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On the Dynamics of Fluid Interfaces

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SCOPE

Under conditions of equilibrium, the property of interfacial tension is sufficient to completely describe fluid-fluid interfaces. However, it has been realized that under dynamic conditions, interfaces exhibit properties that are quite unique. Consequently, in recent years, fluid interfaces in motion have excited the attention of a large number of researchers in a variety of problems of far-reaching interest physically. To mention a few of these, one can list the phenomenon of capillarity in classical hydrodynamics, the damping of water waves by films of oil, the chemistry of surface films, the stability of foams and emulsions, the behavior of drops and bubbles, the enhancement of transfer across interfaces, and a wide variety of other problems.

The unique nature of these dynamic interfacial properties has even led to the characterization of interfaces as a distinct phase. Interfacial mechanics deals with the resistance offered by interfaces to viscous and elastic forces and consequent dynamic properties. In recent years, several mathematical models have been proposed to describe the dynamics of an interface, and these usually incorporate properties such as dilational viscosity and elasticity and shear viscosity and elasticity. Experimental measurement of these and their verification seem very scanty.

The objective of this work is to theoretically and experimentally analyze an interface in motion with a view to throwing a little more light on these properties. The system of dispersed phases oscillating in a continuous medium is chosen to provide a dynamic interface. From the existing theories of interfacial mechanics and the basic theory of oscillating dispersed phases in a continuous medium, the decay and frequency of these oscillations are computed as functions of the dynamic interfacial properties. An experimental system is set up, and the decay and frequency of liquid drops and gas cavities of varying radii are measured. On the belief that these dynamic properties are altered by the presence of surface active agents, the system was maintained very clean, and experiments were performed with triple distilled water, tap water, and accurate aqueous solutions of ionic and nonionic surfactants. A comparison with the theoretical predictions was made in an attempt to estimate some of the interfacial properties.

CONCLUSIONS AND SIGNIFICANCE

The theoretical computations were made by assigning values to the interfacial properties reported in the literature. From the general system of disperse phases oscillating in a continuous medium, two simplified cases were chosen. These were the case of a drop of liquid oscillating in a gas and a gas cavity oscillating in a liquid. The size range of the drops and cavities studied were from 0.8 to 1.5 mm. This range was chosen from experimental consideration. Sizes below 0.8 mm were not studied because of the very high frequency that they exhibit, making measurements inaccurate, and sizes beyond 1.5 mm exhibit deformation from the spherical shape, making the theory inaccurate. Within this size range, it was found that the interfacial viscosities had little effect on the decay and frequency. The dominant interfacial properties in this range are the elasticities. It was found that the dilational elasticity dominated in the case of the drop, and the shear

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elasticity dominated in the case of the cavity. The theory indicates that at much smaller drop and cavity sizes, the interfacial viscosities will dominate. Therefore, by choosing the proper system, namely, a drop in air or a cavity in a liquid, one can study dilational effects or shear effects.

The experimental study was done with triple distilled water, tap water, and aqueous solutions of ionic and nonionic surfactants. In the size range studied, the experimental results show qualitative agreement with the theory and demonstrate that the presence of surface active agents in the interface does impart rheological properties to it. Also, the deviation of the distilled water data from the theoretical predictions for a free interface (an interface with no dynamic properties) does indicate the possibility of an interface having intrinsic rheological character. In all these measurements, it was found that the decay factor was the one that was influenced significantly by the interfacial properties, while the frequency, on the other hand, is dependent only on the interfacial tension.

In all, the present study of the interfacial mechanics of a dispersed phase in forced oscillation demonstrates the system to be a new and promising technique for the quantitative evaluation of the various interfacial viscous and elastic properties.

Part I.

The system of a dispersed phase oscillating in a continuous medium is investigated theoretically with the specific purpose of developing a new technique for the measurement of interfacial viscous and elastic properties. By use of the well-known models of interfacial mechanics, the decay and frequency of liquid drops oscillating in a gas and of gas cavities oscillating in a liquid are computed as functions of dynamic interfacial properties. The results of the theory indicate, for the size range considered, that the elastic properties dominate over the viscous properties and that dilational effects dominate in the case of the drop in air and shear effects dominate in the case of the cavity in a liquid. The frequency does not seem to depend on the dynamic interfacial properties.

In very simple terms, an interface is the boundary between two homogeneous phases, and it is a region of small but finite thickness in which transition occurs from one homogeneous bulk phase to another. In recent years, fluid interfaces have drawn the attention of a large number of research workers owing to a variety of problems of far reaching interest physically. One can list the phenomenon of capillarity in classical hydrodynamics, the damping of water waves by films of oil, the chemistry of surface films, the stability of foams and emulsions, the behavior of drops and bubbles, and a wide variety of other problems. In the description of systems not in equilibrium, it is well known that the interfacial phase can and does play a very significant role. Fluid motion can be sustained by and could originate in an interface in systems that are not in mechanical, thermal, or compositional equilibrium. The dynamic behavior of interfaces in motion has therefore excited a great deal of interest in the past (Thomson, 1855; Plateau, 1872; Gibbs, 1931; Marangoni, 1952; Boussinesq, 1913; Scriven, 1960). The central objective has been to demonstrate the significance (or lack) of peculiar properties that enter into the description of interfaces in motion through the use of a broad theory and a series of experiments.

A detailed look at the interfacial phase is of paramount interest and importance, and such a treatment is the essence of interfacial mechanics. An interface at rest, and in equilibrium, is conveniently described as a geometric surface in tension, and the fundamental equilibrium property of interfacial tension σ is sufficient to characterize it adequately. However, complications arise with motion, and the characteristic resistance offered to deformation introduces additional dynamic properties which have been the subject of interest in recent years (Scriven, 1960; Eliassen, 1963). This resistance to deformation was first observed by the Belgian physicist Joseph Plateau (Plateau, 1872), and he introduced the idea of a superficial viscosity to the interface which was later put on firmer ground by other workers (Gibbs, 1931). The first attempt at quantification of this behavior is attributable to Boussinesq (Boussinesq, 1913). In his attempt at modeling the interface by analogy with bulk fluids, he introduced the concept of interfacial viscosity, one for shear ϵ and one for dilation κ. Furthermore, the elastic nature of the interfacial phase, primarily due to gradients in interfacial tension, led to elastic properties being attributed to the interface (Oldroyd, 1955). The consideration of the interface as a distinct phase and its analogy with the bulk phases has led to the formulation of generalized transport equations for the interface with viscous and elastic properties and associated rheological models of interest (Scriven, 1960; Eliassen, 1963). This approach considers a fluid interface as a distinct phase with its own characteristic properties, interfacial tension, an equilibrium property analogous to the isotropic pressure of a fluid, and viscous and elastic properties which arise out of resistance to dilation, shear, bending, and twisting. The mathematical formulation of the problem is based on the following verbal description of the momentum balance:

> "Normal stress differences across an interface are balanced by the force of interfacial tension, a consequence of Laplace's equation (Davis and Rideal, 1961) and the dynamic forces due to bending and contributions from elongation. Similarly tangential stress differences are balanced by gradients in interfacial tension and dynamic forces arising from interfacial dilation and shear."

The mathematical expressions for these balances depend on the geometric configuration under consideration as shown in general treaties on the subject (Eliassen, 1963; Bupara, 1965). We will consider them for spherical shapes.

In parallel with these theoretical developments, there have been attempts at experimental substantiation of the interfacial properties. The only system that seems to have been considered heretofore seems to be the two-dimensional capillary wave. The capillary wave experiment has with it a long historical background, beginning with attempts at measuring interfacial tension (Kelvin, 1871) to measurements of dynamic interfacial properties (Goodrich, 1961; Davies, 1961; Mann and Hansen, 1963; Mayer, 1969). However, these experiments generally have not been very conclusive.

Another complicating factor in the study of interfaces is the role played by surface active agents. Existing in microscopically small quantities, these are known to alter the interfacial tension. Therefore, it would seem reasonable to expect that they would alter the dynamic character of the interface also. Any attempt at elucidating interfacial properties would therefore necessitate the use of a system whose interfacial characteristics are controllable to a fairly reasonable degree of accuracy.

The central objectives of this work are to study the effect of dynamic interfacial properties on the motion of an interface and to develop a controllable technique of measurement of the characteristics of the motion with a view to estimating the role of these interfacial properties.

The system used is that of dispersed phases oscillating in a continuous medium, the interfacial models applied are the recent work of Scriven and co-workers, the experimental technique is optical, and the controllability is through the use of controlled amounts of known surface active agents.

OSCILLATING DISPERSE SYSTEMS: AN INTERFACE IN MOTION

The movement of a dispersed phase in a continuous medium and the transfer of heat and mass between them have attracted a great deal of attention from many researchers. A droplet or cavity of one fluid immersed in another fluid assumes a static shape that is nearly spherical when gravitational effects are small in comparison with interfacial tension effects. If such a dispersed phase is deformed by an external force which is applied and then removed, it will return back to its former spherical shape. Depending on the properties of the fluids involved and the composition of the interface, this process may involve a series of oscillations about the spherical shape with continuously decreasing amplitude. Such an effect is observed when the dispersed phase is lighter or heavier than the continuous phase. In the present work, both such systems are studied: a drop of liquid in air and a bubble of air in a liquid.

The return of the deformed dispersed phase to the equilibrium spherical shape through a series of oscillations is characteristic of the dynamical response of many systems. When a drop is deformed by an external force, which is applied and then removed, certain restoring forces start operating which tend to bring it back to its equilibrium shape. This restoring force is usually the interfacial tension σ. However, owing to the inertia of the system, the restoring forces cause an overshoot of the equilibrium position. Hence a series of oscillations of decreasing amplitude are observed. These oscillations alternate between an oblate and a prolate form. One would expect the decay to be dependent on the viscous properties of the two fluids and on the dynamic characteristic of the interface itself. On the other hand, the frequency of the oscillation would be expected to be a function mainly of the restoring force, namely, interfacial tension. Theoretical estimates of the decay rate β_R and frequencies β_I have been obtained in the absence of any dynamic interfacial properties (Kelvin, 1871; Lamb, 1945; Miller and Scriven, 1968) and are given by

$$\beta_R = \frac{5\nu_i}{R^2} \tag{1}$$

$$\beta_I = \sqrt{\frac{8\sigma}{R^3\rho_i}} \tag{2}$$

for a drop oscillating in air and

$$\beta_R = \frac{20\nu_o}{R^2} \tag{3}$$

$$\beta_I = \sqrt{\frac{12\sigma}{R^3\rho_o}} \tag{4}$$

for a bubble of a gas oscillating in a liquid. Some experimental measurements of the frequency and decay are also available (Valentine et al., 1965, Schroeder and Kintner, 1965; Loshak and Byers, 1973). The choice of this system for the study of interfacial motion is based on the work of Loshak and Byers, wherein the high speed optical technique of studying droplet oscillations was first developed.

THEORY

The system under consideration is that of dispersed phases oscillating in a continuous medium, the interface of which has characteristic viscous and elastic properties. The experimentally measurable variables of the system are the decay and frequency of the oscillations. Therefore, the theory must be capable of predicting the decay and frequency as a function of the interfacial viscous and elastic properties, the bulk viscosity and density, the interfacial tension, and a characteristic length of the system which would be the diameter of the dispersed phase.

The general hydrodynamic theory is the same as that developed in the literature (Chandrasekhar, 1960; Bupara, 1965; Miller and Scriven, 1968). For the system under consideration, consisting of an incompressible fluid phase dispersed in another, a small displacement theory would lead to the solution of the Navier-Stokes in terms of spherical harmonics and appropriate half-integer Bessel functions (Miller and Scriven, 1968; Abramowitz and Stegun 1960):

$$w_i(r) = a_1 r^b + a_3 \sqrt{\frac{\pi}{2\gamma_i r}}\, J_{b+1/2}(\gamma_i r) \tag{5}$$

w_i : inner radial velocity

$$w_o(r) = a_2 r^{-b-1} + a_4 \sqrt{\frac{\pi}{2\gamma_o r}}\, H^{(1)}_{b+1/2}(\gamma_o r) \tag{6}$$

w_o : outer radial velocity

$$z_i(r) = b_1 \sqrt{\frac{\pi}{2\gamma_i r}}\, J_{b+1/2}(\gamma_i r) \tag{7}$$

z_i : inner radial vorticity

$$z_o(r) = b_2 \sqrt{\frac{\pi}{2\gamma_o r}}\, H^{(1)}_{b+1/2}(\gamma_o r) \tag{8}$$

z_o = outer radial vorticity

where

$$\gamma_i^2 = \frac{\beta_b}{\nu_i} \tag{9}$$

$$\gamma_o^2 = \frac{\beta_b}{\nu_o} \tag{10}$$

where β_b represents the complex frequency of mode b. $J_{b+1/2}(\gamma_i r)$ represents a half-integer spherical Bessel, and $H^{(1)}_{b+1/2}(\gamma_o r)$ represents a half-integer Hankel function of the first kind. To determine the coefficients a_1, a_2, a_3, a_4, b_1, and b_2, six boundary conditions are required.

Our primary interest is the boundary conditions on the interface. It is in here that the dependency of the decay and frequency of oscillations on the interfacial rheological parameters occur. In the analysis of the oscillations of the dispersed phase, one encounters a deformed interface. For such an interface, the interfacial conditions have to be defined. The method outlined by Bupara (1965) is used here. A deformed interface is quite difficult to describe mathematically unless the boundary conditions happen to coincide with a coordinate surface of the system, the so-called natural boundary conditions. Hence the assumption made is that a deformed surface is in fact a perturbation of some reference state or surface of known properties, which also coincides with the coordinate surface of the system. In the current problem, the spherical coordinate system with the radius of the dispersed phase forms the so-called natural reference state. The boundary conditions in spherical coordinates at the perturbed surface are given in terms of conditions at the reference surface by means of a Taylor series approximation (Bupara, 1965).

In the case of spherical systems, the small displacement may be written as

$$R^* = R + B(\theta, \phi, t) \tag{11}$$

Since the oscillations undergo a decay in time, the displacement B is a function of time also. If the interfacial displacement is assumed to be sufficiently small, its time and angular dependence should be of the same form as the radial velocity and vorticity. Hence

$$B = B_{bm} = B_{obm} \exp[-\beta_b t]\, \gamma_b{}^m(\overline{\infty}) \tag{12}$$

Here B_o represents the initial displacement and is also unknown.

In the solution we have seven unknowns, namely, a_1, a_2, a_3, a_4, b_1, b_2, and B_{obm}. Therefore, we need seven equations, and these can be gotten from the kinematic condition, continuity of radial and tangential velocities, and a force balance. It is clear from an earlier work (Miller and Scriven, 1968) that seven equations can be obtained from these boundary conditions. Although these equations have been derived in general form by Miller and Scriven (1968), it might be noted that their equations have been derived based on the inner fluid velocity and vorticity. In this paper, we wish to consider two limiting cases of the general problem. The first would be when the external medium is rarefied, namely, that of a drop oscillating in a gas. The boundary conditions of Miller and Scriven (1968) can be used for this and would lead to an irrational algebraic equation in β containing all the physical properties of the system; that is

$$F_1(\beta, \rho_i, \rho_o, \mu_i, \mu_o, \sigma, R, \kappa, \epsilon, \lambda, M) = 0 \tag{13}$$

To this we can apply the condition of $\rho_o \to 0$ and $\mu_o \to 0$, use for the case of the droplet oscillating in a gas.

However, for the other limiting case of a bubble of gas oscillating in a liquid, we cannot use the boundary conditions of Miller and Scriven (1968) since they are based on the inner fluid velocity which is now rarefied. Hence, similar boundary conditions based on the external fluid velocity were derived (Ramabhadran, 1972) and are given below. It is fairly clear that the kinematic condition, the continuity of radial velocity, the surface divergence of the tangential velocity continuity, and the radial component of the surface curl of the tangential velocity continuity would remain the same. The differences would arise in the force balance boundary conditions only. It is here that the dependence on the interfacial properties occur and hence arises the difference between the two limiting cases. The force balance conditions based on the external fluid velocity (Ramabhadran, 1972) are given below:

Radial component of force balance:

$$\begin{aligned}
&- B_o\beta^{*2}\Gamma/b(b+1) + a_1 R^{b-1}\,[\rho_i\beta/b + 1 \\
&\quad - 2(b-1)\mu_i/R^2] + a_3\sqrt{\pi/2\gamma_i R^3}\,(2\mu_i/R^2) \\
&\quad [(1-b)\, J_{b+1/2}(\gamma_i R) + \gamma_i R\, J_{b+3/2}] \\
&\quad + a_2 R^{-b-2}\,[\rho_o\beta/b + 1 - 2(b+2)(\mu_o - D)/R^2] \\
&\quad - a_4\sqrt{\pi/2\gamma_o R^3}\,[2(\mu_o - D)/R^2][(1-b)\, H^1_{b+1/2}(\gamma_o R) \\
&\quad + \gamma_o R\, H^1_{b+3/2}(\gamma_o R)] = 0
\end{aligned} \tag{14}$$

where

$$\beta^* = \sqrt{\frac{b(b+1)(b-1)(b+2)\sigma}{R^3\{(b+1)\rho_i + b\rho_o\}}} \tag{15}$$

Surface divergence of the tangential force balance:

$$\begin{aligned}
&a_1 R^{b-1}\, 2(b^2-1)\mu_i \\
&\quad + a_3\sqrt{\pi/2\gamma_i R^3}\,\{\mu_i\,[2(b^2-1)\, J_{b+1/2}(\gamma_i R) \\
&\quad - \gamma_i^2 R^2\, J_{b+1/2}(\gamma_i R) + 2\gamma_i R\, J_{b+3/2}(\gamma_i R)]\} \\
&\quad - a_2 R^{-b-2}\, b(b+2)[2\mu_o + S(b+2) + Db] \\
&\quad - a_4\sqrt{\pi/2\gamma_o R^3}\,\mu_o\,[2(b^2-1)\, H^1_{b+1/2}(\gamma_o R) \\
&\quad - \gamma_o^2 R^2\, H^1_{b+1/2}(\gamma_o R) + 2\gamma_o R\, H^1_{b+3/2}(\gamma_o R)] \\
&\quad + S(b+2)(b)\,\{(b+2)\, H^1_{b+1/2}(\gamma_o R) \\
&\quad + \gamma_o R\, H^1_{b+3/2}(\gamma_o R) + Db(b+2)\,[b\, H^1_{b+1/2}(\gamma_o R) \\
&\quad + \gamma_o R\, H^1_{b+3/2}(\gamma_o R)]\} = 0
\end{aligned} \tag{16}$$

Radial component of the surface curl of the tangential force balance:

$$\begin{aligned}
&b_1\sqrt{\pi/2\gamma_i R}\,\mu_i\,[(b-1)\, J_{b+1/2}(\gamma_i R) - \gamma_i R\, J_{b+3/2}(\gamma_i R)] \\
&\quad - b_2\sqrt{\pi/2\gamma_o R}\,\{[(b-1)\mu_o + S(b+2)b]H^1{}_{b+1/2}(\gamma_o R) \\
&\mu_o\gamma_o R\, H_{b+3/2}(\gamma_o R)\} = 0
\end{aligned} \tag{17}$$

Using the boundary conditions based on the external fluid velocity, one can obtain an irrational algebraic equation in β containing all the physical properties of the system; that is

$$F_2(\beta, \rho_i, \rho_o, \mu_i, \mu_o, \sigma, R, \kappa, \epsilon, \lambda, M) = 0 \tag{18}$$

For the analysis of the general problem, either Equation (13) or (18) can be used, but for the limiting case of a drop of liquid in a gas, one has to use Equation (13) and for the case of a bubble in a liquid, one has to use Equation (18). We now wish to solve this transcendental equation for the simpler cases of a drop oscillating in a rarefied medium and a bubble of gas oscillating in a liquid.

A DROP OF LIQUID OSCILLATING IN A GAS

The rarefied nature of the external medium implies that it has no effect on the oscillations. The simplified system is considered for mathematical tractability, and it is also expected that the problem may represent a situation in which some of the interfacial properties may be less im-

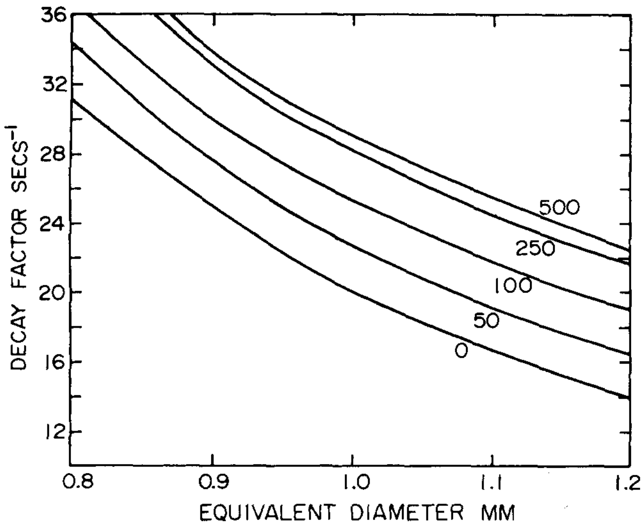

Fig. 1. Plot of the decay factors as a function of size with dilational elasticity λ as parameter.

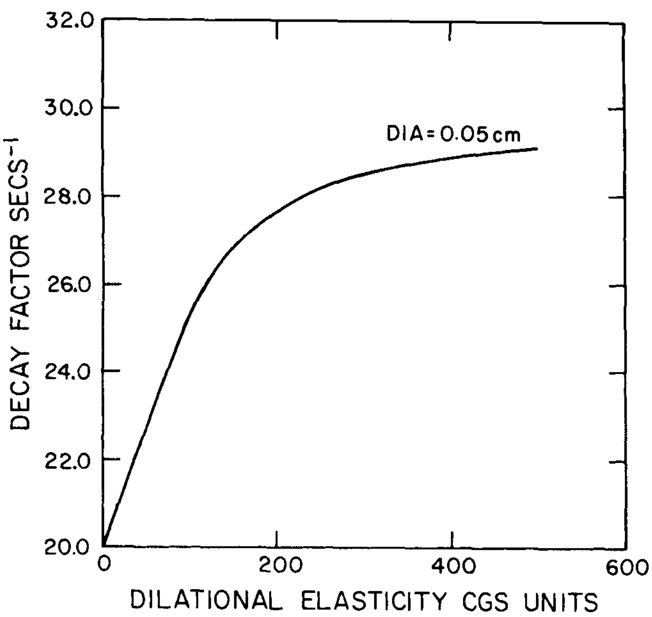

Fig. 3. Plot of the drop decay factor as a function of the dilational elasticity.

portant. By assuming $\rho_o << \rho_i$ and $\mu_o << \mu_i$ in the determinant, Equation (13) results in

$$\beta^{7/2} + \alpha_D Q^J(\gamma_i R)\beta^3 + \gamma_D \beta^{5/2} + \delta_D Q^J(\gamma_i R)\beta^2 + \xi_D \beta^{3/2} + \zeta_D Q^J(\gamma_i R)\beta + \Delta_D Q^J(\gamma_i R) = 0 \quad (19)$$

where

$$Q^J(\gamma_i r) = \frac{J_{b+3/2}(\gamma_i r)}{J_{b+1/2}(\gamma_i r)} \quad (20)$$

The coefficients α_D, γ_D, δ_D, ξ_D, ζ_D, and Δ_D are defined in the appendix. They are functions of the interfacial and internal properties but are independent of the properties of the rarefied external fluid, as would be expected. The real and imaginary parts of β have been solved numerically from Equation (19) by using the modified steepest descent method of Lance (1958). Details of the computation procedure are available (Ramabhadran, 1972). All computations were done for the mode $b = 2$ which is by far the most important one physically. Some computed results are shown in Figures 1 to 3. The decay factor is plotted against the drop size with interfacial dilational

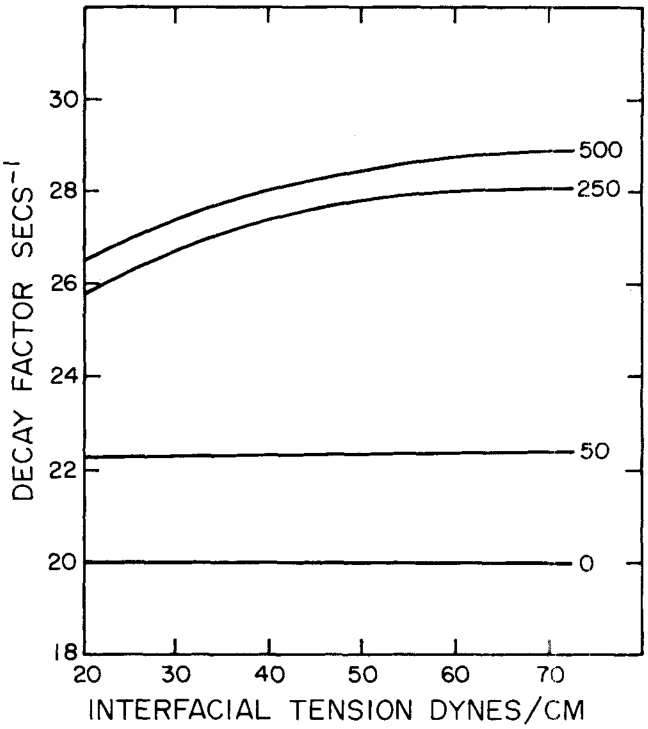

Fig. 2. Plot of the decay factor as a function of the interfacial tension with dilational elasticity λ as parameter.

elasticity as parameter, while the other interfacial properties are maintained constant at zero. It was found that the interfacial viscosities, in the range of sizes considered, had little or no effect on the decay of the oscillations. Figure 2 shows the plot of decay factor as a function of dilational elasticity for a drop of 0.5 mm diameter, while all the other properties were held constant. Figure 3 shows the plot of decay factor as a function of interfacial tension with dilational elasticity as parameter. The computed results indicate that the most dominant property for the liquid drop in a rarefied medium is the interfacial dilational elasticity. The frequency was found to be rather insensitive to interfacial properties other than interfacial tension. These results indicate that the problem of a liquid drop in air would provide a good way of measuring interfacial dilational elasticity in the size range of drops considered. Since the decay factor β_R increases with decreasing radius, it is clear that the dilational elasticity tends to become less important relative to the viscosity. Therefore, the interfacial dilational viscosity should become important with drops of very small size. However, such drops were not considered because of limitations on what could be measured experimentally.

A GAS BUBBLE OSCILLATING IN A LIQUID

The rarefied nature of the internal medium implies that it has no effect on the oscillations. It is hoped that, as in the previous case, this may also unearth a situation in which some of the interfacial properties may be more dominant. It also provides a simpler and mathematically tractable system. By assuming that $\rho_i <<< \rho_o$ and $\mu_i <<< \mu_o$ in the determinant, Equation (18) results in

$$\beta^4 + \alpha_C Q^H(\gamma_o R)\beta^{7/2} + \gamma_C\beta^3 + \delta_C Q^H(\gamma_o R)\beta^{5/2} + \zeta_C Q^H(\gamma_o R)\beta^{3/2} + \xi_C\beta^2 + \pi_C Q^H(\gamma_o R)\sqrt{\beta} + \Delta_C\beta + \nabla_C = 0 \quad (21)$$

where $Q^H(\gamma_o r)$ for the physically realistic mode $b = 2$ is given by

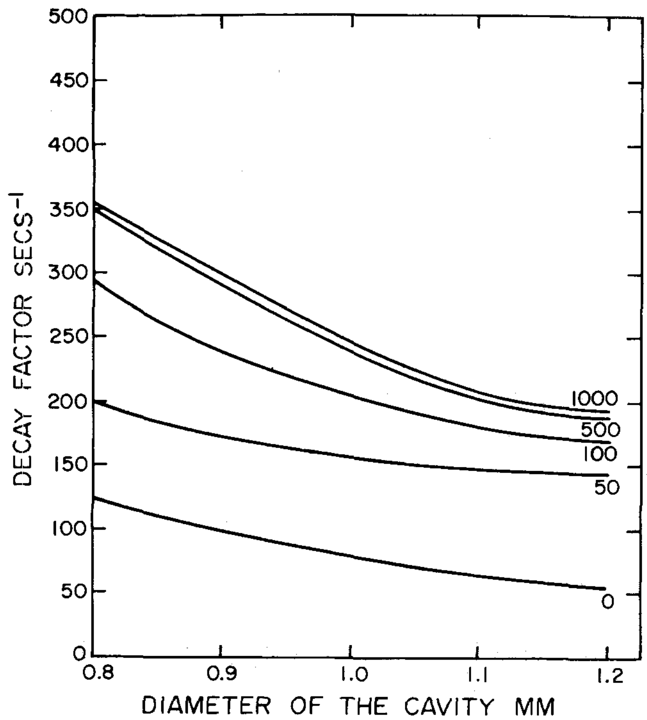

Fig. 4. Plot of the decay factor as a function of the diameter of the cavity with shear elasticity M as parameter.

$$Q^H(\gamma_o r) = \frac{H^{(1)}_{7/2}(\gamma_o r)}{H^{(1)}_{5/2}(\gamma_o r)} \qquad (22)$$

The coefficients α_C, γ_C, δ_C, ξ_C, ζ_C, Δ_C, π_C, and ∇_C of Equation (21) are defined in the appendix.

The real and imaginary parts of the complex number β in Equation (21) have been solved numerically for a range of interfacial properties, close to those which have been reported in the literature. The numerical procedure, which may be found in more detail in Ramabhadran (1972), is based on the method of Muller (1958). Figure 4 plots the decay factor as a function of bubble diameter with interfacial shear elasticity as parameter, all the other properties being held constant at zero. Figure 5 plots the decay as a function of shear elasticity for a bubble of diameter 0.5 mm, and Figure 6 shows the effect of interfacial tension on the decay. As in the case of the drop, the viscous properties seemed to have little or no effect, and the frequencies are generally dependent only on the interfacial tension. The dominant interfacial property affecting the decay seems to be the interfacial shear elasticity.

DISCUSSION

In the range of interfacial properties thought to be important, the analysis indicates that the dynamic interfacial properties affect only the decay of the oscillations and not the frequency. This would be an expected result based on the results of a free interface. The frequency should depend mainly on the restoring force which would be interfacial tension. The decay, on the other hand, is the rate at which the interface relaxes back to equilibrium from a deformation. This would therefore depend on the viscous and elastic properties of the interface.

The dynamic properties considered were the two coefficients of viscosity and the two coefficients of elasticity. In order to remain within experimentally attainable drop and cavity sizes, it was decided to work with diameters in the range 0.5 to 1.5 mm. The computations for both the cases were done in this range. It was found that in this range of drop diameters the interfacial viscosities had little effect

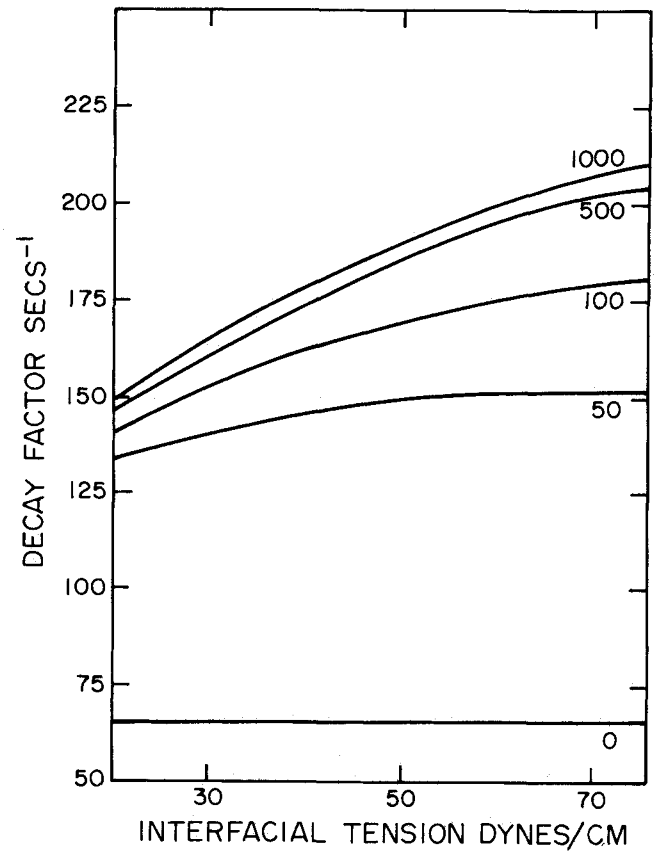

Fig. 5. Plot of the decay factor as a function of the interfacial tension with shear elasticity M as parameter.

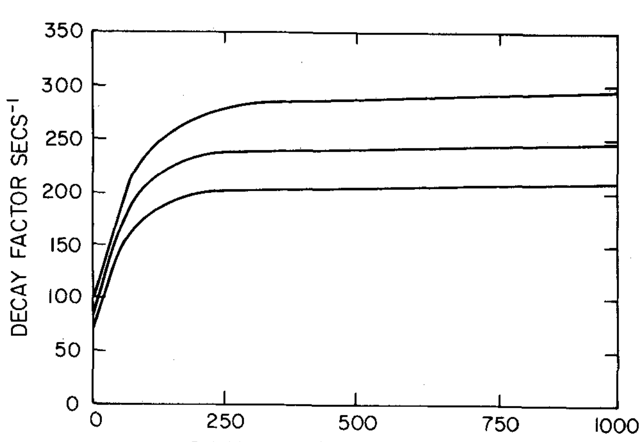

Fig. 6. Plot of the bubble decay factor as a function of the interfacial shear elasticity with the size as a parameter.

on the decay. However, from looking at the expressions for the dilational modulus D and the shear modulus S, it seems possible that these viscosities might exercise their influence on the decay at much smaller diameters when the decay rate is much larger. No attempt was made, however, to work with these smaller sizes owing to experimental limitations (Ramabhadran, 1972).

In the size ranges considered, it seems quite reasonable to conclude that with the experimentally reported values of the dilational and shear elasticities in the literature, the rarefication of the external medium makes the shear insignificant and that of the internal medium makes the dilation insignificant. The size range of drops and bubbles considered are such that it seems to make the tangential shear in the external medium significant, while that in the internal medium seems unimportant. When the external medium is rarefied, as in the case of the drop tangential, shear no longer seems important. Consequently, no tangential shear is transmitted on to the interface, and the only property of importance is the interfacial dilational elasticity. In other words, if the external medium is rarefied, the drop tends to behave more and more like a solid sphere, particularly as the dilational elasticity is increased. However, when the internal medium is rarefied, as in the case of the bubble, tangential shear seems to dominate over the other properties of the system. Further work needs to be done before more concrete conclusions are reached. The preliminary results indicate, therefore, that the drop experiment can be used as a possible method for the measurement of interfacial dilational elasticity. Similarly, the cavity experiment can be used as a method for shear elasticity measurement. Experimentally one can alter the interfacial properties by adding controlled amounts of known surface active agents. This would certainly alter the surface characteristics and hence the interfacial properties. By measuring the decay rates in the appropriate experiment, the induced interfacial properties can be inferred. Part II describes the experiments that have been carried out.

NOTATION

a_i = coefficients in the velocity field, $i = 1, 4$
b_i = coefficients in the vorticity field, $i = 1, 2,$
b = mode of oscillation
B_o = initial displacement of the dispersed phase
D = dilational modulus $= \kappa/R - \lambda/\beta_R$
M = interfacial shear elasticity
r = radial coordinate
R = radius of the drop or bubble
S = shear modulus $= \epsilon/R - m/\beta_R$
t = time
w = radial component of velocity
z = radial component of vorticity

Greek Letters

β_R = decay factor of oscillations
β_I = frequency of oscillations
θ, ϕ = angular coordinates
κ = interfacial dilational viscosity
ϵ = interfacial shear viscosity
λ = interfacial dilational elasticity
μ = viscosity
ρ = density
ν = kinematic viscosity
σ = interfacial tension

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APPENDIX

The coefficients in Equation (34) are

$$\alpha_D = (b+2)(b-1)\epsilon/R^2\sqrt{\rho_i\mu_i} + b(b+1)\kappa/R^2\sqrt{\rho_i\mu_i} - 2\sqrt{\mu_i}/R\sqrt{\rho_i}$$

$$\gamma_D = 2b[b-1-(b^2-1)]\kappa/\rho_i R^3 - 2[b(b-1)+(b^2-1)]\mu_i/\rho_i R^2 - (b^2-1)(b+2)\epsilon/\rho_i R^3$$

$$\begin{aligned}\delta_D = &-4b\sqrt{\mu_i}\,[(b-1)+(b^2-1)]\kappa/R^4\,\rho_i^{3/2} \\ &+ 4[b(b^2-1)+b(b-1)]\mu_i^{3/2}/R^3\,\rho_i^{3/2} \\ &- (b+2)(b-1)\,M/R^2\sqrt{\rho_i\mu_i} \\ &- b(b+1)\lambda/R^2\sqrt{\rho_i\mu_i} \\ &+ 2b(b+2)\sqrt{\mu_i}\,[(b^2-1)-(b-1)^2]\epsilon/R^4\,\rho_i^{3/2} \\ &+ 2b(b+2)[(b-1)^2-(b^2-1)]\kappa\epsilon/R^5\sqrt{\mu_i}\,\rho_i^{3/2}\end{aligned}$$

$$\xi_D = 2b\,[(b^2-1)-(b-1)]\lambda/R^3\rho_i + (b^2-1)(b+2)\,M/R^3\,\rho_i + \beta^{*2}$$

$$\begin{aligned}\zeta_D = &\,2b(b+2)[(b^2-1)-(b-1)^2]\kappa\,M/R^5\sqrt{\mu_i}\,\rho_i^{3/2} \\ &+ 2b(b+2)\sqrt{\mu_i}\,[(b-1)^2-(b^2-1)]\,M/R^4\,\rho_i^{3/2} \\ &+ 4b(b-1)\sqrt{\mu_i}\,(b+2)\lambda/R^4\,\rho_i^{3/2} \\ &+ 2b(b+2)[(b^2-1)-(b-1)^2]\,\epsilon\lambda/R^5\sqrt{\mu_i}\,\rho_i^{3/2} \\ &- 2\sqrt{\mu_i}\,\beta^{*2}/R\sqrt{\rho_i} \\ &+ (b+2)(b-1)\,\beta^{*2}\,\epsilon/R^2\sqrt{\rho_i\mu_i}\end{aligned}$$

$$+ b(b+1)\beta^{*2}\kappa/R^2\sqrt{\rho_i\mu_i}$$

and

$$\Delta_D = -b(b+1)\beta^{*2}\lambda/R^2\sqrt{\rho_i\mu_i}$$
$$-(b+2)(b-1)\beta^{*2}M/R^2\sqrt{\rho_i\mu_i}$$
$$+2b(b+2)[(b-1)^2-(b^2-1)]M\lambda/R^5\sqrt{\mu_i}\rho_i^{3/2}$$

The coefficients in Equation (36) are defined as

$$\alpha_C = -2\sqrt{\mu_o}/R\sqrt{\rho_o} - b(b+2)\epsilon/R^2\sqrt{\rho_o\mu_o}$$
$$-b(b+2)\kappa/R^2\sqrt{\rho_o\mu_o}$$
$$\gamma_C = [2(2b+1)-2(b+1)(b+2)$$
$$-2b(b+2)]\mu_o/\rho_o R^2$$
$$-b(b+2)^2\epsilon/\rho_o R^3$$
$$+[2(b+2)(b-1)-b^2(b+2)]\kappa/\rho_o R^3$$
$$\delta_C = b(b+2)M/R^2\sqrt{\rho_o\mu_o}$$
$$-4(b^2-1)(b+2)\mu_o^{3/2}/R^3\rho_o^{3/2}$$
$$+b(b+2)\lambda/R^2\sqrt{\rho_o\mu_o}$$
$$+4(b+2)(2b-1)(b+1)\sqrt{\mu_o}\kappa/R^4\rho_o^{3/2}$$
$$-4b(b+2)(b+1)\kappa^2/R^4\rho_o^{3/2}\sqrt{\mu_o}$$
$$\xi_C = b(b+2)^2M/R^3\rho_o + \beta^{*2}$$
$$+2(2b+1)(b+2)^2b(b+1)\mu_o\epsilon/R^5\rho_o^2$$
$$+4(b+1)(b+2)(2b+1)(b-1)\mu_o^2/R^4\rho_o^2$$
$$+[b^2(b+2)-2(b+2)(b+1)]\lambda/R^3\rho_o$$
$$+2(b+2)(2b+1)(b^2-2b+2)(b+1)\mu_o\kappa/R^5\rho_o^2$$
$$-2(2b+1)(b+2)b(b+1)(b+2)\kappa\epsilon/R^6\rho_o^2$$
$$-2(2b+1)(b+2)b^2(b+1)\kappa^2/R^6\rho_o^2$$
$$\zeta_C = -2\sqrt{\mu_o}\beta^{*2}/R\sqrt{\rho_o} - b(b+2)\epsilon\beta^{*2}/R^2\sqrt{\rho_o\mu_o}$$
$$-4(b+2)(2b-1)(b+1)\sqrt{\mu_o}\lambda/R^4\rho_o^{3/2}$$
$$+8b(b+2)(b+1)\kappa\lambda/R^4\sqrt{\mu_o}\rho_o^{3/2}$$
$$-b(b+2)\beta^{*2}\kappa/R^2\sqrt{\rho_o\mu_o}$$
$$\Delta_C = -2b(2b+1)(b+2)^2(b+1)\mu_o M/R^5\rho_o^2$$
$$+2(2b+1)(\mu_o)\beta^{*2}/\rho_o$$
$$-2(b+2)(2b+1)(b^2-2b+2)(b+1)\mu_o\lambda/R^5\rho_o^2$$
$$+2(2b+1)(b+2)^2(b+1)b\lambda\epsilon/R^6\rho_o^2$$
$$+2(2b+1)(b+2)^2(b+1)bM\kappa/R^6\rho_o^2$$
$$+4(2b+1)(b+2)(b+1)b^2\kappa\lambda/R^6\rho_o^2$$
$$\pi_C = b(b+1)(M)\beta^{*2}/R^2\sqrt{\rho_o\mu_o}$$
$$+b(b+2)\lambda\beta^{*2}/R^2\sqrt{\rho_o\mu_o}$$
$$-4b(b+2)(b+1)\lambda^2/R^4\sqrt{\mu_o}\rho_o^{3/2}$$
$$\nabla_C = -2(2b+1)(b-2)b(b+1)(b+2)\lambda M/R^6\rho_o^2$$
$$-2b^2(b+2)(b+1)(2b+1)\lambda^2/R^6\rho_o^2$$

Part II.

Ultra high-speed motion picture photography is used to measure the decay and frequency of drops of liquid in air and of air cavities in liquids. Consequent to the belief that surface active agents induce dynamic interfacial properties, a very clean system is used, and experiments are performed with triple distilled water, tap water, and known aqueous solutions of ionic and nonionic surfactants. Experimental results yield good qualitative agreement with the theory. The theoretical and experimental studies show the system to be a new and promising technique for the quantitative evaluation of the various interfacial viscous and elastic properties.

The main objective of the experiment was to accurately measure the decay and frequency characteristics of dispersed phases oscillating in a continuous medium under controlled conditions. The controls that had to be exercised were on the size of the drop or bubble and the characteristics of the interface, namely, the amount of surface active material that is present on it.

The basic requirement of the experimental setup was that an oscillating dispersed phase, once released by suitable means in a continuous medium, could be examined and its behavior recorded. Since the effect of surfactants had also to be studied, the system had to be clean. The equipment was built along the lines outlined by Loshak (1969), and Loshak and Byers (1973). The overall requirements to be met by the apparatus can be listed as follows.

A transparent section woud be needed which would permit visual observation of the motion of the dispersed phase. Plane sheet glass was used for the front and back, while the sides were constructed of aluminum. Provision for controlled and measurable formation and injection of the dispersed phase into the continuous medium would be required. An oscillating mechanism had to be provided to make the dispersed phase oscillate at any desired frequency. A high speed motion picture camera system along with frame by frame analysis facilities would be needed to record rapid decay and frequencies of the oscillations. A choice of surfactants with which the dynamic interfacial properties could be altered had to be provided.

THE EXPERIMENTAL SETUP

The test section was rectangular in cross section, made of aluminum at the sides, and plane sheet glass for the front and back to minimize optical distortion. It was about 19 in. long. Larger square cross-sectional containers at the top and bottom were provided to collect the dispersed phase. Injection mechanisms were provided at three points along the sides of the column, two very near the top and one near the bottom. This would enable us to study both rising and falling media.

The injection mechanism consisted of a tip made out of concentric copper tubes. The end of the tip was a detachable syringe needle made of high quality chromium steels. All sizes ranging from BD18 to BD27 were used. The number refers to the size of the needle; the larger it is the smaller the diameter. A BD22 needle would approximately be about 0.0286 in. diameter and about 3.5 in. long. The needle was bent through 90 deg so that the