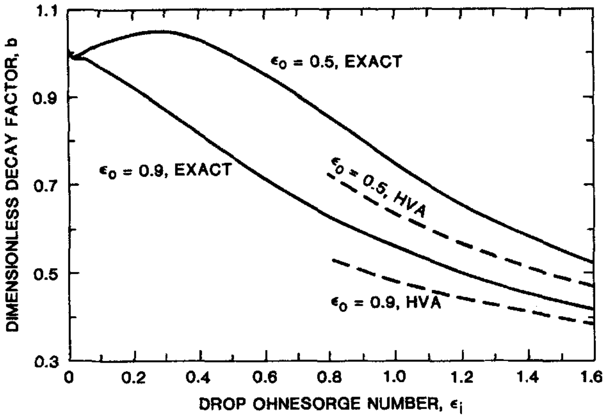

Figure 6. Exact and approximate solutions of Eq. 3 for a drop undergoing second-harmonic oscillations ($\ell = 2$): dimensionless decay factor, b, vs. drop Ohnesorge number, ϵ_i, as a function of the Ohnesorge number for the continuous phase, ϵ_o.
In all cases shown, $\rho_o = \rho_i$.

Thus, $b = 8\epsilon_o$ when $\ell = 2$. The numerical calulations show that when $\epsilon_i \rightarrow 0$, $b = 6.8 \times 10^{-2}$ for $\epsilon_o = 10^{-2}$, $b = 7.6 \times 10^{-3}$ for $\epsilon_o = 10^{-3}$, and $b = 8 \times 10^{-4}$ for $\epsilon_o = 10^{-4}$. Figures 5 and 6 show that the exact results for $\epsilon_o = 0.1, 0.5$, and 0.9 exhibit a shallow minimum as ϵ increases from zero. This behavior is in accord with the classical analysis of the laminar boundary layer between parallel streams (Lock, 1951). The comparison of the exact values of b in Figure 5 is with the LVA and that in Figure 6 is with the HVA because in the latter case the error in the LVA (measured relative to the exact solution) is several hundred percent. Figures 5 and 6, as well as Figure 2, show that the HVA is most accurate when ϵ_i and ϵ_o are both large and are also of the same order of magnitude. When ϵ_o is sufficiently large, the decay factor decreases as ϵ_i increases, which is characteristic of highly overdamped oscillators.

Table 2 shows the effect of interchanging drop and ambient fluid viscosities, while holding everything else constant, for a drop undergoing second-harmonic oscillations ($\ell = 2$). The results of Table 2 make plain that increasing the viscosity of the continuous phase has a larger effect on the complex frequency than increasing the viscosity of the drop phase by the same amount while holding the continuous-phase viscosity fixed. This finding is in agreement with the experimental results of Trinh et al. (1982): see Table 3 in their paper. Moreover, Table 2 also shows that the prediction by the LVA of both the decay factor and the frequency when the viscosity of the surrounding fluid is greater than that of the drop is worse than those when the viscosity of the drop is the larger of the two viscosities, which was hitherto unsuspected. This is because the LVA greatly overestimates viscous dissipation outside the boundary layer in the continuous phase. When $\mu_o/\mu_i = 10$, the error in the decay factor is 38% for $R = 0.1$ cm and it is 100% for $R = 0.01$ cm. Moreover, the LVA is unable to account properly for the variation of the frequency with viscosity because β_I in Eq. 9 is invariant when μ_i and μ_o are swapped for one another provided $\rho_i = \rho_o$. Table 2 also shows that the error incurred by Miller and Scriven in omitting a term in the LVA to the decay factor is in general small, as discussed previously.

Table 2. Effect of Interchanging Drop and Ambient Fluid Viscosities*

β	$R = 10^{-2}$ m (1 cm)	$R = 10^{-3}$ m (10^{-1} cm)	$R = 10^{-4}$ m (10^{-2} cm)
		$\mu_i/\mu_o = 1$	
Exact	$0.248 + 6.70i$	$14.64 + 206.0i$	$893.1 + 6{,}186i$
P&M**	$0.248 + 6.70i$	$14.65 + 206.0i$	$892.0 + 6{,}193i$
M&S†	$0.264 + 6.70i$	$16.21 + 206.0i$	$1{,}048.2 + 6{,}193i$
Lamb	$6.93i$	$219.1i$	$6{,}928i$
		$\mu_i/\mu_o = 10$	
Exact	$0.486 + 6.57i$	$33.10 + 198.8i$	$2{,}550 + 5{,}417i$
P&M**	$0.504 + 6.57i$	$34.90 + 199.2i$	$2{,}622 + 5{,}810i$
M&S†	$0.540 + 6.57i$	$38.50 + 199.2i$	$2{,}982 + 5{,}810i$
Lamb	$6.93i$	$219.1i$	$6{,}928i$
		$\mu_o/\mu_i = 10$	
Exact	$0.686 + 6.50i$	$46.10 + 188.0i$	$2{,}702 + 4{,}436i$
P&M**	$0.790 + 6.57i$	$63.50 + 199.2i$	$5{,}479 + 5{,}810i$
M&S†	$0.826 + 6.57i$	$67.10 + 199.2i$	$5{,}840 + 5{,}810i$
Lamb	$6.93i$	$219.1i$	$6{,}928i$

*$\gamma = 10^{-2}$ N/m (10 dyne/cm); $\rho_i = \rho_o = 10^3$ kg/m^3 (1 g/cm^3); min (μ_i, μ_o) = 10^{-3} kg/(m · s) [10^{-2} g/(cm · s)]

**LVA of Prosperetti (1980) and Marston (1980)

†LVA of Miller and Scriven (1968)

When they did not observe quantitative agreement between the predictions of the LVA, Eq. 9, and their experimental measurements, Trinh et al. (1982) state that this is quite reasonable because contamination of the interface could not be avoided. Figure 7 compares a set of experimental measurements of decay factors by Trinh et al. (1982) with various solutions of Eq. 3: the exact solution, the LVA of P&M and the LVA of Miller and Scriven (LVA of M&S). The experimental data are from the fifth column of Table 2 of the paper by Trinh et al. (1982). Figure 7 shows that the measurements of Trinh et al. (1982) are in excellent agreement with the exact solution. Once more, the discrepancy between the two LVA's is small.

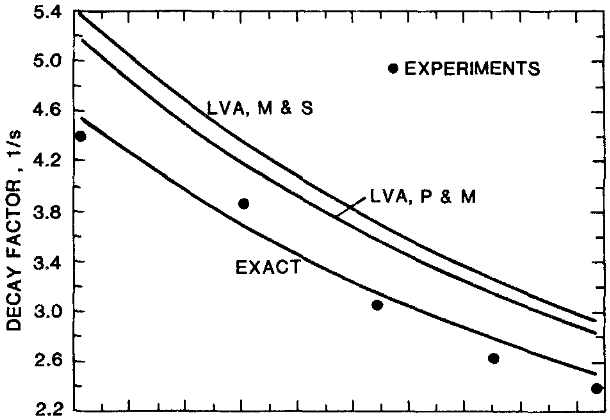

Figure 7. Experiments of Trinh et al. (1982) with exact and approximate solutions of Eq. 3 for a drop of Silicone/CCl$_4$ mixture undergoing second-harmonic oscillations ($\ell = 2$) in distilled water: dimensional decay factor vs. drop radius.
$\gamma = 37.5$ dyne/cm, $\nu_i = 0.368$ cm^2/s, and $\nu_o = 0.011$ cm^2/s.

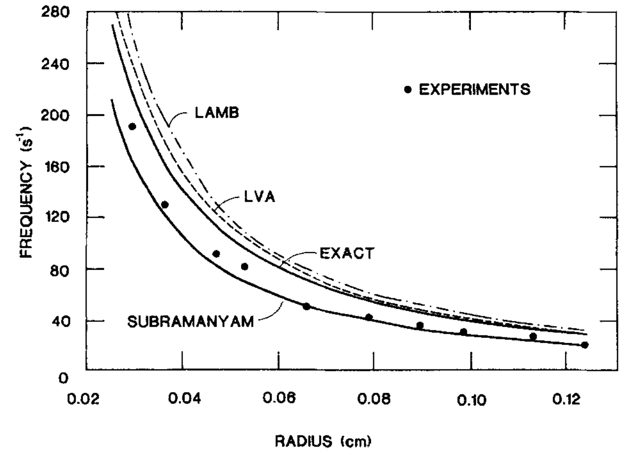

Figure 8. Frequencies of second-harmonic oscillation (ℓ = 2) as a function of radius for water drops falling in 2EtOH: experiments and theory.
See the "Introduction" Section for the properties of the two fluids.

Figure 8 shows the frequencies of oscillation of water drops falling in 2EtOH. The experimental data were obtained from the apparatus described previously. When drop radius is large, the exact solution of Eq. 3 does a poor job of representing the experimental measurements. However, Subramanyam's (1969) dispersion relation, Eq. 11, which accounts for the flow past the oscillating drop is in excellent agreement with the experiments for large drop radii. The predictions of the exact solution of Eq. 3 improve and those of Eq. 11 worsen as drop radius gets smaller, in accordance with the earlier discussion.

Figure 9 shows how the dimensionless angular frequency, w, varies with the Ohnesorge number for the drop phase as a function of the Ohnesorge number for the continuous phase for drops undergoing third-harmonic oscillations ($\ell = 3$). The corresponding decay factors are shown in Figure 10. As $\epsilon_i, \epsilon_o \rightarrow 0$ but $\epsilon_i \ll \epsilon_o$, Figure 10 shows that $b \rightarrow 15\,\epsilon_o$.

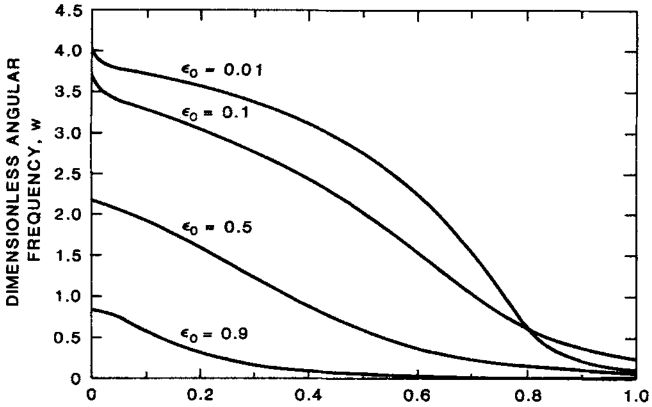

Figure 9. Exact solution of Eq. 3 for a drop undergoing third-harmonic oscillations ($\ell = 3$): dimensionless angular frequency, w, vs. drop Ohnesorge number, ϵ_i, as a function of the Ohnesorge number for the continuous phase, ϵ_o.
In all cases shown, $\rho_o = \rho_i$.

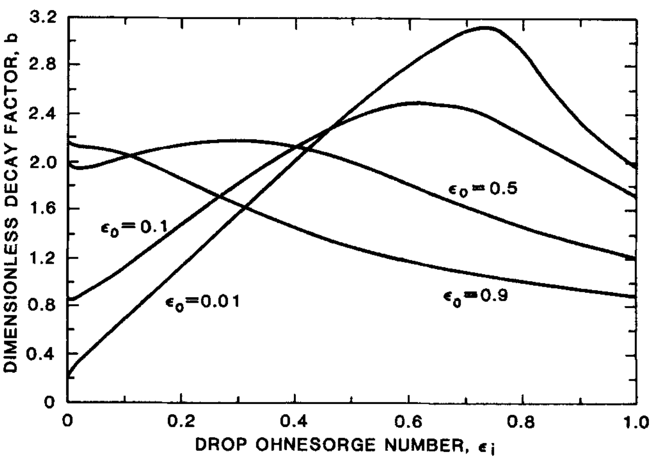

Figure 10. Exact solution of Eq. 3 for a drop undergoing third-harmonic oscillations ($\ell = 3$): dimensionless decay factor, b, vs. drop Ohnesorge number, ϵ_i, as a function of the Ohnesorge number for the continuous phase, ϵ_o.
In all cases shown, $\rho_o = \rho_i$.

Calculations for mode numbers other than $\ell = 2$ and 3 show that when ϵ_o is finite, the exact solution of Eq. 3 does not predict a transition to aperiodic motion for any value of the mode number ℓ. That is, for large ϵ_i (or μ_i), the curves for w tend to zero only asymptotically. Thus, a liquid drop oscillating in another liquid behaves qualitatively more similar to a bubble oscillating in a liquid than a liquid drop oscillating in a vacuum or a rarefied gas, where a transition to aperiodic motion does occur. (See Prosperetti, 1980, who presents numerical solutions of Eq. 3 for the bubble and drop cases for several values of ℓ.)

The frequency of oscillation for two inviscid fluids increases with mode number ℓ (Eq. 4). From Figures 3, 4 and 9, it is evident that this is also true for any ϵ_o when ϵ_i is small. For example, for $\epsilon_o = 0.5$ and $\epsilon_i = 0.1$, $w = 0.983$ for $\ell = 2$, $w = 1.932$ for $\ell = 3$, and $w = 2.81$ for $\ell = 4$. However, the situation is reversed for large values of ϵ_i. For example, for $\epsilon_o = 0.5$ and $\epsilon_i = 0.8$, $w = 0.234$ for $\ell = 2$, $w = 0.147$ for $\ell = 3$, and $w = 0.0384$ for $\ell = 4$. This reversal in behavior for a liquid drop oscillating in another liquid has also been found for a bubble oscillating in a liquid and a drop oscillating in a vacuum or a rarefied gas (Prosperetti, 1980).

By contrast, decay factors always increase with mode number ℓ for a liquid drop oscillating in another liquid, see Figures 5, 6 and 10. For example, for $\epsilon_o = 0.5$ and $\epsilon_i = 0.1$, $b = 1.022$ for $\ell = 2$, $w = 2.040$ for $\ell = 3$, and $w = 3.34$ for $\ell = 4$. For $\epsilon_o = 0.5$ and $\epsilon_i = 0.8$, $w = 0.85$ for $\ell = 2$, $w = 1.468$ for $\ell = 3$, and $w = 1.88$ for $\ell = 4$. This behavior is identical to that observed for a bubble oscillating in a liquid and also a liquid drop oscillating in a vacuum or a rarefied gas when the relevant Ohnesorge number is either small or large (Prosperetti, 1980).

Concluding Remarks

According to the foregoing results, agreement between theory and experiment can be improved by solving the dispersion equation, Eq. 1 or Eq. 3, numerically, instead of relying on approximations to it. With the aid of the exact (numerical) solutions presented in this paper, one would then be able to say with certainty for the first time that observed discrepancies between theoretical predictions and experimental measurements are due to other important effects such as finite-amplitude oscillations, surface tension gradients, and variation of physical properties other than surface tension.

The LVA has been found to be especially inaccurate in the context of solvent extraction where drops of one liquid having properties like those of water are dispersed in a continuous phase which is slightly less dense but much more viscous than the drop phase. As shown in Table 2, use of the LVA can result in large errors in the frequencies of oscillation and even larger errors in decay rates when the viscosity of the continuous phase is say ten times that of the dispersed phase. Moreover, the error in the LVA increases as drop radius decreases. Thus, use of either the exact solutions of Eq. 3 or those of Eq. 11 are a must in the context of electric-field-enhanced solvent extraction where: 1) accurate knowledge of natural frequencies of oscillation is necessary for proper operation of the extraction device (see, e.g., Scott, 1987); and 2) the typical drop size is much smaller than that in ordinary solvent extraction in the absence of electric field (see, e.g., Scott and Wham, 1989).

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Notation

b = real part of $\bar{\beta}$
B = gravitational Bond number, $gR^2\Delta\rho/\gamma$
C = function defined in Eq. 5
F = function defined in Eq. 6
g = gravitational acceleration, cm/s^2
G = function defined in Eq. 7
i = imaginary unit
K = ratio of fluid densities, ρ_i/ρ_o
ℓ = mode number
Q^H = ratio of fractional order Hankel functions of the first kind, Eq. 8
Q^J = ratio of fractional order Bessel functions of the first kind, Eq. 8
R = drop radius, cm
Re_i = Reynolds number, UR/ν_i
U = drop center-of-mass velocity relative to continuous phase, cm/s
w = imaginary part of $\bar{\beta}$
We_i = Weber number, $\rho_i RU^2/\gamma$

Greek letters

β = complex frequency, s^{-1}
β_I = oscillation frequency, s^{-1}
β_R = decay factor, s^{-1}
$\underline{\beta}^*$ = Lamb frequency, Eq. 4, s^{-1}
$\bar{\beta}$ = dimensionless complex frequency, $\beta\sqrt{\rho_i R^3/\gamma}$
γ = interfacial tension, dyne/cm
Γ = density function, $\rho_o\ell + \rho_i(\ell + 1)$, g/cm^3
Δ = free interface complex frequency determinant, Eq. 3
ϵ = Ohnesorge number, $\nu\sqrt{\rho/\gamma R}$
λ = viscosity ratio, μ_i/μ_o
μ = viscosity, poise
ν = kinematic viscosity, cm^2/s
σ = complex frequency, $i\beta$, s^{-1}
σ' = dimensionless complex frequency, $\sigma R/U$
ρ = fluid density, g/cm^3
ω = $\sqrt{\beta/\nu}$, cm^{-1}

Subscripts

i = referring to the droplet phase
o = referring to the continuous phase

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