

Vibrations of microemulsion droplets and vesicles with compressible surface layer

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The surface vibration spectra of liquid droplets with flexible interfaces, like microemulsion droplets or vesicles, are studied. As distinct from the previous theories, we proceed with exact solutions of hydrodynamic equations for incompressible bulk fluids inside and outside the droplet. The dynamical equations for the interface are those obtained by Lebedev and Muratov [JETP **68**, 1011 (1989)] but with the improved continuity equation for the surface layer. Within the Helfrich's concept of the interfacial elasticity and taking into account the compressibility of the surface layer, the exact equation is obtained for the frequencies of the droplet vibrations. The equation describes uniformly a broad region of frequencies from the lowest, almost purely relaxation modes, up to the modes determined mainly by the change of the area per molecule of the layer. The dispersion laws for some of the modes are obtained analytically in the limits of large and small penetration depths of the corresponding waves. Our analysis corrects the previous results concerning the relaxation modes, the capillary wave frequency and the frequency of the mode connected with the fluctuations of molecules in the surface layer. An additional mode of this kind is obtained for almost incompressible layers. In the region corresponding to large penetration depths, a couple of modes exist with frequencies depending both on the surface elasticity and compressibility. In the limit of infinite compressibility of the layer, the lower of the two modes disappears. The conditions necessary for the existence of all the modes were specified. Some representative numerical solutions of the obtained equation are presented as depending on various values of the model parameters including those for realistic microemulsion systems. [S1063-651X(98)06812-3]

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I. INTRODUCTION

In the past years, a voluminous literature has appeared dealing with the physical properties of microemulsion and vesicle systems [1,2]. Although there are many experimental probes for the static structure, the dynamics of these supramolecular systems is less well understood. To access the dynamics, in particular, thermal fluctuations of droplet microemulsions that provide a dynamical probe of the bending properties of surfactant interfaces, the highest resolution spectroscopy methods are needed. Among them, spin-echo neutron scattering, which only can access the fluctuations on a local scale, has been employed to study the shape fluctuations of microemulsion droplets [3]. However, so far only the lowest overdamped mode of the fluctuations has been investigated [4,5]. Based on the theory [6] and with comparison of the dynamic and static measurements, the experiments yielded the bending moduli of the surfactant layer. Together with the spontaneous curvature C_s , these moduli (the mean rigidity κ and Gaussian modulus $\bar{\kappa}$) are the main parameters within the context of Canham-Helfrich model of interfacial elasticity representing a very successful approach to understanding the behavior of microemulsions and vesicles [7,8]. However, there are other important parameters characterizing the surfactant film or vesicle membrane and their dynamics in the low-frequency region. So, it is known [9] that the adsorbed surfactant layer can essentially influence hydrodynamic properties of the droplet. The changes of the droplet shape are connected with the stretches and compressions of the layer and thus with the changes of the concentration of molecules in the layer. These changes are usually assumed to belong to the higher-frequency range of the fluctuations and

on the basis of a separation of energy scales [6] are not considered. However, the characteristics of real systems are quite different and a more general theory must take into account fluctuations of the molecules of the surface film with a change of the area per molecule, e.g., the fluctuations of the surfactant. A parameter controlling these concentration changes is essentially the surface elastic modulus B , connected with the surface compressibility $1/B$ ($B = -n_s \partial \alpha / \partial n_s > 0$, where n_s is the equilibrium number of molecules per unit area of the surface [10–12]), and α is the surface tension for a flat interface [13]. The latter constant is often zero or anomalously low for vesicles and microemulsions but for some droplets with large radii, $\gg 10^2$ Å (note that only droplets with radii larger or comparable with 100 Å can be considered within the phenomenology when the thickness of the layer is neglected), α can become significant in the expansion of the surface energy density,

$$\varepsilon_s = \alpha - \beta \left(\frac{1}{R_1} + \frac{1}{R_2} \right) + \frac{\kappa}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2 + \frac{\bar{\kappa}}{R_1 R_2}. \quad (1)$$

Here R_i are the principal local curvature radii, and $\beta = C_s \kappa$ is connected with the spontaneous curvature $C_s = 2/R_s$ (R_s is the spontaneous radius of curvature). The coefficients in Eq. (1) are widely used in the literature. We only note that $\alpha = \sigma + 2\kappa/R_s^2$ (σ is the microscopic interfacial tension), $\kappa > 0$, $2\kappa + \bar{\kappa} > 0$, and $\beta > 0$ for microemulsion droplets (if R_i are measured from the interior to exterior of the droplet). For vesicles, described by much of the same physics, $\beta = 0$ (for a free vesicle in conditions when the symmetry consideration is applicable). In this case there is no genuine surface tension α , but rather a constraint on the total area [2]. If the vesicle

membrane is incompressible, the total area is constant while the opposite is not true. Usually, the membrane is thought to be almost incompressible. In our description the area constraint is not used, the membrane is, in general, compressible, and the limit of incompressible membrane is obtained when $B \rightarrow \infty$.

The stability of the droplet with respect to small perturbations is ensured by the condition

$$\alpha_l = \alpha - 2\beta/R_0 + \kappa l(l+1)/R_0^2 > 0, \quad (2)$$

where the orbital number l appears after the expansion of the distance R from the center of mass of the droplet to its surface,

$$R(\vartheta, \varphi) - R_0 = u(\vartheta, \varphi) = R_0 \sum_{lm} a_{lm}(t) Y_{lm}(\vartheta, \varphi), \quad (3)$$

where R_0 is a radius of the sphere with the same volume as the droplet, and Y_{lm} are spherical harmonics. The index m runs from $-l$ to l , and $l=2, \dots, l_{\max}$, where l_{\max} is usually assumed $\sim R_0/d$, d being a typical molecular diameter [10]. The phenomenology of the microemulsion droplet formation can be found in [12,13]. The statistical mechanics of microemulsions (but neglecting the surface compressibility) in the case when a dilute droplet phase coexists with an excess phase of the dispersed fluid has been developed in [14]. In that work the contributions of the modes with large numbers l are suppressed more exactly and the renormalization of the parameters C_s , κ , and $\bar{\kappa}$ due to the shape fluctuations is calculated. In what follows we assume all the parameters α , κ , $\bar{\kappa}$, and R_s are already renormalized. Except for α their dependence on the surface density n_s can be neglected [12]. One more parameter that is usually neglected in the description of the microemulsion droplet or vesicle dynamics is the surface mass density of the interfacial layer, ρ_s . Again, this is not always justified, at least for higher numbers l since, as will be seen below, the quantities to be compared are ρ_s/R_0 , ρ_1/l , and $\rho_2/(l+1)$, where ρ_1 and ρ_2 are densities of the bulk fluids inside and outside the droplet, respectively.

The role of the discussed parameters is well seen considering the dispersion laws of the normal mode frequencies connected with the fluctuations of the droplet surface film. Such modes were studied in a number of papers. Usually, only the lowest relaxational mode is considered (e.g., [15,6,16]). A mode determined by the compressibility of the layer and thus reflecting the surfactant concentration fluctuations has been predicted in Ref. [11] for Langmuir films at plane water-air interfaces and later a similar mode has been calculated also for droplet microemulsions [12,17]. The character of this mode that has a very specific dispersion law is fully determined by the character of conservation of the molecules on the curved droplet surface. In [12,17,18] the continuity equation for the surfactants at the interface was used in the traditional form [9] which is, for two-dimensional liquid interfaces, only a special case as discussed in detail in [19] and [16].

The aim of this work is to calculate the spectra of the vibration modes connected with flexible interfaces of microemulsion and emulsion droplets or vesicles, with the attention given to the effects of the fluctuations of the molecules

on the surface. Due to this, we do not use the concept of the excess area conservation as in [15,6]. While [15,6] were devoted to the study of shape fluctuations of such vesicle droplets as are not spherical in equilibrium, we consider the fluctuations of spherical droplets coated with a compressible film. The most general approaches for our purposes were developed in [12] and [10]. Nevertheless, the former theory has to be improved as discussed above, and the latter one does not take into account the curvature energy that is essential for microemulsions.

We assume the bulk fluids to be incompressible since in the frequency range of interest the compressibility effects on the dispersion laws and dynamical structure factors of scattering are small [18,20]. We consider fluctuations of the droplets not influenced by other droplets in the solution. The model assumes impenetrable interfaces, that is, the flow of the molecules between the surface and the bulk phase is absent. These slow processes must be taken into account when the frequencies $\omega \rightarrow 0$ are considered [11]. Since we study the dynamics of an individual droplet, the thermodynamics of the system is of less importance; particularly, the results are applicable for both one- and two-phase microemulsions [13]. The thermodynamics becomes essential in calculations of the dynamical structure factors when the results must be averaged over the equilibrium distribution in the droplet radii. Within the discussed model, using exact solutions of the hydrodynamic equations, we obtain an exact equation for the surface vibration frequencies of the droplet. This equation, depending on the parameters for real systems, describes a broad range of frequencies and can be solved numerically. Here we obtain its analytical solutions for some interesting limiting cases. The character of the studied collective modes is determined by the relation between the droplet size R_0 , the penetration depth of the corresponding viscous wave $\delta \sim (\eta/\rho\omega)^{1/2}$, and the parameters of the surface energy. In this way we obtain dispersion relations for two almost purely relaxational (overdamped) modes, the capillary wave frequency, and two frequencies connected with the fluctuations of the molecules in the surface layer, one of them not discussed in the literature so far. The two overdamped modes depend both on the elasticity and compressibility of the surface and the lower of them disappears only when the compressibility modulus B is equal to 0. As opposite to the frequency of the capillary wave, the highest two modes are determined mainly by the surface compressibility. To our knowledge, our approach allowed us to give the conditions necessary for the existence of all these modes in more detail than had been possible thus far. We also solved the obtained characteristic equation for the surface vibration frequencies of the droplet numerically. Some representative numerical solutions are presented for the frequencies as depending on the orbital number l and various values of the model parameters including those for realistic microemulsion systems experimentally studied in the literature.

II. CHARACTERISTIC EQUATION FOR THE SURFACE VIBRATION FREQUENCIES

For further progress in the study of the dynamics of microemulsion and vesicle systems it is important to firmly establish the consequences of the existing theories. In par-

ticular, the interpretation of dynamic experiments requires detailed knowledge of the vibration spectra of fluctuating droplets. As discussed above, we proceed with the theory of Ref. 12 (later developed in [19,16]). The method of analysis comprises a solution of the linearized hydrodynamic (Navier-Stokes and continuity) equations for the fluid inside and outside the droplet, and the boundary conditions at the interface. The general method of their derivation was described in detail in [11] and applied for plane interfaces. In the case of the droplets with finite radii, the Helfrich curvature energy (1) must be taken into account [12]. The linearized variant of these equations (the velocities and deviations of the surface density of molecules from its equilibrium value are assumed to be small) is as follows:

$$\rho_s \frac{\partial v_r^s}{\partial t} - \frac{\Delta_{\perp} + 2}{R_0^2} \left[\alpha - \frac{2\beta}{R_0} - \frac{\kappa \Delta_{\perp}}{R_0^2} \right] u = p'_1 - p'_2 - 2 \frac{\partial}{\partial r} (\eta_1 v_{r1} - \eta_2 v_{r2}), \quad (4)$$

$$\rho_s \frac{\partial v_{\vartheta}^s}{\partial t} - \frac{1}{R_0} \frac{\partial \alpha}{\partial n_s} \frac{\partial n'_s}{\partial \vartheta} = \frac{1}{R_0} \frac{\partial}{\partial \vartheta} (\eta_2 v_{r2} - \eta_1 v_{r1}) + \left(\frac{\partial}{\partial r} - \frac{1}{R_0} \right) (\eta_2 v_{\vartheta 2} - \eta_1 v_{\vartheta 1}), \quad (5)$$

$$\rho_s \frac{\partial v_{\varphi}^s}{\partial t} - \frac{1}{R_0 \sin \vartheta} \frac{\partial \alpha}{\partial n_s} \frac{\partial n'_s}{\partial \varphi} = \frac{1}{R_0 \sin \vartheta} \frac{\partial}{\partial \varphi} (\eta_2 v_{r2} - \eta_1 v_{r1}) + \left(\frac{\partial}{\partial r} - \frac{1}{R_0} \right) (\eta_2 v_{\varphi 2} - \eta_1 v_{\varphi 1}). \quad (6)$$

In addition to the quantities already discussed, $\vec{v}^s(v_r^s, v_{\vartheta}^s, v_{\varphi}^s)$ is the velocity of the interface in spherical coordinates, Δ_{\perp} is the angle part of the operator $r^2 \Delta$ in spherical coordinates, \vec{v} is the velocity of bulk fluids, p' is the variable part of the pressure p , η is the viscosity, and the indices 1 and 2 refer to the interior and exterior of the droplet. The deviation of the number density of (e.g., surfactant) molecules of the surface from its equilibrium value is n'_s that can be expanded in spherical harmonics as

$$n'_s = n_s \sum_{l>0, m} v_{lm} Y_{lm}. \quad (7)$$

After differentiation, all the variables are related to $r=R_0$. In addition, we have $\vec{v}_1 = \vec{v}_2 = \vec{v}^s$ at $r=R_0$, $\partial u / \partial t = v_r^s$, and the continuity equation differs from that used in [9,12,17] by a term proportional to the radial velocity of the surface,

$$\frac{\partial n'_s}{\partial t} + \frac{n_s}{R_0} \left(\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} v_{\vartheta} \sin \vartheta + \frac{1}{\sin \vartheta} \frac{\partial v_{\varphi}^s}{\partial \varphi} + 2 v_r^s \right) = 0. \quad (8)$$

Together with the well-known hydrodynamic equations for incompressible bulk fluids [9], Eqs. (3)–(8) represent a full set for the determination of the frequency spectrum of small vibrations of the droplet. The velocity can be searched for in the form (since only poloidal solutions of the problem exist)

$$\vec{v} = \sum_{lm} \left(\vec{e}_r \frac{l(l+1)}{r^2} + \vec{e}_{\vartheta} \frac{1}{r} \frac{\partial^2}{\partial r \partial \vartheta} + \vec{e}_{\varphi} \frac{1}{r \sin \vartheta} \frac{\partial^2}{\partial r \partial \varphi} \right) u_{lm}(r, t) Y_{lm}(\vartheta, \varphi). \quad (9)$$

We rewrite all the equations for the Fourier components $\sim \exp(-i\omega t)$ of time-dependent quantities. It is suitable to express the exact solutions of the Navier-Stokes equations for both regions in terms of the spherical Bessel functions [21] $j_l(z_1)$ and $h_l^{(1)}(z_2)$,

$$u_{lm}^{(1)}(r, 0) = C_{lm}^{(1)} r j_l(z_1) - i \beta_l^{(1)} \frac{r^{l+1}}{\rho_1 \omega}, \quad 0 \leq r \leq R_0; \\ u_{lm}^{(2)}(r, 0) = C_{lm}^{(2)} r h_l^{(1)}(z_2) + i \beta_l^{(2)} \frac{r^{-l}}{\rho_2 \omega}, \\ r \geq R_0, \quad z_j = r(i\omega \rho_j / \eta_j)^{1/2}. \quad (10)$$

Here C and β are constants of integration, and $\beta = B(t=0)$ comes from the expansion of the pressure:

$$p'_1 = \sum_{lm} B_l^{(1)} (l+1) r^l Y_{lm}, \quad p'_2 = \sum_{lm} B_l^{(2)} l r^{-l-1} Y_{lm}. \quad (11)$$

The solution (10) is chosen to be finite as $r \rightarrow 0$. To exclude also the exponential divergence at $r \rightarrow \infty$, one must use $h_l^{(1)}$ if $\text{Re}[i(\omega)^{1/2}] < 0$ (when the second of the possible roots is taken, $h_l^{(1)}$ has to be replaced by $h_l^{(2)}$). Substituting Eq. (10) in equations containing the velocities \vec{v} , and combining them, we obtain the following exact equation with respect to ω :

$$\left\{ \frac{\rho_1}{l} + \frac{1}{2l+1} \frac{z_1 j_{l+1}}{j_l} \left[\frac{A_l}{\omega^2} - \rho_1 - 2(l+2)P \right] \right\} \\ \times \left\{ \frac{1}{2l+1} \frac{z_2 h_{l-1}^{(1)}}{h_l^{(1)}} \left[\frac{n_l(l-1)}{\omega^2} + \frac{\rho_s(l+1)}{R_0} - 2(l^2-1)P \right] - \rho_2 \right\} \\ = \left\{ \frac{1}{2l+1} \frac{z_2 h_{l-1}^{(1)}}{h_l^{(1)}} \left[\frac{A_l}{\omega^2} - \rho_1 + 2(l-1)P \right] + \frac{\rho_2}{l+1} \right\} \\ \times \left\{ \rho_1 - \frac{1}{2l+1} \frac{z_1 j_{l+1}}{j_l} \left[\frac{n_l(l+2)}{\omega^2} + \frac{\rho_s l}{R_0} + 2l(l+2)P \right] \right\}, \quad (12)$$

$$A_l = \alpha_l(l-1)(l+2)R_0^{-3}, \quad n_l = n_s \frac{\partial \alpha}{\partial n_s} l(l+1)R_0^{-3},$$

$$\rho_l = \frac{\rho_1}{l} + \frac{\rho_2}{l+1} + \frac{\rho_s}{R_0}, \quad P = \frac{\rho_1}{z_1^2} - \frac{\rho_2}{z_2^2}, \quad (13)$$

and z_j hereafter are taken at $r=R_0$. Now we can prove that the mode $l=1$ does not appear in the characteristic equation (12). This mode corresponds to the translational motion of the droplet without its deformation. Then in the system connected with the droplet, with the origin in its center of mass, $u=0$ [Eq. (3)]. With this condition our system of equations is self-consistent only in the case when also $\nu_{1m}=0$. For $l=1$ there is no motion in the surface layer and the expansions (7) (as distinct from [12] and [10]) and (3) both begin with $l=2$. Finally, it has been discussed in [11,12] that in the region of very low frequencies the exchange of the molecules between the layer and the surroundings must be taken into account. This would change the continuity equation (8), and correspondingly Eq. (12) and its solutions. Together with other authors we neglect this exchange: the validity of such an approximation (impermeability of the surface film) has been proven in [16] for the lowest-frequency modes (the higher the modes the better justified this approximation is).

III. ANALYTICAL SOLUTIONS FOR THE NORMAL MODE FREQUENCIES

Equation (12) gives wide possibilities for the analysis of the surface spectra. Below we consider a few examples that can be treated analytically. The most often studied case in the literature corresponds to large penetration depths of the shear waves inside and outside the droplet: $\delta \gg R_0$, which means small $|z_i|$. Using the asymptotic expansions for the Bessel functions [21] for $|z_i| \rightarrow 0$, we obtain a quadratic equation with respect to ω , which is truly neglecting the fourth-order terms in z_i ,

$$1 - \frac{\omega_{\text{rel}}}{\omega} - i\omega \Sigma_l \approx 0,$$

$$\Sigma_l = \frac{R_0^2}{(2l-1)(2l+3)} \left\{ 2\rho + \frac{\rho_s}{R_0} \frac{4l^2 + 4l + 3}{2l+1} \right\}. \quad (14)$$

The expression for Σ_l , which is rather complicated in the general case, is shown here in the case of vesicles. From two solutions of Eq. (14) the solution consistent with the used approximation is a purely relaxation mode $\omega \approx \omega_{\text{rel}}$ with small corrections of the order $\sim z^2$. Here

$$\omega_{\text{rel}} \approx -\frac{i}{2l+1} \frac{R_0^2}{p_l q_l} \{ A_l l(l+1)(p_l + q_l) - n_l [(l^2-1)p_l + l(l+2)q_l] \}, \quad (15)$$

$$p_l = \eta_1(2l^2 + 4l + 3) + 2\eta_2 l(l+2),$$

$$q_l = 2\eta_1(l^2 - 1) + \eta_2(2l^2 + 1). \quad (16)$$

Now, let us take into account the fourth-order terms of small z_i in the asymptotic expansion of the Bessel functions in Eq. (12). Then the characteristic equation (12) simplifies to

$$1 - \frac{\omega_{\text{rel}}}{\omega} - \frac{\Xi_l}{\omega^2} \approx 0, \quad \Xi_l = -\frac{A_l n_l R_0^2 l(l+1)}{\eta^2 (2l-1)(2l+1)^2 (2l+3)}. \quad (17)$$

Here also a complicated expression for Ξ_l is given in the case of vesicles. The solutions of Eq. (17) depend on the relation $\xi = 4\Xi_l/|\omega_{\text{rel}}|^2$ that can be smaller than or of the order of unity. The simplest case, which includes physically interesting limits $B = -n_s \partial \alpha / \partial n_s \rightarrow 0$ and $B \rightarrow \infty$, corresponds to $\xi \ll 1$ when we have again one of the solutions $\omega \approx \omega_{\text{rel}}$, and the new frequency is $\omega \approx \varpi_{\text{rel}}$,

$$\varpi_{\text{rel}} \approx i \frac{A_l n_l R_0^4}{p_l q_l |\omega_{\text{rel}}|} l(l+1), \quad (18)$$

$|\varpi_{\text{rel}}| \ll |\omega_{\text{rel}}|$. This mode exists only for nonzero compressibility modulus B . In the limits of small and large B , the analytical expressions for ϖ_{rel} are as follows:

$$|\varpi_{\text{rel}}| \approx \frac{-n_l R_0^2 (2l+1)}{p_l + q_l}, \quad B \rightarrow 0,$$

$$|\varpi_{\text{rel}}| \approx \frac{A_l R_0^2 l(l+1)(2l+1)}{(l^2-1)p_l + l(l+2)q_l}, \quad B \rightarrow \infty. \quad (18a)$$

When $B \rightarrow 0$, Eq. (15) is in agreement with our calculations [17] and the results found in the theories [16,22] (if the capillary or generalized Laplace condition [13] $p_1 - p_2 = 2\alpha/R_0 - 2\beta/R_0^2$ is taken into account), that neglect from the beginning the inertia terms in the hydrodynamic equations. On the other hand, ω_{rel} differs from the frequency found by Lebedev and Muratov [12,23]. It is to be noted that in a number of previous less general studies, e.g., [15,6,22], the droplet dynamics is calculated using equations for a sphere neglecting the fluctuations of molecules in the surface layer, i.e., the model equations do not contain terms $\sim B$. This means that if we formally put $B=0$ in Eq. (15), our expression for ω_{rel} (since in this case ϖ_{rel} does not exist) should correspond to frequencies found in these works. While the frequency found in [22] (see also references there) for microemulsions is exactly Eq. (16) with $B=0$, the frequency obtained in the often cited work [6] is different. To compare the latter result by Milner and Safran for vesicles with ω_{rel} , we have to set $\eta_1 = \eta_2 = \eta$ and formally identify their Lagrange multiplier $-\gamma$ with our σ (microscopic interfacial tension). However, their frequency still differs from ω_{rel} by the factor $(4l^2 + 4l - 3)/(4l^2 + 4l - 2)$. Moreover, the concept of the constant mean excess area Δ [6] leads in the limit $\Delta \rightarrow 0$ (corresponding to spherical droplets in equilibrium) to $\omega \rightarrow \infty$. The same can be related to the result by Schneider, Jenkins, and Webb [15], who have $C_s = 0$. As to the lower frequency ϖ_{rel} , we did not find its analytical expression (18) in the literature. The second of the limits (18a), $B \rightarrow \infty$ (incompressible layer [10,16]), corresponds to the result given in [23] but differs from the frequencies obtained in [16]. The result [6] is thought to describe incompressible

vesicle membranes. Then it should coincide with Eq. (18a) for $B \rightarrow \infty$. However, it differs from ω_{rel} by the factor $(2l^2 + 2l - 1)/(2l^2 + 2l - 3)$.

When $B \neq 0$, fluctuations of the molecules in the surface layer can significantly influence both the ω_{rel} and ω_{rel} and could be, in principle, determined from dynamical experiments like inelastic scattering of neutrons. The neutron scattering experiments [3–5] on microemulsions were interpreted so far within the model [6] with an incompressible surfactant layer and the curvature elasticity as the restoring force. However, these studies yielded values of the bending rigidity κ higher than measured with indirect macroscopical or optical methods [24]. We thus suppose that it would be interesting to reconsider the interpretation of the neutron scattering experiments on microemulsions [3–5] with the account for surface compressibility.

Now, let the penetration depth of the shear waves outside and inside the droplet be small. In the main approximation for $|z_i| \rightarrow \infty$ we have from Eq. (12)

$$(A_l - \rho_l \omega^2)(n_l + \rho_s \omega^2 / R_0) \approx 0. \quad (19)$$

Thus one of the characteristic frequencies ω_{cap} corresponds to the capillary wave. It is to be expected that the other frequency ω_ρ is much higher since usually we have $\rho_s / R_0 \ll \rho_l$ (and $n_l \gg A_l$). The equation that describes the region of frequencies from the capillary frequencies to ω_ρ is (corrections to it are of the order of z^{-4}):

$$\begin{aligned} & \rho_l \left(\frac{\omega_{\text{cap}}^2}{\omega^2} - 1 \right) \left\{ \frac{\rho_s}{R_0} \left(1 - \frac{\omega_\rho^2}{\omega^2} \right) \right. \\ & \times \left(-1 + i \frac{l+1}{z_1} + \frac{il}{z_2} \right) - \frac{i\rho_1}{z_1} - \frac{i\rho_2}{z_2} \left. \right\} \\ & + \frac{i\rho_1 \rho_s}{l z_1 R_0} \left[l+1 - (l-1) \frac{\omega_\rho^2}{\omega^2} \right] \\ & + \frac{i\rho_2 \rho_s}{(l+1) z_2 R_0} \left[l - (l+2) \frac{\omega_\rho^2}{\omega^2} \right] \approx 0. \quad (20) \end{aligned}$$

The solution describing weakly damped capillary waves does not depend on the surface compressibility,

$$\begin{aligned} \omega \approx \omega_{\text{cap}} \left[1 - \frac{1+i}{2R_0 \rho_l \sqrt{2} \omega_{\text{cap}}} \left(\frac{l-1}{l} \sqrt{\rho_1 \eta_1} + \frac{l+2}{l+1} \sqrt{\rho_2 \eta_2} \right) \right], \\ \omega_{\text{cap}}^2 = \frac{A_l}{\rho_l}. \quad (21) \end{aligned}$$

This solution is a generalization of the well-known classical result [25].

The region of frequencies much higher than ω_{cap} is described by the equation

$$\delta_1 \frac{R_0 \rho_l}{\rho_s} \left(\frac{i\omega_\rho}{\omega} \right)^{1/2} + \left(\frac{\omega_\rho^2}{\omega^2} - 1 \right) \left[\left(\frac{i\omega_\rho}{\omega} \right)^{1/2} \delta_2 - 1 \right] \approx 0, \quad (22)$$

where the small quantities δ_1 and δ_2 (of order $\sim 1/z$) are

$$\begin{aligned} \delta_1 = \frac{1}{R_0 \rho_l \sqrt{\omega_\rho}} \left\{ \sqrt{\rho_1 \eta_1} \left(1 + \frac{2\rho_s}{l R_0 \rho_l} \right) \right. \\ \left. + \sqrt{\rho_2 \eta_2} \left(1 - \frac{2\rho_s}{(l+1) R_0 \rho_l} \right) \right\}, \quad (23) \end{aligned}$$

$$\begin{aligned} \delta_2 = \frac{1}{R_0 \rho_l \sqrt{\omega_\rho}} \left\{ \sqrt{\frac{\eta_1}{\rho_1}} \left[(l+1) \rho_l - \rho_1 \frac{l-1}{l} \right] \right. \\ \left. + \sqrt{\frac{\eta_2}{\rho_2}} \left[l \rho_l - \rho_2 \frac{l+2}{l+1} \right] \right\}. \end{aligned}$$

When not only δ_1 is small but also $\delta_1 R_0 \rho_l / \rho_s \ll 1$, the solution of Eq. (22) is

$$\omega \approx \omega_\rho \left(1 - \frac{1+i}{2\sqrt{2}} \delta_1 \frac{R_0 \rho_l}{\rho_s} \right), \quad \omega_\rho = \left(-\frac{n_l R_0}{\rho_s} \right)^{1/2}. \quad (24)$$

This frequency did not appear in previous papers, particularly in [12], where the surface density ρ_s was neglected. There has been found another surface mode in [12], connected with the fluctuations of molecules in the surface. A similar mode can be obtained here also from Eq. (22) as a special case when the fifth-order equation is reduced assuming small $x = |\omega/\omega_\rho| \ll 1$, $\delta_2 \ll x^{1/2}$, and $\delta_2 \ll x^2 \delta_1 R_0 \rho_l / \rho_s$. In contrast to the previous case, the quantity $\delta_1 R_0 \rho_l / \rho_s$ is much larger than unity. Then the solution is $\omega \approx \omega_n = \omega_\rho (-i)^{1/3} (\delta_1 R_0 \rho_l / \rho_s)^{-2/3}$, that is,

$$\begin{aligned} \omega_n \approx \frac{1}{2} (\pm \sqrt{3} - i) \left\{ \frac{1}{-n_l R_0} \left[\sqrt{\rho_1 \eta_1} \left(1 + \frac{2\rho_s}{l R_0 \rho_l} \right) \right. \right. \\ \left. \left. + \sqrt{\rho_2 \eta_2} \left(1 - \frac{2\rho_s}{(l+1) R_0 \rho_l} \right) \right] \right\}^{-2/3}. \quad (25) \end{aligned}$$

Finally, there are no solutions for the frequencies in the region much higher than ω_ρ .

IV. SIMPLE ESTIMATIONS, NUMERICAL SOLUTIONS, AND DISCUSSION

The variety of the model parameters for real systems is broad, so we shall only briefly summarize the conditions at which the calculated modes could exist. The first assumption to be taken into account is that the droplet radii must be large enough, at least R_0 must be larger or of the order of 100 Å. For simplicity, in the estimations we assume that the parameters of the bulk fluids, η and ρ , are close to those for water, which is true exactly for vesicles and approximately for many systems of interest.

First, consider the mode ω_{rel} [Eq. (15)] that is most frequently studied in the literature. It was found here using the asymptotics $|z| \rightarrow 0$. In fact, the obtained quadratic equation (14) (as seen from the asymptotic expansion of the Bessel functions [21]) serves as a good approximation to Eq. (12) when $|z_2| \ll \sqrt{3}$ and $|z_1|$ can be less or even of the order of unity, $|z_1| \ll 8$ (for all values of l including $l=2$), or $|z_i| \ll 2l$ (if only large $l \gg 2$ are considered). In addition, to obtain ω_{rel} we require $4|\omega_{\text{rel}} \Sigma_l| \ll 1$, where $\Sigma_l \sim R_0^2 \rho / 10 \eta$ ($l=2$) and $\Sigma_l \sim R_0^2 (\rho/l + \rho_s/R_0) / 2l \eta$ ($l \gg 2$). Note that for

largest possible l the term ρ_s/R_0 is not negligible in comparison with ρ/l and should be taken into account. Usually, for microemulsion or vesicle systems, α is very small, $<10^{-4} \text{ J m}^{-2}$. But when it dominates in α_l from Eq. (2), and the modulus B is negligible, the above requirements are satisfied if $\alpha R_0(\rho/l + \rho_s/R_0)/2\eta^2 \ll 1$, for all values l . For realistic values of α ($\sim 10^{-2} \text{ SI}$ or smaller) and ρ_s , this condition holds for radii up to $\sim 5 \cdot 10^2 \text{ \AA}$ ($l=2,3,\dots$). When l is large, we need $R_0 < l(2 \times 10^{-5} - \rho_s)10^{-3} \text{ m}$ which is always satisfied for highest numbers l . Other possible cases can be analyzed analogously. So, when the bending terms dominate ω_{rel} , the approximation requires $\kappa\rho/R_0\eta^2 \ll 1$ ($l=2$) or $\kappa l^2(\rho/l + \rho_s/R_0)/4R_0\eta^2 \ll 1$ (large l) that is well satisfied for known systems. The frequency then scales with $1/R_0^3$ [3–6]. When the compressibility term $\sim B$ dominates in Eq. (15), the estimation for ω_{rel} is $\sim Bl/4R_0\eta$, for both $l=2$ and $l \gg 2$. In the literature [12], B is often assumed to be of the order of the usual surface tensions $\sim 10^{-2} \text{ J m}^{-2}$, so the conditions for the existence of such a mode are similar to the above case when the surface tension dominates ω_{rel} . The mode can exist for droplets with radii up to 500 \AA or proportionally larger with decreasing $B < 10^{-2} \text{ J m}^{-2}$. For high numbers l the radius can be approximately $l/2$ times larger, except for the case when ρ_s is unusually large, larger than $10^{-5} \text{ kg m}^{-2}$. Thus we see that the discussed mode in the case when the surfactants show appreciable changes in the area per molecule can exist in microemulsions. However, it cannot be the frequency of the mode observed in neutron scattering experiments [3–5] where the relevant frequencies scaled with $1/R_0^3$. In any case, there is a wide region of the values of B when the surface compressibility significantly influences the relaxation mode. This fact should be taken into account in the interpretations of dynamic experiments. The scaling $1/R_0^3$ can be shown also by the frequency ϖ_{rel} from Eq. (18). This is possible in the case when the higher relaxation frequency ω_{rel} is determined mainly by the compressibility and can be estimated as $\omega_{\text{rel}}(B \rightarrow \infty) \sim Bl/4R_0\eta \sim \varpi_{\text{rel}}(B \rightarrow 0)$ and $A_l \sim R_0^{-5}$ [Eqs. (13) and (2)] is given by the curvature elasticity. In this case ϖ_{rel} practically does not depend on the compressibility modulus B and its estimation is $|\varpi_{\text{rel}}| \sim (\alpha_l/4R_0\eta)l$, which coincides with the expression for ω_{rel} in the opposite case when $B=0$. If the conditions for the existence of the frequency ω_{rel} are satisfied, the quadratic equation (17) also holds. Its solutions are governed by the parameter ξ , small in both the considered cases of small and large B , when the above estimations are valid. For intermediate values of B ($-n_l$ comparable to A_l , so that ξ becomes comparable to 1), the solutions $\omega \approx (\omega_{\text{rel}}/2)[1 \pm (1 - \xi)]^{1/2}$ can differ quite significantly from ω_{rel} and ϖ_{rel} .

The above discussed results are demonstrated by Figs. 1 and 2. Figure 1 shows numerical solutions of the characteristic equation (12) with parameters corresponding to water-in-oil (decane) microemulsion systems studied in Ref. [5]: at the temperature $20 \text{ }^\circ\text{C}$ the bulk densities and viscosities are $\eta_1 = 10^{-3} \text{ Pa s}$, $\eta_2 = 0.648 \times 10^{-3} \text{ Pa s}$, $\rho_1 = 10^3 \text{ kg m}^{-3}$, $\rho_2 = 0.73 \times 10^3 \text{ kg m}^{-3}$, and the equilibrium radius is $R_0 = 100 \text{ \AA}$. The spin echo experiments [5] yielded the following bending moduli for the AOT sodium di-2-ethylhexyl sulfosuccinate surfactant layer: $\kappa = 3.8k_B T$, and $\bar{\kappa}$ close to -1.9κ . The remaining parameters R_s and α (the spontaneous

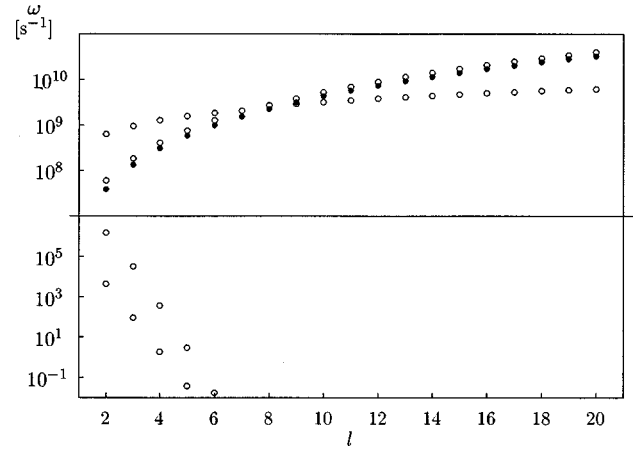


FIG. 1. Numerical solutions of Eq. (12) for the frequency $\omega = \text{Re } \omega + i \text{Im } \omega$ depending on the orbital number l . The system parameters correspond to water-in-oil microemulsion described in the text: $\eta_1 = 10^{-3} \text{ Pa s}$, $\eta_2 = 0.648 \times 10^{-3} \text{ Pa s}$, $\rho_1 = 10^3 \text{ kg m}^{-3}$, $\rho_2 = 0.73 \times 10^3 \text{ kg m}^{-3}$, $\rho_s = 0$, $R_0 = 100 \text{ \AA}$, $\kappa = 3.8k_B T$, $\bar{\kappa} = -1.9\kappa$ [5], and the quantities R_s and α are calculated for the case of two-phase coexistence: $R_s = 2\kappa R_0/(2\kappa + \bar{\kappa})$ and $\alpha = (2\kappa + \bar{\kappa})/R_0^2$. The lower and upper parts of the figure show $|\text{Re } \omega|$ and $|\text{Im } \omega|$, respectively. When the surface compressibility modulus $B = 0$ (dark circles), $|\text{Im } \omega|$ is indistinguishable from the analytical solution ω_{rel} (Eq. 15). For $B = 10^{-2} \text{ J m}^{-2}$ (open circles), the higher frequency is well described by the expression for ω_{rel} , and the lower one corresponds to ϖ_{rel} from Eq. (18).

radius of curvature and the surface tension coefficient) are calculated for the case of two-phase coexistence [13], $R_s = 2\kappa R_0/(2\kappa + \bar{\kappa})$ and $\alpha = (2\kappa + \bar{\kappa})/R_0^2$. The surface density ρ_s did not affect the calculations and can be neglected. For these parameters the used approximation (large penetration depths of the waves) is well satisfied and leads to almost purely relaxational modes. Figure 1 gives the dependence of the real and imaginary parts of the frequency ω on the orbital

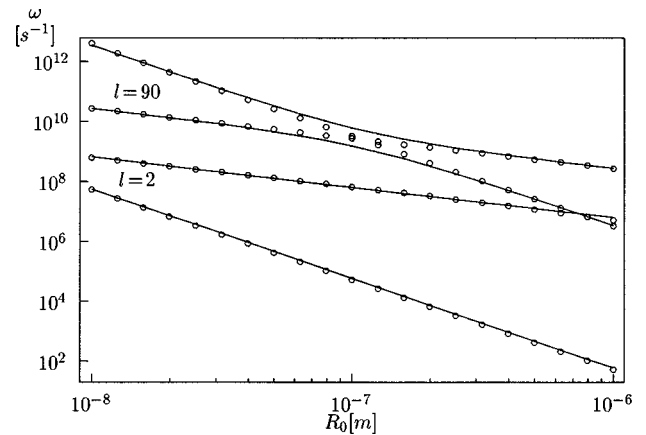


FIG. 2. The dependence of $|\text{Im } \omega|$ on the droplet radius for $B = 0.01 \text{ J m}^{-2}$ and two values of l ($l=2$ and $l=90$). Numerical (open circles) solutions to Eq. (12) and analytical (solid line) solutions ω_{rel} and ϖ_{rel} (Eqs. 15 and 18) are shown, ϖ_{rel} being the lower frequency. The used parameters correspond to oil-in-water microemulsion system [26]: $\eta_1 = 0.648 \times 10^{-3} \text{ Pa s}$, $\eta_2 = 10^{-3} \text{ Pa s}$, $\rho_1 = 0.73 \times 10^3 \text{ kg m}^{-3}$, $\rho_2 = 10^3 \text{ kg m}^{-3}$, and $\rho_s = 10^{-6} \text{ kg m}^{-2}$. The Gaussian modulus $\bar{\kappa} = -1.75\kappa$, $2\kappa + \bar{\kappa} = 0.9k_B T$ [27], and the parameters R_s and α are determined as in Fig. 1.

number l . In the case when the compressibility modulus $B = 0$, the absolute value of the imaginary part of the frequency cannot be distinguished on the graphs from the analytical solution ω_{rel} given by Eq. (15) (the difference from the analytical solution [6] used in the interpretation of the experimental data [4,5] is, however, appreciable and grows with the number l when the conditions for the existence of the mode become less well satisfied). In agreement with our analytical analysis, when $B \neq 0$ (we used the value $B = 10^{-2} \text{ J m}^{-2}$), numerical calculations possess two solutions: one of them well described by the expression for ω_{rel} and the solution with lower values of $|\text{Im } \omega|$ corresponds to ϖ_{rel} from Eq. (18). The real part of the calculated frequency is relatively very small and sharply decreases to zero with increasing l . It could be, however, observable for the lowest l (the maximum of $|\text{Re } \omega| \approx 1.6 \times 10^6 \text{ s}^{-1}$, when $B = 10^{-2} \text{ J m}^{-2}$ and $l=2$) in dynamic experiments by a frequency shift from the central peak of the scattering. Figure 2 shows the dependence of $|\text{Im } \omega|$ on the droplet radius for $B = 0.01 \text{ J m}^{-2}$ and two values of l ($l=2$ and large $l=90$). The parameters used here are the same as in Ref. [26] for the oil (decane)-in-water surfactant (C_8E_3) system: $\eta_1 = 0.648 \times 10^{-3} \text{ Pa s}$, $\eta_2 = 10^{-3} \text{ Pa s}$, $\rho_1 = 0.73 \times 10^3 \text{ kg m}^{-3}$, $\rho_2 = 10^3 \text{ kg m}^{-3}$, and $2\kappa + \bar{\kappa} = 0.9k_B T$. Now the Gaussian modulus $\bar{\kappa}$ is chosen as in [27], $\bar{\kappa} = -1.75\kappa$, and as above, the parameters R_s and α are determined for the case of two-phase coexistence [26]. The surface layer thickness 11 \AA determined in [26] allowed us to estimate the surface density ρ_s , which cannot be neglected for large l , by the value $10^{-6} \text{ kg m}^{-2}$. In agreement with our estimations for large B , for $l=2$ (and $l=90$ but large R_0) the frequency ω_{rel} scales with $1/R_0$ and $\varpi_{\text{rel}} \sim 1/R_0^3$. For large l and small radii the bending term is dominant in ω_{rel} so it scales $\sim 1/R_0^3$, and $\varpi_{\text{rel}} \sim 1/R_0$. Our analytical results describe very well the numerical solutions of Eq. (12), especially in the case $l=2$. The only exception is a small region around the radius 10^{-7} m when the parameter $\xi = 4|\varpi_{\text{rel}}||\omega_{\text{rel}}|^{-1}$ [introduced after Eq. (17)] becomes for large l very close to unity and the determinant of the quadratic equation (17) close to zero. In such a case the small terms which were neglected in obtaining Eq. (17) should be taken into account to obtain a correspondence with the exact equation (12).

Now consider the frequencies calculated with the assumption $|z| \rightarrow \infty$ (it is seen from the asymptotics of the Bessel functions that the approximation works well if we have $|z| \gg l+1$). The frequency ω_{cap} does not depend on B so we have to distinguish the two following cases. For the first one, when the bending terms dominate in α_l , the used asymptotics cannot serve as a good approximation for known systems since it requires unrealistic (too large) bending moduli. When α is large and dominates α_l , the approximation can be good for very large droplets and works better for small l according to the inequalities $\alpha R_0 \gg 10^{-8} \text{ J/m}$ ($l=2$), or $\alpha R_0/l \gg 2 \times 10^{-9} \text{ J/m}$ ($l \gg 2$). The conditions at which the surface frequency ω_ρ exists [Eq. (24)], can be satisfied for large enough values of the modulus B . It is seen from two inequalities that for both $l=2$ and $l \gg 2$ read (all quantities are in SI units) $5 \times 10^{-4} (10/B\rho_s)^{1/4} \ll (\rho_s l/R_0)^{-1/2} \ll (B\rho_s/10)^{1/4}$. Thus for surface densities ρ_s in the range $10^{-7} - 10^{-6} \text{ kg m}^{-2}$ the modulus B must be much larger than

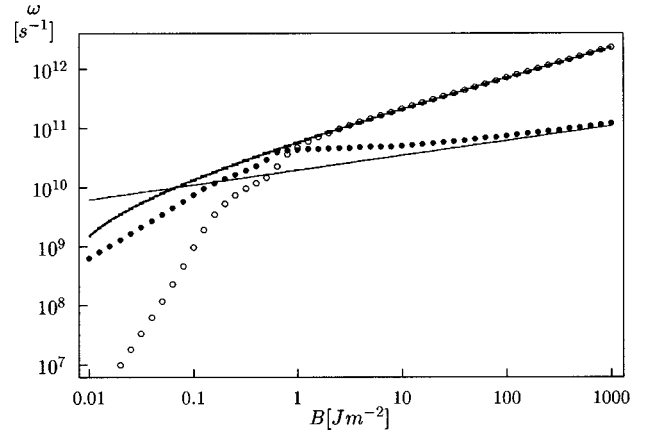


FIG. 3. Absolute values of imaginary (dark circles) and real parts (open circles) of the frequencies calculated numerically from Eq. (12) and analytically according to Eq. (24) for $\omega \approx \omega_\rho$ (the solid line is for $|\text{Im } \omega|$ and the thicker line for $|\text{Re } \omega|$) as depending on the compressibility modulus B . Other parameters are as in Fig. 1, except for $\rho_s = 10^{-5} \text{ kg m}^{-2}$.

usual surface tensions. A good approximation for the calculation of the frequency ω_n [Eq. (25)] can be reached for droplets with large radii R_0 and/or small surface density ρ_s . Depending on the system parameters, the following inequalities have to be satisfied: $BR_0 \gg 10^{-8}$ ($l=2$) or $BR_0 \gg 2l \times 10^{-9} \text{ J m}^{-1}$ (large l), and $10(BR_0/l)^{1/2} \gg (10B\rho_s)^{3/4}$ or $3 \times 10^3 (BR_0/l)^{1/2} \gg 2(10B\rho_s)^{1/4}$ (the last two conditions applicable for both $l=2$ and $l \gg 2$). It is then seen that for values of B close to those of the usual surface tension [10,12] the required radius is very large, much larger than 10^4 \AA ; in this case the mode cannot exist in microemulsions. Figures 3 and 4 show the dependence of the solutions to Eq. (12) on the compressibility modulus B . To present the analytical solutions for the frequencies ω_n and ω_ρ , the orbital number l is chosen to be small, because in the opposite case it is difficult to satisfy the conditions $|z_{1,2}| \gg l+1$. Figure 3 shows the absolute values of imaginary and real parts of the frequencies calculated numerically and according to Eq. (24). The drop-

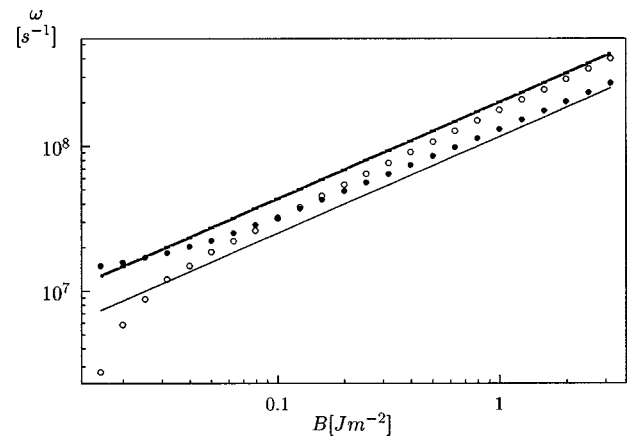


FIG. 4. Absolute values of imaginary (dark circles) and real parts (open circles) of the frequencies calculated numerically from Eq. (12) and analytically according to Eq. (25) for $\omega \approx \omega_n$ (the solid line is for $|\text{Im } \omega|$ and the thicker line for $|\text{Re } \omega|$), as depending on the compressibility modulus B . Other parameters are as in Fig. 2, but with $\rho_s = 10^{-7} \text{ kg m}^{-2}$ and $R_0 = 10^{-6} \text{ m}$.

lets are small, $R_0 = 10^{-8}$ m, the surface density rather high, $\rho_s = 10^{-5}$ kg m $^{-2}$, and the modulus B takes large values up to 10^3 J m $^{-2}$. Other parameters are the same as for water-in-oil droplets illustrated by Fig. 1. As already discussed, in the literature the surface layer is usually considered as incompressible, which corresponds to infinite B . In agreement with the estimations, the picture shows that as B increases to very large values, the frequency becomes well described by our solution ω_ρ , not found in previous works on the droplet dynamics. The data in Fig. 4 are calculated for oil-in-water droplets with much larger radii, $R_0 = 10^{-6}$ m, small $\rho_s = 10^{-7}$ kg m $^{-2}$, and B changing from 0.01 to a few J m $^{-2}$. Other parameters are as in Fig. 2. For such systems, in the region of larger B , the solution of Eq. (12) shows the tendency to become close to the frequency ω_n from Eq. (25), which corresponds to the mode predicted in Ref. [12] as a mode connected with the redistribution of the surfactant molecules on the droplet surface.

In conclusion, we have calculated the surface vibration spectra of liquid droplets within the hydrodynamic phenomenology more exactly than it has been done so far. First of all, the inclusion of the compressibility and mass density of the surface layer makes the calculated frequency spectra richer. We have considered the low-frequency region from almost purely the relaxation modes to the modes connected mainly with the change of the surface area per molecule in the layer and described this region uniformly by one equation. This equation was solved numerically and some limiting cases were treated analytically. It was found that for finite compressibility of the layer, in conditions when the

penetration depths of the waves are large, two relaxational modes simultaneously exist instead of one overdamped mode described in the literature. We have also predicted a mode that can exist in the opposite situation of small penetration depth, if the layer is almost incompressible. In other cases our analytical solutions correct the results already known from the literature and the approach allowed us to specify the conditions of applicability of the solutions more precisely. Except for the capillary wave mode, the compressibility of the layer significantly affects the surface modes. We believe that some of the predicted features of the surface vibration spectra (such as the existence of the couple of overdamped but not purely relaxational modes) could stimulate more attention to this influence in further investigations, especially in the dynamic scattering experiments capable of possessing some of the quantitative characteristics of the liquid drop systems such as microemulsion, emulsion, and vesicle systems, which have long been of great interest in physics and applications.

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