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Dynamic equilibrium fluctuations of fluid droplets

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The frequency spectrum of the thermal fluctuations in the shape of fluid droplets is derived when the droplets are coated with a thin film such as a surfactant monolayer or lipid bilayer. The surface viscosity and compressibility and the inertia and viscosity of the bulk fluids interior and exterior to the droplet are taken into account, and their effects on the decay of the surface modes is discussed in detail.

I. INTRODUCTION

There is a wide variety of phenomena for which the dynamics of fluid-fluid interfaces plays an important role. The nature of the interface is an important factor in many industrial applications such as oil-displacement mechanisms in enhanced oil recovery,[1] coalescence of fluid droplets[2] and the rheology of emulsions.[3] Amphiphilic molecules tend to adsorb at oil-water interfaces, and the orientation and interactions between these molecules result in an interfacial behavior different from that in the bulk phases. The dynamics of interfaces containing thin surface films cannot be explained on the basis of surface tension alone, and thin surface films can behave as two-dimensional Hookean solids, Newtonian fluids, or can have much more complex viscoelastic behavior.[4]

In this paper we consider the thermal fluctuations in the shape of small fluid bodies immersed in a fluid with different properties. The droplets are coated with a thin film which behaves as a two-dimensional compressible Newtonian fluid, and which is insoluble in the adjacent bulk phases. Important examples include lipid vesicles[5] and oil-water emulsions where the dispersed phase exists in the form of droplets which are stabilized by a surfactant monolayer. In addition, coated fluid droplets are a reasonable approximation to biological cells when modeling many types of hydrodynamic phenomena.[6–9]

The thermal fluctuations in planar surfaces covered with monomolecular films have been discussed, for example, by Bouchiat and Langevin,[10] and light scattering experiments have been performed to determine the surface rheological parameters,[11,12] but the rheology of the surface has not been fully accounted for in work on spherical interfaces. Ljunggren and Erikkson[13] have discussed the thermal fluctuations in the shape of micelles with low surface tension; however, they included no dissipation. Schneider *et al.*[14] and Milner and Safran[15] have considered the dynamic shape fluctuations in small fluid droplets correctly neglecting the inertia of the surrounding fluid media and also neglecting the viscosity of the surface layer. A constant surface density was assumed in the theoretical calculations which is experimentally justified for the systems studied by these authors. There are situations however, where the compressibility of the surface layer cannot be neglected, such as in the vicinity of a surface phase transition. The density fluctuations associated with a large surface compressibility can have important consequences in several biological contexts, for example, in affecting the permeability of the cell membrane to ions[16] or the reactivity of enzymes bound to the lipid bilayer,[17] and some bacterial lipid membranes appear to exist within the phase-transition region at growth temperatures.[18] In addition, lipid vesicles can have rather large surface compressibilities, and increases in surface area up to 10% have been reported in osmotic swelling experiments.[19] For generality we therefore do not assume that the surface layer is incompressible and further take into account damping by both the surface viscosity and the viscosity of the adjacent bulk fluids. The inertia of the bulk fluids, important for large droplets, is also included.

If $\mathbf{R}=R(\theta,\phi,t)\hat{\mathbf{r}}$ is the position vector to a point on the surface, then in equilibrium $\langle R\rangle=R_0=\text{const}$, and we define a fluctuation δR in the shape of the surface by $\delta R(\theta,\phi,t)=(R-R_0)/R_0$, where θ and ϕ are the polar and azimuthal angles and $\delta R \ll 1$. Using the Laplace transform and expanding δR in a series of spherical harmonics Y_{lm}, the fluctuations in the mode amplitudes $\delta R_{lm}(z)$ can be found by solving the linearized hydrodynamic equations for the fluids interior and exterior to the droplet. Momentum balance equations for the adsorbed surface film are imposed as boundary equations on the stress. The time dependence of the fluctuations is given by the correlation function

$$S_{lm,l'm'}(t,t')=\langle \delta R_{lm}(t)\delta R_{l'm'}(t')\rangle \ ,$$

the average being taken over an equilibrium ensemble. The static, or equal time, correlation function $S_{lm,l'm'}(t,t)$ gives the amplitude of the fluctuations and can be found from thermodynamics, and the angular correlations

$S(\theta,\theta',\phi,\phi',t,t')$ are found by summing over the modes.

The spectral density of the fluctuations cannot be understood without an examination of the normal mode frequencies. The dynamics of inviscid fluid spheres was discussed long ago by Rayleigh[20] (see also Lamb[21]). The normal mode frequencies for a viscous fluid droplet, neglecting the stress exerted by the external fluid medium and considering only the surface tension of the interface, were analyzed by Reid;[22] a good discussion is given in Chandrasekhar.[23] Miller and Scriven[24] extended the analysis to fluid droplets immersed in another fluid medium, also taking into account the surface viscosity and elasticity. They obtained some general results for the frequencies of the normal modes, but owing to the wide range of possible behavior, they considered in detail only imcompressible surface fluids and surfaces with vanishing viscosity. They did not perform the numerical calculations which are required in the general case. Here we discuss the normal mode frequencies in some detail in the case when the damping is due only to the surface viscosity, and then show how the viscous coupling to the adjacent fluids affects the decay of the surface modes. This analysis reveals some interesting features which, owing to the complexity of the system, have not yet been thoroughly explored.

We begin in Sec. II by deriving the amplitude of the static equilibrium fluctuations in the shape of the surface and the surface density from thermodynamics. In Sec. III we solve the hydrodynamic boundary-value problem and obtain the dispersion relation for the normal mode frequencies and the Laplace transform of the correlation function. The normal mode frequencies are discussed in Sec. IV, and analytical expressions are given in several approximations. In Sec. V we obtain the spectral density of the fluctuations in the shape of the surface and also discuss the angular correlations using parameter values typical of biological cells, and in Sec. VI we make some concluding remarks.

II. STATIC EQUILIBRIUM FLUCTUATIONS

The equal time or static correlation functions for the surface and density fluctuations can be found from thermodynamic arguments as discussed, for example, by Reichl.[25] At equilibrium the average total area of the droplet is A_0 and the average surface density is $\Gamma_0=\text{const}$ and we consider fluctuations in the total area $\Delta A=A-A_0$ and surface density $\delta\Gamma(\theta,\phi,t)=[\Gamma(\theta,\phi,t)-\Gamma_0]/\Gamma_0$. Assuming that the total number of molecules on the surface remains constant and considering only isothermal changes, the total change in free energy can be written

$$\Delta F=\sigma_0\Delta A+\frac{KR_0^2}{2}\int[\delta\Gamma(\theta,\phi)]^2d\Omega\ , \tag{2.1}$$

where σ_0 is the equilibrium surface tension, R_0 is the equilibrium radius of the droplet, and $K=-\Gamma_0(\partial\sigma/\partial\Gamma)_T$ is the isothermal elastic modulus ($C=1/K$ is the isothermal surface compressibility). The integration is over the undeformed surface and $d\Omega=\sin\theta\, d\theta\, d\phi$.

We will consider a surface which encloses an incompressible fluid. In this case the total change in area of the interface must be found subject to the constraint that the volume enclosed by the surface remain constant. It is shown in Ref. 13 that under this constraint the total change in area of the interface is

$$\Delta A=\frac{R_0^2}{2}\int\delta R(L^2-2)\delta R\, d\Omega\ , \tag{2.2}$$

where L^2 is the square of the angular momentum operator

$$L^2=-\nabla_0\cdot\nabla_0=-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}-\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\ . \tag{2.3}$$

The fluctuations δR and $\delta\Gamma$ can be expanded in a series of spherical harmonics,

$$\begin{aligned}\delta R(\theta,\phi,t)&=\sum_{l,m}\delta R_{lm}(t)Y_{lm}(\theta,\phi)\ ,\\ \delta\Gamma(\theta,\phi,t)&=\sum_{l,m}\delta\Gamma_{lm}(t)Y_{lm}(\theta,\phi)\ ,\end{aligned} \tag{2.4}$$

where $L^2Y_{lm}=l(l+1)Y_{lm}$. The total free energy then becomes a sum over the mode amplitudes

$$\Delta F=\frac{R_0^2}{2}\sum_{\substack{l=2\\ -l\le m\le l}}^{l_{\max}}\sigma_0(l+2)(l-1)|\delta R_{lm}(t)|^2+\frac{R_0^2K}{2}\sum_{\substack{l=1\\ -l\le m\le l}}^{l_{\max}}|\delta\Gamma_{lm}(t)|^2\ . \tag{2.5}$$

The mode $l=0$ is excluded since by assumption the surface encloses an incompressible fluid and there is no change in the total amount of surface material. In the first term $l=1$ is also excluded since it corresponds to motion of the center of mass of the droplet. The maximum mode number will be of order $l_{\max}\sim R_0/d$, where $d\sim5$ Å is a typical molecular diameter.

Application of the equipartition theorem to Eq. (2.5) yields the amplitudes of the static fluctuations

$$\langle\delta R_{lm}(t)\delta R^*_{l'm'}(t)\rangle=\frac{k_BT}{\sigma_0R_0^2(l+2)(l-1)}\delta_{ll'}\delta_{mm'}\ , \tag{2.6}$$

$$\langle\delta\Gamma_{lm}(t)\delta\Gamma^*_{l'm'}(t)\rangle=\frac{k_BT}{KR_0^2}\delta_{ll'}\delta_{mm'}\ , \tag{2.7}$$

$$\langle\delta\Gamma_{lm}(t)\delta R^*_{l'm'}(t)\rangle=\langle\delta\Gamma^*_{lm}(t)\delta R_{l'm'}(t)\rangle=0\ , \tag{2.8}$$

where k_B is Boltzmann's constant and T is the temperature. Equation (2.6) has also been derived elsewhere.[13] The fluctuations δR and $\delta\Gamma$ are uncorrelated in equilibrium, and fluctuations with different mode numbers are also uncorrelated. The surface density fluctuations are proportional to the surface isothermal compressibility, analogous to the density fluctuations in bulk fluids. The fluctuations in shape can be quite large for very small droplets with low surface tensions as in microemulsions[26] and the curvature energy must be taken into account, however, this will not be discussed here.

III. DYNAMIC FLUCTUATIONS

The time dependence of the fluctuations for each l,m mode is given by the correlation function of the radial displacement at two different times t and t'

$$S_{lm,l'm'}(t,t')=\langle \delta R_{lm}(t)\delta R^{*}_{l'm'}(t')\rangle \; . \tag{3.1}$$

Since equilibrium correlations are time translation invariant we can equivalently write (see, e.g., Forster[27])

$$S_{lm,l'm'}(t)=\langle \delta R_{lm}(t)\delta R^{*}_{l'm'}(0)\rangle = S_{lm,l'm'}(-t) \; . \tag{3.2}$$

Equilibrium fluctuations decay according to the linearized hydrodynamic equations. There are two different but equivalent ways of finding the equilibrium correlation functions in finite systems. In the first method, one adds a fluctuating stress tensor to the hydrodynamic equations. This is treated as a source term, and the equations can be solved as a boundary value problem using a Green function. The correlation functions can be expressed in terms of the correlation functions of the components of the fluctuating stress tensor. This method is well suited for Dirichlet problems for which the velocities are prescribed over the boundary, but is inappropriate for problems such as we have here in which the stresses must satisfy conditions on the boundary. Alternatively, the boundary-value problem can be solved as an initial-value problem where the initial values are random variables distributed according to an equilibrium ensemble. The solutions are linear in the initial values, and the time-dependent correlation function can be found if the static correlation function, which determines the amplitude of the fluctuations, is known. Thus we obtain the spectral density of the fluctuations in the shape of the surface by solving the hydrodynamic initial-value problem for the interior and exterior fluids with linearized surface balance equations imposed as boundary conditions on the stress.

We begin by finding general expressions for the velocity fields of the fluids interior and exterior to the sphere which are assumed to be incompressible and at constant temperature. The development here follows closely that given by Chandrasekhar.[23] Writing the Laplace transform of a function $f(r,\theta,\phi,t)$ as

$$f(r,\theta,\phi,z)=\int_0^{\infty} e^{-zt} f(r,\theta,\phi,t)\,dt \tag{3.3}$$

the velocities $\mathbf{u}^{i}(r,\theta,\phi,z)$ $[\mathbf{u}^{e}(r,\theta,\phi,z)]$ of the interior (exterior) fluids are solutions to the Laplace transformed hydrodynamic equations

$$\begin{gathered}\rho_{i,e} z \mathbf{u}^{i,e} = -\nabla p^{i,e} + \eta_{i,e}\nabla^2 \mathbf{u}^{i,e} + \mathbf{u}^{i,e}(0) \; , \\ \nabla\cdot\mathbf{u}^{i,e}=0 \; ,\end{gathered} \tag{3.4}$$

where $\mathbf{u}(0)\equiv\mathbf{u}(r,\theta,\phi,t=0)$ and $p=p(r,\theta,\phi,z)$ is the pressure. Here and in what follows quantities referring to the interior (exterior) fluids will be labeled with an i (e); $\rho_{i,e}$ are the equilibrium densities and $\eta_{i,e}$ are the shear viscosities. The Laplace transform introduces the initial value of the velocity fluctuation. The correlation function is obtained by multiplying by $\delta R(t=0)$ and averaging over an equilibrium ensemble. Since the static correlation $\langle \mathbf{u}(0)\delta R(0)\rangle$ is odd under time reversal it vanishes in equilibrium,[27] and we may without loss of generality set the initial values $\mathbf{u}(0)$ equal to zero.

Equations (3.4) are to be solved subject to boundary conditions derived from the surface momentum balance and continuity equations which describe the dynamics of the interface. Neglecting the inertia of the adsorbed surface layer, the general form of the surface momentum balance equation is

$$\nabla_S\cdot\mathbf{T}+\hat{\mathbf{n}}\cdot(\mathbf{P}^{e}-\mathbf{P}^{i})=0 \; , \tag{3.5}$$

where ∇_S is the surface gradient operator, $\mathbf{T}$ is the surface stress tensor, $\hat{\mathbf{n}}$ is the normal to the interface and $\mathbf{P}^{i}(\mathbf{P}^{e})$ is the stress tensor of the interior (exterior) fluid. We assume that the surface layer behaves as a compressible Newtonian surface fluid and that deviations from sphericity are small. Then Eq. (3.5) can be linearized and the normal and tangential components of the surface momentum balance equations become[28,29]

$$\begin{aligned}-\frac{2\sigma}{R_0}+\sigma_0(2-L^2)\frac{\delta R}{R_0}-\frac{2\kappa}{R_0^2}(\nabla_0\cdot\mathbf{v}_s+2v_n)& \\ =P^{i}_{rr}-P^{e}_{rr}\big|_{r=R_0} \; ,&\end{aligned} \tag{3.6}$$

$$\begin{aligned}\frac{\nabla_0\sigma}{R_0}+\frac{\kappa+\epsilon}{R_0^2}\nabla_0(\nabla_0\cdot\mathbf{v}_s)+\frac{2\kappa}{R_0^2}\nabla_0 v_n+\frac{2\epsilon}{R_0^2}\mathbf{v}_s& \\ +\frac{i\mathbf{L}\epsilon}{R_0^2}\hat{\mathbf{r}}\cdot\nabla_0\times\mathbf{v}_s=\hat{\mathbf{r}}\cdot(\mathbf{P}^{i}-\mathbf{P}^{e})\cdot\mathbf{I}_0\big|_{r=R_0} \; ,&\end{aligned} \tag{3.7}$$

where $\mathbf{I}_0=\hat{\boldsymbol{\theta}}\hat{\boldsymbol{\theta}}+\hat{\boldsymbol{\phi}}\hat{\boldsymbol{\phi}}$, $\nabla_0=\hat{\boldsymbol{\theta}}\,\partial/\partial\theta+\hat{\boldsymbol{\phi}}/\sin\theta\,\partial/\partial\phi$, $i\mathbf{L}=\hat{\mathbf{r}}\times\nabla_0$, and ϵ and κ are the shear and dilational surface viscosities. The surface velocity is $\mathbf{v}=\mathbf{v}_s(\theta,\phi,z)+v_n(\theta,\phi,z)\hat{\mathbf{r}}$, where $\mathbf{v}_s$ is the velocity tangent to the surface, and to lowest order $v_n(\theta,\phi,t)=\partial_t R(\theta,\phi,t)$.

The radial components of the stress tensors $\mathbf{P}^{i,e}$ are[30]

$$\begin{aligned}P_{rr}&=-p+2\eta\frac{\partial u_r}{\partial r} \; , \\ \hat{\mathbf{r}}\cdot\mathbf{P}\cdot\mathbf{I}_0&=\frac{\eta}{r}\nabla_0 u_r+\eta r\frac{\partial}{\partial r}\left[\frac{u_\theta\hat{\boldsymbol{\theta}}+u_\phi\hat{\boldsymbol{\phi}}}{r}\right] ,\end{aligned} \tag{3.8}$$

since the fluids are assumed incompressible. The surface tension can be eliminated by using the continuity equation and writing $\sigma=\sigma_0-K\,\delta\Gamma$, where K is the surface elastic modulus. The surface density can be expressed in terms of the velocities by using the Laplace-transformed surface-continuity equation

$$z\,\delta\Gamma(\theta,\phi,z)-\delta\Gamma(0)+\frac{\Gamma_0}{R_0}(\nabla_0\cdot\mathbf{v}_s+2v_n)=0 \; , \tag{3.9}$$

where $\delta\Gamma(0)\equiv\delta\Gamma(\theta,\phi,t=0)$. In Sec. II we saw that the static correlation function $\langle\delta\Gamma(0)\delta R(0)\rangle$ vanishes in equilibrium. Thus any term involving the initial value of the fluctuations in the surface density will vanish when we compute the correlation function $\langle\delta R_{lm}(z)\delta R_{l'm'}(0)\rangle$ and we may set it equal to zero.

Equations (3.6) and (3.7) are boundary conditions to be imposed on the stress when solving the hydrodynamic equations for the velocities of the bulk fluids. In addition, the velocity must be continuous across the interface, thus

$$\mathbf{u}^i(R_0,\theta,\phi,z)=\mathbf{u}^e(R_0,\theta,\phi,z)=\mathbf{v}(\theta,\phi,\mathbf{z}) , \tag{3.10}$$

where $\mathbf{u}(R)\sim\mathbf{u}(R_0)$ to lowest order. The general solution to Eq. (3.4) is discussed in Ref. 20; here we give only the main results. Since the fluids are incompressible the pressure is a solution to Laplace's equation $\nabla^2\delta p=0$, where the total pressure is $p=p_0+\delta p$, and p_0 is the constant equilibrium pressure. Note that for the reference surface the discontinuity in pressure across the interface is given by $(p^i-p^e)_0=2\sigma_0/\mathbf{R}_0$. General solutions for δp are superpositions of functions of the form $r^l Y_{lm}$ and $r^{-(l+1)}Y_{lm}$ and well-behaved solutions for the pressures $\delta p^{i,e}$ are given by

$$\begin{aligned}\delta p^i(r,\theta,\phi,z)&=\delta p^i_{lm}(z)(r/R_0)^l Y_{lm}(\theta,\phi) ,\\ \delta p^e(r,\theta,\phi,z)&=\delta p^e_{lm}(z)(R_0/r)^{l+1} Y_{lm}(\theta,\phi) .\end{aligned} \tag{3.11}$$

The velocities in the inner and outer regions can be written in terms of two scalar functions $U_{i,e}=U_{i,e}(r,z)$ as

$$\mathbf{u}^{i,e}(r,\theta,\phi,z)=\frac{l(l+1)}{r^2}U_{i,e}Y_{lm}(\theta,\phi)\hat{\mathbf{r}}+\frac{1}{r}\frac{dU_{i,e}}{dr}\nabla_0 Y_{lm} \tag{3.12}$$

and the scalar functions are given by

$$\begin{aligned}U_i(r,z)&=C_i r j_l(q_i r)-\frac{\delta p^i_{lm} r^{l+1}}{z\rho_i(l+1)R_0^l} ,\\ U_e(r,z)&=C_e r h_l^{(1)}(q_e r)+\frac{\delta p^e_{lm} R_0^{l+1}}{z\rho_e l r^l} ,\end{aligned} \tag{3.13}$$

where j_l is a spherical Bessel function of the first kind, $h_l^{(1)}$ is a spherical Hankel function, and $q_a^2=-z\rho_a/\eta_a$, $a=i,e$. The coefficients $C_{i,e}$ are determined by the boundary conditions which to first order may be taken on the surface of the undeformed sphere. The continuity conditions allow us to write the surface velocity in the form

$$\mathbf{v}(\theta,\phi,z)=w_{lm}(z)Y_{lm}\hat{\mathbf{r}}+v_{lm}(z)\nabla_0 Y_{lm} . \tag{3.14}$$

Using Eqs. (3.6)–(3.14) we find after a considerable amount of algebra that the tangential components of the momentum-balance equation, Eq. (3.7), can be written as

$$\frac{\tau_s}{R_0}(A+\lambda B)v_{lm}(\zeta)+\zeta(C+\lambda D)\delta R_{lm}(\zeta)=(C+\lambda D)\delta R_{lm}(0) , \tag{3.15}$$

where $\tau_s=\kappa/\sigma_0$, $\zeta=z\tau_s$ is a dimensionless frequency, and $\delta R_{lm}(0)\equiv\delta R_{lm}(t=0)$. The dimensionless parameter $\lambda=\eta R_0/\kappa$ is a measure of the relative importance of the dissipation in the bulk fluids and the surface dissipation. The normal component, Eq. (3.6), can be written in the form

$$\frac{\tau_s}{R_0}b_l(C+\lambda D)v_{lm}(\zeta)-\zeta\left[a_l\left[1+\frac{\zeta^2}{\Omega_l^2}\right]+2C-\lambda E\right]\delta R_{lm}(\zeta)=\left[\lambda E-2C-a_l\frac{\zeta^2}{\Omega_l^2}\right]\delta R_{lm}(0) , \tag{3.16}$$

where $b_l=l(l+1)$ and $a_l=b_l-2$. We have also defined a dimensionless frequency Ω_l

$$\Omega_l=\Omega_0\left[\frac{2a_l b_l}{2l+1+\Delta\rho}\right]^{1/2} , \tag{3.17}$$

where $\Omega_0=\omega_0\tau_s$ and $\omega_0=(\sigma_0/\rho R_0^3)^{1/2}$ is a natural frequency associated with the inertia of the bulk fluids. If all sources of dissipation are neglected the modes oscillate with the capillary frequency ω_0. We have further defined $\rho=\rho_i+\rho_e$, $\eta=\eta_i+\eta_e$, and the dimensionless parameters $\Delta\rho=(\rho_i-\rho_e)/\rho$ and $\Delta\eta=(\eta_i-\eta_e)/\eta$. The functions A, B, C, D, and E in Eqs. (3.15) and (3.16) are

$$\begin{aligned}A&=-b_l\beta-\zeta(\mu a_l+b_l) ,\\ C&=2(\zeta+\beta) ,\\ B&=2\zeta\,\Delta\eta+\frac{\tau_F}{2\tau_s}\zeta^2(Q_i+Q_e) ,\\ D&=-2\zeta\,\Delta\eta-\frac{\tau_F}{2\tau_s}\zeta^2\left[\frac{Q_i}{l}-\frac{Q_e}{l+1}\right] ,\\ E&=4\zeta\,\Delta\eta+\frac{\tau_F}{2b_l\tau_s}\zeta^2[(l+1)^2Q_i+l^2Q_e] ,\end{aligned} \tag{3.18}$$

where $\mu=\epsilon/\kappa$ and $\beta=K/\sigma_0$ is a dimensionless surface elasticity. The functions $Q_{i,e}$ in Eq. (3.18) are

$$\begin{aligned}Q_i&=\frac{1+\Delta\rho}{x_i}\frac{j_l(x_i)}{j_{l+1}(x_i)} ,\\ Q_e&=(1-\Delta\rho)\left[2l+1-\frac{x_e h_{l+1}^{(1)}(x_e)}{h_l^{(1)}(x_e)}\right]^{-1} ,\end{aligned} \tag{3.19}$$

where

$$x_i^2=-z\tau_F\frac{1+\Delta\rho}{1+\Delta\eta},\quad x_e^2=-z\tau_F\frac{1-\Delta\rho}{1-\Delta\eta} . \tag{3.20}$$

We have also defined the characteristic time $\tau_F=\rho R_0^2/\eta$, which is roughly the time for the bulk fluids to reach steady state following some disturbance of the surface. Note that $\tau_s/\tau_F=\lambda\Omega_0^2$, thus the inertia of the bulk fluids will be important when either λ or Ω_0 is small.

If we eliminate v_{lm} between Eq. (3.15) and Eq. (3.16), multiply by $\delta R^*_{l'm'}(0)$ and average over an equilibrium ensemble, we arrive at the final result for the Laplace transform of the correlation function $S_{lm,l'm'}(\zeta)=\langle\delta R_{lm}(\zeta)\delta R^*_{l'm'}(t=0)\rangle$,

$$S_{lm,l'm'}(\zeta)=S_{lm,l'm'}(t=0)\tau_s\frac{\Delta(\zeta)+a_l(A+\lambda B)}{\zeta\,\Delta(\zeta)} \tag{3.21}$$

where

$$\Delta(\zeta)=(A+\lambda B)\left[\lambda E-2C-a_l\left[1+\frac{\zeta^2}{\Omega_l^2}\right]\right]-b_l(C+\lambda D)^2 \tag{3.22}$$

and the equal time or static correlation function, given by Eq. (2.6), determines the amplitude of the fluctuations.

IV. NORMAL-MODE FREQUENCIES

The dispersion relation for the frequencies of the normal modes is found by setting $\Delta(\zeta)=0$. Functions A and C depend only on the compressibility and viscosity of the surface, the $O(\lambda^2)$ terms arise from the damping by the bulk fluids, and the $O(\lambda)$ terms are the coupling between the surface and bulk fluids. Thus the dispersion relation for a surface when only surface tension is considered is obtained by setting $K=\epsilon=\kappa=0$ which is equivalent to setting $A=C=0$. If, in addition, the exterior fluid is neglected, we set $\rho_e=\eta_e=0$, and the dispersion relation then reduces to the case considered by Reid and others.[22–24]

The dispersion relation when the bulk fluids are inviscid can be obtained from (3.22) by setting $\lambda=0$. The mode analysis for the general case $\lambda\neq0$ is better understood by first considering this case in some detail. In addition, if the surface viscosities are very large compared to the viscosities of the bulk fluids or if the droplets are very small, the damping of the surface modes depends primarily on the surface dissipation. Thus there are situations where to a good approximation the bulk fluids may be treated as inviscid.

When $\lambda=0$, the dispersion relation becomes

$$\Delta(\zeta)=\frac{\mu a_l^2+a_l b_l}{\Omega_l^2}\zeta^3+\left[4\mu a_l+\frac{\beta b_l a_l}{\Omega_l^2}\right]\zeta^2+(4\mu\beta a_l+\mu a_l^2+a_l b_l)\zeta+\beta a_l b_l=0\ . \tag{4.1}$$

If the surface viscosity is neglected there is only one pair of imaginary roots, $\zeta=\pm i\Omega_2$. Note that if we pass to the limit of a planar surface by taking $l\to\infty$, $R_0\to\infty$, and $l/R_0\to q$, then $\omega_0\to(\sigma/\rho)^{1/2}q^{3/2}$, which is the well-known result[31] for the frequency of capillary waves of wave vector q. For the $\lambda=0$ case, there will always be one real root which is sensitive to the surface elasticity and approaches a constant for large mode numbers; we will label this root ζ_e. If there is a complex conjugate pair, we will denote it by ζ_c,ζ_c^*, and when the complex root splits into two real roots they will be denoted $\zeta_\pm$.

Even if the inertia is small $(\Omega_0 \gg 1)$ it can be shown from Eq. (4.1) that $\mathrm{Im}(\zeta_c)\to\Omega_0 l^{3/2}$ for sufficiently large mode number $l>l^*$, where $l^*\sim4\mu^2\Omega_0^2/(1+\mu)^2$. The large l modes therefore oscillate with a frequency which is the same as when the surface viscosity is neglected. If the inertial effects are large $(\Omega_0^2 \ll 1)$, the decay is oscillatory for all $l\geq2$. The situation is actually more complicated than this; in certain cases there can be oscillatory decay for both large and small mode numbers, modes with intermediate values of the mode number being overdamped. This will be discussed in more detail later.

The modes are linear combinations of surface velocity and radial displacement of the interface and depend on three time scales, τ_s, τ_s/β, and ω_0^{-1}. The decay times τ_s and τ_s/β are analogous to the RC decay times in an electric circuit: $\tau_s=\kappa/\sigma_0$ is the time for the elastic energy stored in a radial displacement of the interface to dissipate, and $\tau_s/\beta=\kappa/K$ is the time for the elastic energy stored in a density fluctuation to dissipate. The frequency ω_0 depends on the inertia of the bulk fluids and the surface tension.

Before proceeding with the analysis, we give some examples of the magnitudes of the various parameters for a few physical systems. There is a wide variety of rheological behavior for surface films which depends on the chemical nature of the surfactant and the temperature, pH, and ionic strength of the fluid media. Among the common surfactants are the fatty acids and alcohols. For example, palmitic acid (C_{16}) at 25 °C and spread as a monolayer on a water subphase of pH 2 has a surface shear viscosity $\epsilon=10^{-4}$ g/s when the surface area per molecule is 26 Å^2 (Ref. 4). At this molecular area the surface pressure $\Pi=0.5$ dyn/cm (Ref. 32) and the surface elasticity $K=24$ dyn/cm. Droplets of oil in water (or water in oil) stabilized by a monolayer of this type at a similar surface pressure have a surface tension $\sigma=\sigma_{ow}-\Pi=49.5$ dyn/cm, where $\sigma_{ow}=50$ dyn/cm is a typical value for the surface tension of an oil-water interface. Assuming $\kappa\sim\epsilon$ and considering droplets of radius $R=0.01$ cm, a typical relaxation time is $\tau_s=2\times10^{-6}$ s and the dimensionless parameters have the values $\beta=0.5$, $\lambda=1$, and $\Omega_0=0.01$ when the fluid media have properties similar to that of water ($\rho\sim1$ g/cm^3, $\eta\sim0.01$ poise). For the same acid but with a molecular area of 22 Å^2, $\Pi=14.9$ dyn/cm, $K=120$ dyn/cm (Ref. 32), and $\epsilon=2.5\times10^{-4}$ g/s.[4] Then $\sigma=35$ dyn/cm, $\tau_s=7\times10^{-6}$ s, and the dimensionless parameters are $\beta=3$, $\lambda=4$, and $\Omega_0=0.04$.

Phospholipid vesicles of radius 100–200 nm have surface elasticities $K\sim3-150$ dyn/cm as determined by osmotic swelling experiments.[19] From the measured pressure difference Δp across the bilayer the surface tension can be estimated at $\sigma\sim0.05-12$ dyn/cm, thus $\beta\sim4-16$ for these systems. At a surface pressure of $\Pi=5$ dyn/cm the surface shear viscosity for phospholipid monolayers is 3×10^{-4} g/s (Ref. 33). At surface pressures on the order of 30 dyn/cm (Ref. 34) we assume a value for the surface viscosity which is larger by an order of magnitude or so. Taking $\epsilon\sim\kappa\sim0.001$ g/s, $\sigma=1$ dyn/cm, $K=10$ dyn/cm, and $R=10^{-5}$ cm leads to the values $\tau_s=0.001$ s, $\beta=10$, $\lambda=10^{-4}$, and $\Omega_0=3\times10^4$. In addition to these examples, the rheological parameters for red blood cells are given in a later section.

The relative magnitudes of the characteristic time scales τ_s, τ_s/β, and ω_0^{-1} determine the manner in which the system relaxes back to equilibrium when $\lambda=0$, and in the following we discuss some limiting cases.

(1) $\Omega_0 \gg 1$. In this case the inertial resistance to the motion of the interface is small, which happens, for example, when the droplets are very small. For $l < l^*$ all the roots are real, and keeping only the highest-order terms in Ω_0 they are given to a good approximation by

$$\zeta_+ = -\frac{4\mu\Omega_l^2}{\mu a_l + b_l} , \tag{4.2}$$

$$\zeta_- = -X - \left[X^2 - \frac{\beta b_l}{4\mu} \right]^{1/2} ,$$
$$\zeta_e = -X + \left[X^2 - \frac{\beta b_l}{4\mu} \right]^{1/2} , \tag{4.3}$$

where

$$X = \frac{4\mu\beta + b_l + \mu a_l}{8\mu} . \tag{4.4}$$

The rapid transient behavior associated with the inertial resistance of the bulk fluids decays at a rate ζ_+ which is independent of the surface compressibility and increases linearly with the mode number when $l \gg 2$. Both ζ_- and ζ_e decrease as μ increases, and increase as β increases. If $4\mu\beta \ll b_l + \mu a_l$

$$\zeta_e \sim -\frac{\beta b_l}{b_l + \mu a_l} , \tag{4.5}$$

$$\zeta_- \sim -\frac{b_l + \mu a_l}{4\mu} , \tag{4.6}$$

and the decay rate of the slow mode, ζ_e becomes independent of the shape of the interface when $l \gg 2$. The frequencies, Eqs. (4.2), (4.5), and (4.6), correspond to a wide separation of time scales, $\omega_0^{-1} \ll \tau_s \ll \tau_s/\beta$. When $4\mu\beta \gg b_l + \mu a_l$

$$\zeta_e \sim -\frac{b_l}{4\mu} , \tag{4.7}$$

$$\zeta_- \sim -\beta , \tag{4.8}$$

thus when the compressibility is small there is a fast mode which decays on the viscoelastic time scale and is independent of mode number, and a slower mode with a decay rate which is independent of the compressibility and dilational viscosity. The effects of surface elasticity are more important for the higher l modes $l > [4\mu\beta/(1+\mu)]^{1/2}$ since these correspond to larger increases in surface area.

(2) $\Omega_0 \ll 1$. In this case the inertia of the bulk fluids is large, and there is one real root and a complex conjugate pair for all $l > 2$. To lowest order in Ω_0

$$\zeta_c = -\frac{2\mu\Omega_l^2}{b_l} + i\Omega_l \tag{4.9}$$

The complex root is independent of the compressibility of the interface with an oscillation frequency which is the same as that obtained when the dissipation is completely neglected. The other mode ζ_e is independent of Ω_0 and is again given by Eq. (4.5). When $l \gg 2$, $\mathrm{Re}(\zeta_c)$ becomes linear in the mode number and $\mathrm{Im}(\zeta_c) \sim \Omega_0 l^{3/2}$. The oscillation frequency is not sensitive to either β or μ when the inertial effects dominate.

(3) When $\beta \ll 1$, ζ_e is again given by Eq. (4.5) and the other roots are given by

$$\zeta_\pm = \frac{-2\mu\Omega_l^2}{\mu a_l + b_l} \left\{ 1 \pm \left[1 - \left[\frac{\mu a_l + b_l}{2\mu\Omega_l} \right]^2 \right]^{1/2} \right\} . \tag{4.10}$$

Oscillatory decay is possible when

$$\Omega_0 < \frac{b_l + \mu a_l}{2\mu} \left[\frac{2l + 1 + \Delta\rho}{2a_l b_l} \right]^{1/2} . \tag{4.11}$$

For typical values of the parameters for large droplets $\epsilon \sim 0.01$ g/s, $\sigma_0 \sim 50$ dyn/cm (Ref. 4), and assuming $\mu \sim 1$, the $l = 2$ mode is oscillatory when $R_0 \sim 0.01$ cm or larger. When $\Omega_0 \ll 1$ the two real roots $\zeta_\pm$ become a complex conjugate pair ζ_c, ζ_c^*, where

$$\zeta_c = -\frac{2\mu\Omega_l^2}{\mu a_l + b_l} + i\Omega_l . \tag{4.12}$$

When $l \gg 2$

$$\zeta_c \sim -\frac{2\mu\Omega_0^2 l}{1+\mu} + i\Omega_0 l^{3/2} \tag{4.13}$$

and Eq. (4.13) is also the limiting form for the complex root for sufficiently large values of l, regardless of the values of the parameters. When $\Omega_0 \gg 1$ the conjugate pair splits into two real roots which are given by Eqs. (4.2) and (4.6) in case (1) above.

The mode frequencies are plotted versus mode number in Figs. 1–3 for various values of the parameters and for the intermediate case $\Omega_0 \sim 1$. Since there are so many parameters we will restrict our attention to cases where the interior and exterior fluids have similar properties, thus we have set $\Delta\rho = \Delta\eta = 0$ in most of the numerical calculations. Unless specified otherwise we have also taken $\beta = \mu = 1$, which are reasonable values for many surface films,[4] and have plotted the negative of the real part of the mode frequencies on the graphs.

When the inertia of the bulk fluids is in the intermediate range ($\Omega_0 \sim 1$) there can be three real roots or a real root and a complex conjugate pair for small values of the mode number. When $l \geq l^*$, the real roots $\zeta_\pm$ coalesce into a complex conjugate pair ζ, ζ^*. An example of this is shown in Fig. 1 where we have plotted $\zeta_\pm$ versus mode number when $\beta = 1$. For these values of the parameters $l^* = \Omega_0^2$ and oscillatory decay occurs for all $l > 2$ when $\Omega_0 = 1$. As Ω_0 increases, l^* increases, and when $\Omega_0 = 4$ the modes with $l < l^* = 16$ are overdamped. Immediately after the two roots collide the real part becomes linear in l. The asymptotic region $\mathrm{Im}(\zeta) \sim l^{3/2}$ has not yet been reached for the larger values of Ω_0. Similar behavior occurs for larger values of Ω_0.

The effect of the surface elasticity on the decay modes is shown in Fig. 2. As β increases, another region of oscillatory decay appears for small values of l, and when $\beta = 120$ only those modes with mode numbers in the range $11 \leq l < 16$ are overdamped. The oscillation frequency in the smaller-l region depends primarily on β, thus these oscillations are not the capillary oscillations $\omega=\Omega_0 l^{3/2}$. With further increases in β (not shown), the small-l region of oscillatory decay eventually disappears, and the small-l modes are again overdamped.

We also find (not shown) that the behavior as μ is varied is similar to that shown in Fig. 1 in that l^* increases as μ increases. Thus the small-l modes tend to be overdamped for surface films with large values of μ.

The other mode, ζ_e, is not sensitive to the inertia when Ω_0 is either very large or very small. However, when $\Omega_0 \sim 1$ the real root and the complex root can collide and exchange real parts. An example of this is shown in Fig. 3. The upper curves (a, b, and c) correspond to the real root ζ_e, and the lower curves (f, g, and h) correspond to the complex root. As Ω_0 increases, ζ_e decreases and $\mathrm{Re}(\zeta_c)$ increases until they collide near $\Omega_0 \sim 1$. When $\Omega_0=1$ there are three real roots for $l \leq 5$ for these values of the parameters.

We see from these examples that the conditions under which there are damped oscillations are by no means simple. In general, the decay will be oscillatory when Ω_0 and μ are small, and the low modes can oscillate when β is large (but not too large). This would correspond, for example, to large droplets coated with a film which has small compressibility. Regardless of the values of the parameters, for large enough values of the mode number the decay will be oscillatory. We note that when inertial effects are neglected, the decay rates are independent of the droplet radius when $\lambda=0$.

We now show how the damping by the bulk fluids alters the mode frequencies. The dispersion relation is transcendental and the roots must be found numerically. There are an infinite number of roots; the large roots are associated with the zeros of the Bessel functions, but we will restrict our attention to those which reduce to ζ_e, ζ_c, or ζ_- when $\lambda=0$. These are the smallest and most important roots. Before discussing the results in the general case, let us first consider the case when the inertia of the bulk fluids is small compared to the dissipation.

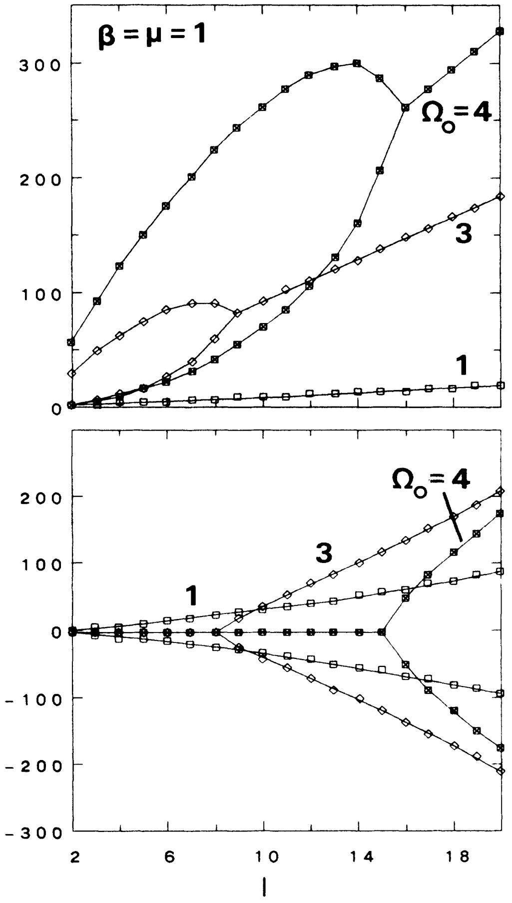

FIG. 1. Coalescence of the two real roots ζ_- and ζ_+ into a complex root ζ_c for various values of Ω_0 and $\beta=\mu=1$. The negative of the real part of the mode frequency and the imaginary part are plotted vs mode number l. In the top graph, the upper (lower) curves correspond to ζ_+ (ζ_-), the straight lines to $\mathrm{Re}\zeta_c$.

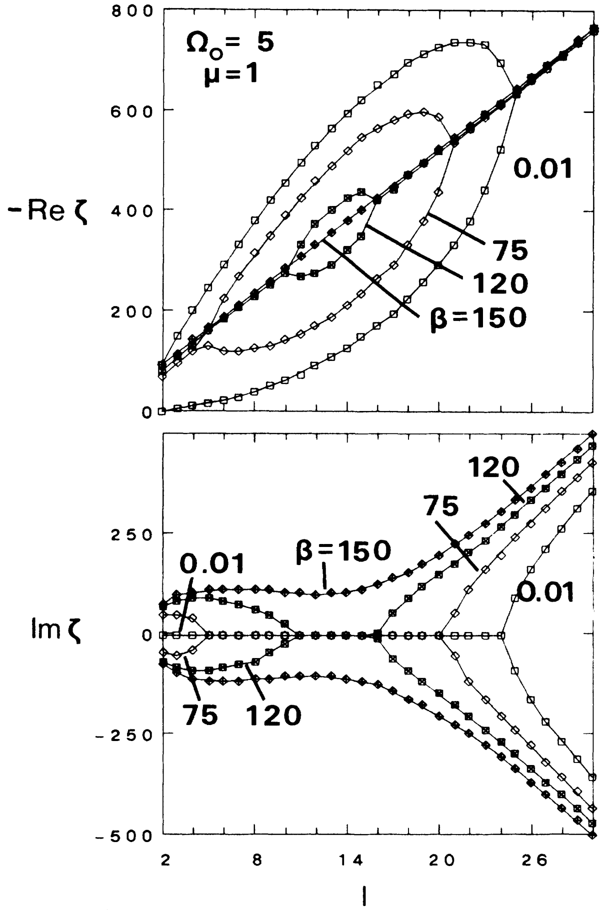

FIG. 2. Coalescence of the two real roots ζ_- and ζ_+ into a complex root ζ_c for various values of β and $\Omega_0=5$, $\mu=1$. The negative of the real part of the mode frequency and the imaginary part are plotted versus mode number l. In the top graph, the upper (lower) curves correspond to ζ_+ (ζ_-), the straight lines to $\mathrm{Re}\zeta_c$.

When the fluids have viscosity, the relative importance of inertia and dissipation is determined by the ratio of time scales $\tau_s/\tau_F=\lambda\Omega_0^2$. If $\tau_s/\tau_F \gg 1$ the transient response time of the bulk fluids in responding to a deformation of the surface is short, and the bulk fluids rapidly reach steady state. In this limit the surface processes are relatively slow, and the bulk fluids essentially follow the motion of the interface. Analytical results can be found for the frequencies of the slow modes which satisfy $\zeta \ll \tau_s/\tau_F$. In this approximation the terms in the dispersion relation involving the spherical Bessel functions are considerably simplified.

For $x_{i,e} \ll 1$ we can replace $Q_{i,e}$ in Eq. (3.19) by

$$\begin{aligned} z\tau_F Q_i &\rightarrow -(1+\Delta\eta)(2l+3) , \\ z\tau_F Q_e &\rightarrow -(1-\Delta\eta)(2l-1) . \end{aligned} \tag{4.14}$$

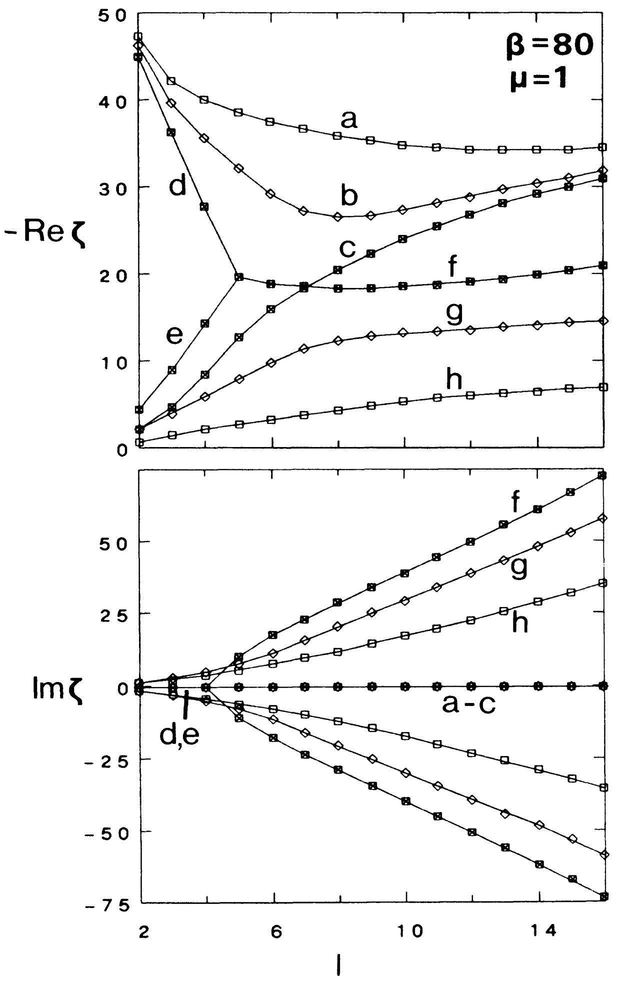

FIG. 3. Collision of the real root ζ_e with the complex conjugate pair as Ω_0 varies. The negative of the real part of the mode frequency and the imaginary part are plotted vs mode number l and $\beta=80$, $\mu=1$. Curves a, b, and c correspond to ζ_e, d and e to ζ_+ and ζ_-, respectively, and f, g, and h to the complex root ζ_c. $\Omega_0=0.5$ (a and h), $\Omega_0=0.8$ (b and g), and $\Omega_0=1$ (c, d, e, and f).

Since this is equivalent to neglecting the time derivatives in the hydrodynamic equations the modes will not depend on the densities of the bulk fluids. With this approximation the dispersion relation for the slow modes becomes

$$\Delta(\zeta)=(4\mu a_l+\lambda c_1+\lambda^2 c_2)\zeta^2 + (4\mu\beta a_l + b_l a_l + \mu a_l^2 + \lambda c_0)\zeta + \beta b_l a_l = 0 , \tag{4.15}$$

where the constants are given by

$$\begin{aligned} c_0 &= (2l+1)a_l + \frac{\beta}{2}[C_l - 4(2l+1) - 12\,\Delta\eta] , \\ c_1 &= \frac{b_l+\mu a_l}{2b_l} C_l - 2(2l+1+3\,\Delta\eta) , \\ c_2 &= \frac{(2l+1)}{2b_l} C_l - \frac{9}{4b_l}(2l+1+\Delta\eta)^2 , \end{aligned} \tag{4.16}$$

and

$$C_l=(l+1)^2(2l+3)+l^2(2l-1)+3\,\Delta\eta . \tag{4.17}$$

There is another fast mode with magnitude on the order of τ_s/τ_F which cannot be found using this approximation.

The limiting case in which the surface viscosity is completely negligible compared to the damping by the bulk fluids is obtained from Eq. (4.15) by considering only the highest order terms in λ. The dispersion relation in this limit is

$$\Delta(\zeta)=\lambda^2 c_2 \zeta^2 + \lambda c_0 \zeta + \beta b_l a_l = 0 \tag{4.18}$$

and the mode frequencies

$$\begin{aligned} \zeta_e &= -\frac{c_0}{2\lambda c_2} + \frac{1}{2\lambda c_2}(c_0^2 - 4\beta c_2 a_l b_l)^{1/2} , \\ \zeta_- &= -\frac{c_0}{2\lambda c_2} - \frac{1}{2\lambda c_2}(c_0^2 - 4\beta c_2 a_l b_l)^{1/2} , \end{aligned} \tag{4.19}$$

are real. Equation (4.19) gives the mode frequencies obtained by using the steady-state hydrodynamic equations and setting $\epsilon=\kappa=0$ in the surface equations. They describe the damping of shape fluctuations for a small fluid body coated with a purely elastic membrane. Note that $z=\zeta/\tau_s$ depends only on the viscosities of the bulk fluids. For a droplet containing no surface film, and if the stress exerted by the exterior medium is neglected, we set $\Delta\eta=1$ and $\beta=0$. In this case there is one mode

$$\zeta_- = -\frac{(2l+1)la_l}{2(l-1)(2l^2+4l+3)\lambda} \tag{4.20}$$

in agreement with the results for this case obtained elsewhere.[22-24] When $l \gg 2$ the modes become

$$\begin{aligned} \zeta_e &\sim -\frac{(1+\beta)l}{4\lambda} + \frac{l}{4\lambda}|\beta-1| , \\ \zeta_- &\sim -\frac{(1+\beta)l}{4\lambda} - \frac{l}{4\lambda}|\beta-1| , \end{aligned} \tag{4.21}$$

therefore the mode frequencies both vary linearly with mode number when the damping is due entirely to the bulk fluids, and the modes decay slowly when the viscosity of the bulk fluids is large. Thus the correlation time for the fluctuations is large when the viscous coupling to the exterior medium is large, and is also largest for the $l=2$ mode. The surface elasticity and surface tension contribute in a similar way, and regardless of the value of β, there will be one mode with frequency $\beta l/2\lambda$ and another with frequency $l/2\lambda$. Note that the damping is due only to the viscosity of the bulk fluids, the decay rates depend inversely on the droplet radius.

The roots of the dispersion relation for intermediate values of λ were obtained numerically using a complex zero finder. Some caution must be taken since the dispersion relation involves functions with branch points. The velocity in the exterior region goes as e^{iqr} at large r, with $q \sim (-\zeta)^{1/2}$. With the branch cut taken along the positive ζ axis q will have a positive imaginary part, giving the correct behavior for $r \rightarrow \infty$.

Figures 4–7 show the mode frequencies ζ_e and ζ_- versus l for several values of λ when the inertia of the bulk fluids is small ($\Omega_0 = 100$). Figures 4 and 5 correspond to a very compressible surface film ($\beta = 0.01$). The large λ result $\zeta_- \sim -l/2\lambda$ is a good approximation when $\lambda \sim 4$ for the larger root ζ_- (Fig. 4), thus the decay of this mode is primarily due to the damping by the bulk fluids for fairly small values of λ. As in the $\lambda = 0$ case, we have found that ζ_- is fairly insensitive to β when β is small. The other mode frequency ζ_e (Fig. 5) is smaller and therefore more important. The asymptotic behavior $\zeta_e \sim -\beta l/2\lambda$ is reached only when $\lambda \gtrsim 100$, thus the surface viscosity is significant in the damping of this mode. We also see that the $\lambda = 0$ approximation gives a fairly accurate description of the low-frequency behavior of the interface when the elasticity and the inertia are small. The approximations to the modes obtained from Eq. (4.15) coincide with the exact numerical results except in some cases when λ is very small and the boundary-layer effects are important as discussed below. When the interface has no surfactant then $\beta = 0$ and the fast mode ζ_- is the only mode of decay.

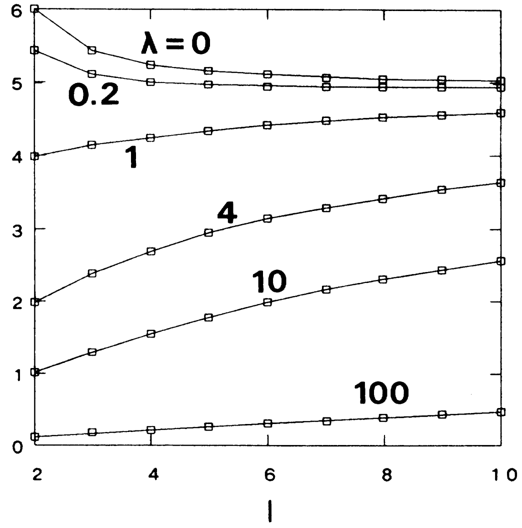

FIG. 5. Negative of the real root ζ_e vs mode number l for various values of λ. Parameters as in Fig. 4.

Figure 6 shows ζ_e for a larger value of β ($\beta = 10$), corresponding to a surface phase with a much smaller compressibility. The other mode frequency ζ_- is similar to that shown in Fig. 4, except that the asymptotic value $\zeta_- \sim -\beta l/2\lambda$ is reached only when $\lambda \sim 100$. When $\lambda \sim 10$ or larger, $\zeta_e \sim -l/2\lambda$ is independent of β and surface viscosity, thus the effect of surface viscosity is less important for this mode. Regardless of the value of β,

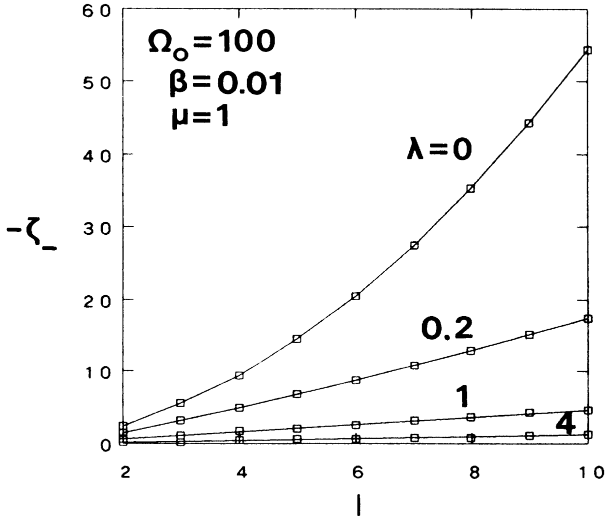

FIG. 4. Negative of the real root ζ_- vs mode number l for various values of λ. $\Omega_0 = 100$, $\beta = 0.01$, and $\mu = 1$.

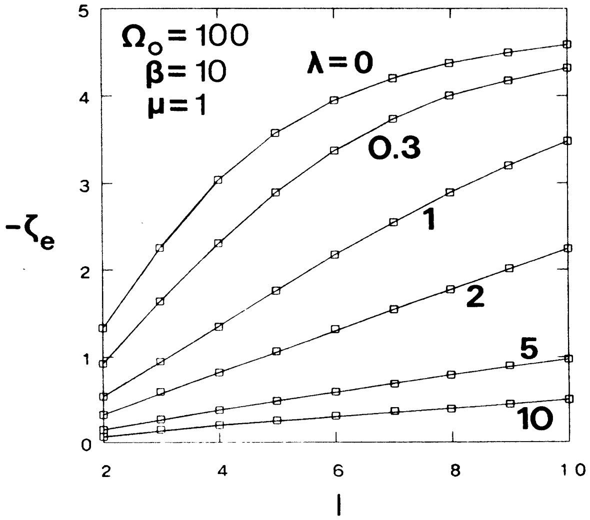

FIG. 6. Negative of the real root ζ_e vs mode number l for various values of λ. $\Omega_0 = 100$, $\beta = 10$, and $\mu = 1$.

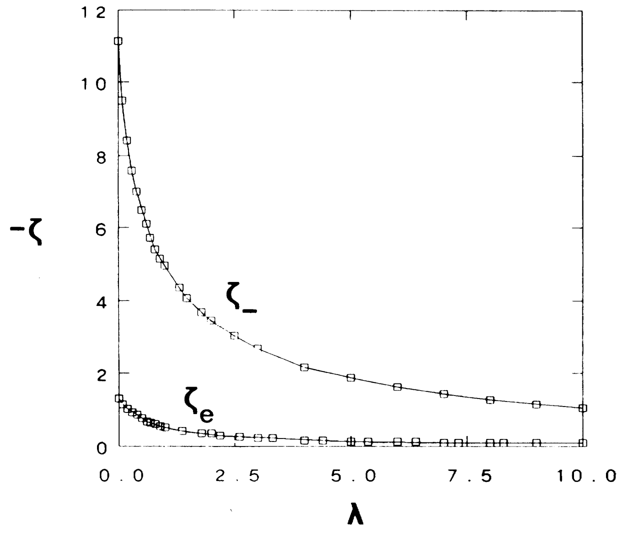

FIG. 7. Negative of the real root ζ_- (upper curve) and ζ_e (lower curve) vs λ. Parameters as in Fig. 6, and $l=2$.

the mode which depends asymptotically on the surface elasticity is also the one for which the effects of surface viscosity are most important. The modes are also sensitive to λ when λ is very small. This can be seen in Fig. 7 where we have plotted the $l=2$ mode frequencies as a function of λ for $\beta=10$. When $\lambda \ll 1$, the difference $[\zeta(\lambda)-\zeta(\lambda=0)]\sim\lambda^{1/2}$. This dependence on $\lambda^{1/2}$ indicates that when the viscosities of the adjacent fluids are small the primary source of dissipation is in the boundary layer on either side of the interface.[35] This is in agreement with similar results obtained elsewhere[24] for the case when the surface viscosity and compressibility are neglected.

We now consider the case when the inertial effects are large. We have seen that if Ω_0 is small there is one real root and a complex conjugate pair for all mode numbers when $\lambda=0$. Figure 8 shows the dependence of the complex root ζ_c on the mode number when λ is nonzero and for an intermediate value of β ($\beta=1$); similar behavior is found for other values of β. Re(ζ_c) first increases with λ,

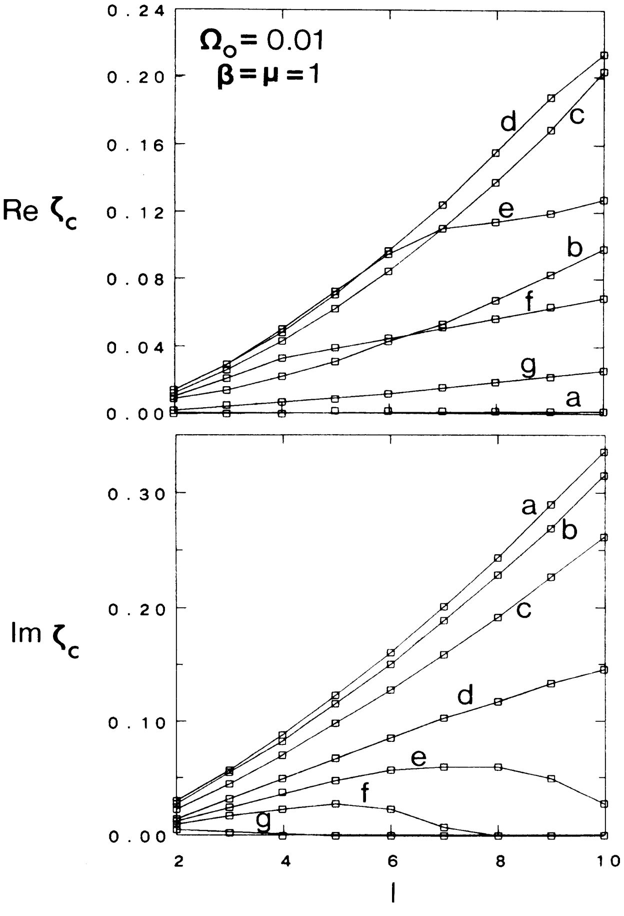

FIG. 8. Complex root ζ_c vs mode number l for various values of λ. $\Omega_0=0.01$ and $\beta=\mu=1$. The curves labeled a–g correspond to $\lambda=0$, 1, 10, 30, 40, 50, and 80, respectively.

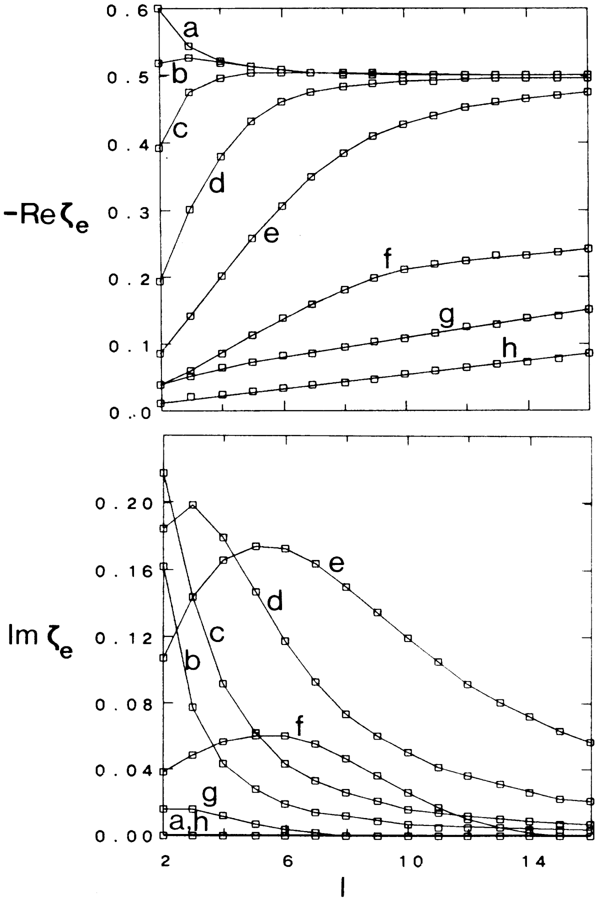

FIG. 9. Complex root ζ_e versus mode number l for various values of λ. $\Omega_0=0.01$ and $\beta=\mu=1$. The curves labeled a–h correspond to $\lambda=0$, 0.002, 0.01, 0.1, 1, 20, 40, and 100, respectively.

then decreases when $\lambda \sim 40$ or larger. The imaginary part is fairly insensitive to λ when λ is $O(1)$ or smaller. As λ increases the complex root splits into two real roots. One of them (not shown) is large and proportional to λ. The higher-l modes are overdamped, and oscillatory decay occurs only for small values of l until eventually ($\lambda \gtrsim 100$) all the modes are overdamped. This is in contrast to the $\lambda=0$ case where the modes oscillate at large values of l. Similar behavior is found for the larger-l modes when $\Omega_0 \sim 1$. Neglecting the viscosity of the bulk fluids is a reasonable approximation when λ is small for the lower mode numbers.

The other root, ζ_e, is real when $\lambda=0$ and has an imaginary part which rapidly increases from zero when λ is small. This is shown in Fig. 9 for $\beta=1$. For this case the elasticity and surface tension are comparable, and the damping rates and oscillation frequencies of the two modes are the same order of magnitude when the mode number is small. When $\lambda \ll 1$, $[\mathrm{Re}\zeta_e(\lambda)-\mathrm{Re}\zeta_e(\lambda=0)] \sim \beta\lambda^{1/2}$, and eventually $\mathrm{Re}\zeta_e$ becomes linear in the mode number for large values of λ. $\mathrm{Im}(\zeta_e) \sim \beta\lambda^{1/2}$ when λ is small, and for very large values of λ it approaches zero. Again the dependence on $\lambda^{1/2}$ indicates a boundary-layer effect, and it is interesting that this can lead to the appearance of a second oscillating mode. As the surface elasticity increases the interface behaves somewhat more like a rigid boundary; the velocity gradients will be larger in the vicinity of the interface. This may account in part for the enhancement of the boundary layer effect when $\beta \gg 1$. Similar behavior occurs when $\Omega_0 \sim 1$, although we have found that these effects are most important when the inertia is large.

V. DYNAMIC CORRELATION FUNCTION

Since $S_{lm,l'm'}(t)$ is an even function of time, the frequency spectrum of the fluctuations

$$S_{lm,l'm'}(\omega)=\int_{-\infty}^{\infty} e^{i\omega t} S_{lm,l'm'}(t)\,dt \tag{5.1}$$

is an even function of ω, and the stability of the equilibrium state also requires that it be positive. Its amplitude is determined by the static correlation function which is diagonal. $S_{lm}(\omega) \equiv S_{lm,lm}(\omega)$ is given by the real part of $S_{lm}(\zeta)$ (Ref. 27),

$$S_{lm}(\omega)=2\,\mathrm{Re}S_{lm}(\zeta=-i\omega+\epsilon) \ . \tag{5.2}$$

Here ω is a real, dimensionless frequency expressed in units of τ_s^{-1}. The spatial correlation function between two points on the surface is

$$S(\theta,\theta',\phi,\phi',\omega)=2\,\mathrm{Re}S(\theta,\theta',\phi,\phi',\zeta)|_{\zeta=-i\omega+\epsilon} \ , \tag{5.3}$$

where $S(\theta,\theta',\phi,\phi'\zeta)$ is found by summing over the modes

$$\begin{aligned} S(\theta,\theta',\phi,\phi',\zeta) &= \langle \delta R(\theta,\phi,\zeta)\delta R^*(\theta',\phi',t=0)\rangle \\ &= \sum_{\substack{l=2 \\ -l\le m\le l}}^{l_{\max}} \sum_{\substack{l'=2 \\ -l'\le m'\le l'}}^{l'_{\max}} S_{lm,l',m'}(\zeta) Y_{lm}(\theta,\phi) \\ &\quad \times Y^*_{l'm'}(\theta',\phi') \ . \end{aligned} \tag{5.4}$$

Using Eq. (2.6) for the amplitude of the static fluctuations and Eq. (3.21), our final result for the spectral density of the two-point correlation function is

$$\begin{aligned} S(\gamma,\omega) &= \frac{2k_B T\tau_s}{\sigma_0 A_0}\mathrm{Re}\sum_{l=2}^{l_{\max}} \left. \frac{\Delta(\zeta)\ a_l(A+\lambda B)}{\zeta\,\Delta(\zeta)} \right|_{\zeta=-i\omega+\epsilon} \\ &\quad \times \frac{(2l+1)}{a_l}P_l(\cos\gamma) \ , \end{aligned} \tag{5.5}$$

where $A_0=4\pi R_0^2$, $P_l(\cos\gamma)$ is a Legendre polynomial, and $\Delta(\zeta)$ is given by Eq. (3.22). The angle γ is defined by $\hat{\mathbf{r}}(\theta,\phi)\cdot\hat{\mathbf{r}}'(\theta',\phi')=\cos\gamma$, where $\hat{\mathbf{r}}$ and $\hat{\mathbf{r}}'$ are unit vectors to two points on the surface and $\cos\gamma=\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi-\phi')$. In deriving this we have made use of the fact that S_{lm} is independent of the mode number m and have used the addition theorem for spherical harmonics.[36] Since the Legendre polynomials have the normalization $P_l(1)=1$, the equal point ($\gamma=0$) correlation function $S(0,\omega)$ is given by Eq. (5.5) with $P_l(\cos\gamma)=1$.

With $\Delta(\zeta)$ given by Eq. (4.1), the correlation function for $\lambda=0$ is

$$S(\gamma,\omega)=\frac{k_B T}{\sigma_0 A_0}\tau_s \sum_{l=2}^{l_{\max}} \frac{[8\mu\beta^2 b_l+8\mu\omega^2(\mu a_l+b_l)]\dfrac{2l+1}{a_l}P_l(\cos\gamma)}{\left[\beta b_l\left[1-\dfrac{\omega^2}{\Omega_l^2}\right]-4\mu\omega^2\right]^2+\omega^2\left[4\mu\beta+(\mu a_l+b_l)\left[1-\dfrac{\omega^2}{\Omega_l^2}\right]\right]^2} \ . \tag{5.6}$$

In the general case there are several peaks in $S(0,\omega)$. These are resonance peaks near $\omega \sim \Omega_l$; the widths are proportional to $\Omega_0^2 l$, and the heights to $l^{-1}\Omega_0^{-2}$. When $\Omega_0 \gg 1$ the only peak is at $\omega=0$ with a height $\propto \epsilon k_B T/(\sigma_0^2 A_0)$, which is independent of β and proportional to R_0^{-2}.

When $\lambda\Omega_0^2 \gg 1$ the surface dissipation is negligible and the damping is large and due entirely to the interior and exterior fluids. In this limit inertial effects are negligible, $\Delta(\zeta)$ is given by Eq. (4.18), and the correlation function is

$$S(\gamma,\omega)=\frac{2k_B T}{\sigma_0 A_0}\lambda\tau_s \sum_{l=2}^{l_{\max}} \frac{(2l+1)}{a_l}\left[\frac{\lambda^2 c_2(2l+1)a_l\omega^2+[c_0-(2l+1)a_l]\beta b_l a_l}{(\lambda^2\omega^2 c_2-\beta b_l a_l)^2+(\lambda c_0\omega)^2}\right]P_l(\cos\gamma) \ . \tag{5.7}$$

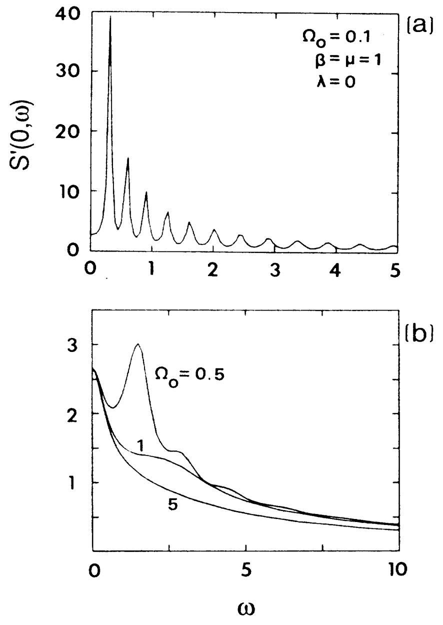

FIG. 10. Dimensionless spectral density $S'(0,\omega)$ for $\beta=\mu=1$ and $\lambda=0$. (a) $\Omega_0=0.1$, (b) $\Omega_0=0.5$, 1, 5.

The peak is at $\omega=0$ with a height $\propto \eta R_0 k_B T/(\sigma_0^2 A_0)$, which is again independent of surface elasticity and proportional to R_0^{-1}.

In Figures 10–12 we plot the dimensionless correlation function $S'(\gamma,\omega)=S(\gamma,\omega)\sigma_0 A_0/(k_B T\tau_s)$ versus frequency ω; we take $\Delta\rho=\Delta\eta=0$ and $\mu=\beta=1$ unless specified otherwise. Figures 10 and 11 show the one-point correlation function $S'(\gamma,\omega)$ [Eq. (5.6)] for the case $\lambda=0$. When the inertia is large all the modes are oscillatory, and the spectrum shows many resonance peaks corresponding to the capillary frequencies Ω_l [Fig. 10(a)], which become smaller as Ω_0 increases [Fig. 10(b)]. When $\Omega_0 \sim 0.5$, the effects of both surface tension and surface elasticity can be seen, and the width of the peak at $\omega=0$ is proportional to β when β is small. As Ω_0 increases further, the spectrum becomes dominated by the slow modes, and the peak shifts to zero frequency. The damping by the bulk fluids particularly affects the high frequency, large mode-number oscillations as shown in Fig. 11. Since Ω_0 is small here, the exact expression for $\Delta(\xi)$ [Eq. (3.22)] must be used in computing the correlation function.

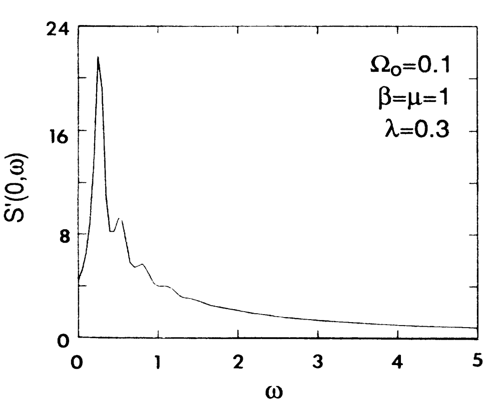

FIG. 11. Dimensionless spectral density $S'(0,\omega)$ for $\beta=\mu=1$, $\lambda=0.3$, and $\Omega_0=0.1$.

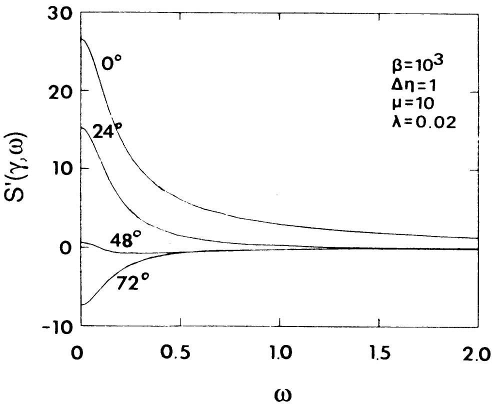

FIG. 12. Dimensionless spectral density $S'(\gamma,\omega)$ of the angular correlations for different values of the angle γ. Inertial effects are neglected and $\beta=10^3$, $\Delta\eta=1$, $\mu=10$, and $\lambda=0.02$.

In Fig. 12 we have plotted the two-point spectral density using surface rheological parameters typical of red blood cells which have been the most extensively studied.[37] We therefore take $\epsilon=0.01$ g/s, $K=100$ dyn/cm, and will assume $\sigma_0=0.1$. We use a typical cell radius $R_0=2\times10^{-4}$ cm and neglect the viscosity of the surrounding aqueous medium compared to the viscosity of the interior fluid. The dilational viscosities are not known; we shall assume $\kappa\sim0.1\epsilon$. In addition, we neglect inertial effects and use Eq. (5.5) with $\Delta(\xi)$ given by Eq. (4.15). These values correspond to the dimensionless parameters $\beta=1000$, $\lambda=0.02$, $\Delta\eta=1$, and $\mu=10$. The angular correlations are shown in Fig. 12 for various values of the angle γ. We see that the correlation function becomes negative when $\gamma\sim48°$. When the angular separation of two points on the surface is in this neighborhood, on the average one point will have a positive radial displacement and the other a negative one. This is due to the fact that when the inertial effects are small the primary contribution to the spectrum is from the small-l modes. For $l=2$ for example, $P_2(\cos\gamma)$ is positive when $\gamma<55°$, and negative when $\gamma>55°$. Thus information about the dominant shape fluctuations can be inferred from the angular dependence of the two-point correlation function.

VI. SUMMARY AND CONCLUSIONS

We have investigated in some detail the fluctuations in a fluid droplet immersed in a fluid medium when the interface between the two fluids has viscosity and compressibility in addition to surface tension. We considered an interface containing a compressible Newtonian surface fluid which is a fairly simple model, but even in this case the dynamics of the interface can be quite complex.

The frequencies of the normal modes depend on the surface rheological parameters, the extent of the coupling to the adjacent fluids and the shape of the interface. When $\lambda=0$ there will be damped oscillations for large enough values of the mode number regardless of the extent of the surface dissipation. This is no longer the case when the fluids have viscosity, and the viscous drag by the adjacent fluids on the interface leads to the vanishing of the large mode-number oscillations. When λ is small the boundary layer effects can be important and are enhanced when both the fluid inertia and surface elasticity are large. In this case there are two oscillatory modes of decay. One of these is associated with the surface tension and is fairly insensitive to λ when λ is small. The other mode is associated with the surface elasticity, has an oscillation frequency which is dependent on the viscous coupling to the bulk fluids, and is strongly affected by the boundary layer. Neglecting the viscosity of the bulk fluids cannot account for this second mode and in this case is a poor approximation to the much more complex behavior which actually occurs.

Even in the simpler case $\lambda=0$ we found that there is no simple condition which determines the way in which the fluid droplet relaxes back to the equilibrium spherical shape. In some cases the low mode-number oscillations decay in a manner which is very different from the higher-frequency capillary oscillations which are associated primarily with the surface tension. These depend on the surface elasticity and may be related to the second oscillatory mode which was found in the nonzero-λ case. Regardless of the values of the parameters, for large enough values of the mode number the decay will be oscillatory. For small droplets, oscillations occur only for very large values of the mode number and are very rapidly damped, and will therefore not be important in any practical sense. When the inertial effects are small, the decay rates depend inversely on the droplet radius if the surface viscosity is neglected and are independent of the droplet radius if the viscosity of the bulk fluids is neglected.

The spectral density of the fluctuations in the shape of the surface has a complicated dependence on frequency owing to the presence of the spherical Bessel functions. The stochastic variable $\delta R(t)$ is therefore non-Markovian, and the memory effects arise in part from the coupling to the adjacent bulk fluids. Since the inner and outer fluids are incompressible the radial motion of the surface induces tangential flow in the inner and outer fluids, and if they have viscosity, this causes a tangential surface flow since the tangential component of velocity must be continuous. The tangential surface flow in turn induces a radial displacement of the interface. There is therefore an interesting hydrodynamic feedback, and the radial displacement at time t depends in a complex way on the radial displacement at an earlier time $t'<t$, especially if the fluids have inertia and do not respond instantaneously to the motion of the interface. When the inertia is large the spectral density of the fluctuations in the shape of the surface shows many resonance peaks each of which corresponds to a different Y_{lm} normal mode. We expect these oscillations primarily when the droplets are large. In this case though the results are not so interesting from the point of view of thermal fluctuations. However, the equilibrium fluctuations decay by the same dynamical processes which determine the response to some small external perturbation. Thus the spectral density $S(0,\omega)$ also describes the response of the droplet to an impulsive force if the static correlation function is replaced with the initial value of the radial displacement. The spectral density in this case summarizes the subsequent dynamical behavior.

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