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Thermal hydrodynamic fluctuations in microemulsions

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Collective thermal excitations in microemulsions are studied within the hydrodynamic correlation theory. Spherical microemulsion droplets (micelles) are coated with a thin film and immersed in a fluid with different properties. The compressibility and viscosity of the bulk fluids are taken into account as well as the curvature energy and the redistribution of the surfactant concentration on the micelle surface. The method of analysis comprises a solution of the linearized dynamic (hydrodynamic and boundary) equations with random (bulk and surface) sources and application of the fluctuation-dissipation theorem. The spectral densities of correlation functions are obtained for both the hydrodynamic fluctuations in the bulk fluids and the shape fluctuations of micelles. The dynamic structure factor of the model microemulsion is calculated.

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I. INTRODUCTION

In the past years, the physics of microemulsions has been of great interest [1–6]. The microemulsions are formed after the surface-active substances (surfactants) are added into the mixture of two liquid components that are, under usual conditions insoluble in each other (usually oil and water). At some critical concentrations of the surfactants, the components yield a homogeneous solution of high stability. In oil-water microemulsion the dispersed phase exists in the form of droplets (micelles) of one liquid (oil) in the other (water). The micelles are stabilized by a surfactant monolayer of amphiphilic molecules. Dynamic properties of such systems depend on the nature of the fluid-fluid interface which can have complex viscoelastic behavior [7]. Even within the phenomenological approach when the surface layer is considered to be infinitely thin, the dynamics of the interface cannot be explained on the basis of surface tension alone [6,7]. The coefficient of the micelle surface tension is anomalously low and the dependence of the surface energy density on the curvature should be taken into account [5,8,9]. The phenomenological treatment requires the length scales of the problem to be much larger than that of a molecular size. This is true for microemulsions with the characteristic size of the droplets of the order 10^3 Å. Lipid vesicles [5,10,11] in aqueous solution have even much larger linear sizes and within the phenomenological theory the micelles in "good" microemulsions and vesicles can be considered simultaneously [9].

In this paper, we are interested in the thermal fluctuations in microemulsions and in solutions of vesicles. The micelles and vesicles are assumed to have a spherical shape in equilibrium. They will be modeled by fluid droplets immersed in a fluid with (generally) different properties and coated with a thin film. Assuming dilute solutions of the droplets, we can focus our attention on the study of the dynamic properties of a separate droplet. Only the low-frequency collective excitations in these systems will be considered. We suppose that in this case, the description is possible in terms of the usual hydrodynamics. The relaxation of the micelle or vesicle surface to its equilibrium spherical form has been already investigated in a number of theoretical papers, e.g., [7,9,12–17]. In these works, the dispersion laws of the relaxation modes have been calculated in various approximations; a good discussion of the theories can be found in Refs. [7,9,16]. The most general approaches have been developed in Refs. [7] and [9]. In the first of these papers, the fluctuations in a fluid droplet immersed in a fluid medium are investigated in detail assuming the interface between the two fluids has viscosity and compressibility in addition to surface tension. In the latter work [9], the dynamic properties of spherical micelles and vesicles with anomalously low surface tension are considered. Describing their surface, the terms depending on the curvature were retained in the surface energy expansion. The boundary conditions at the interface have been found which also depend on the curvature. Moreover, the redistribution of the surfactants on the micelle surface was included into the consideration which corresponds to the surface compressibility as considered in (Ref. [7]). As a result, a specific surface mode connected with the dynamics of surfactants was predicted. Within the linear hydrodynamic theory [9], we have obtained in our previous paper [18] an exact equation for the proper surface modes of spherical micelles and vesicles. This equation allowed us to calculate the surface vibration spectra more precisely compared with the previously known results. However, in all the above mentioned papers the fluids inside and outside the droplets were assumed to be incompressible and only the fluctuations of local quantities connected with the deviations of the surface form from its equilibrium shape have been studied. For this reason, for example, the spectrum of the density fluctuations does not differ from that of the fluctuations of the dielectric permitivity. Moreover, among the collective excitations two contributions can be distinguished. The first one is connected with the bulk hydrodynamic modes and the second with the surface modes. The dispersion law of the last modes is determined by the local surface energy of the droplets and the hydrodynamic flows in the bulk fluid layers close to the interface. In our recent paper [19], we have already developed a hydrodynamic correlation theory of the thermally fluctuating micelles and vesicles assuming the bulk fluids are compressible. Both the hydrodynamic and the surface modes have been considered. However, we have not taken into account the dependence of the surface energy on the curvature and the dynamics of the surfactants. The present paper significantly generalizes the theory [19]. The redistribution of the surfactants at the micelle surface is now taken into account as well as the dependence on the curvature. We present a correlation theory of the thermal fluctuations of micelles and vesicles assuming bulk fluids inside and outside the droplets. The method of analysis comprises a solution of the linearized hydrodynamic (Navier-Stokes and continuity) equations with random (thermal) stresses (Sec. II). The equations are solved with boundary conditions which seem to be appropriate for micelles and model vesicles with impenetrable surface layers. The boundary conditions contain the thermal surface sources. The spectral densities of the correlation functions for hydrodynamic variables are found based on the fluctuation-dissipation theorem: in Sec. III, the bulk modes are considered and in Sec. IV, we find the generalized susceptibilities and spectral densities of the fluctuating hydrodynamic fields determined by the random sources acting at the interface. In Sec. V the spectra of the collective excitations of micelles and vesicles are studied in some detail for various relations between the droplet sizes, the penetration depth of the viscous wave, and the sound wavelength. Section VI deals with calculations of the dynamic structure factor of microemulsions within the used hydrodynamic model.

II. FORMULATION OF THE BOUNDARY-VALUE PROBLEM

Let us assume that the motion of the fluctuating velocities, density and pressure fields is desribed by the linearized continuity equation and Navier-Stokes equation containing random stresses σ_{ik} [20]:

$$\frac{\partial}{\partial t}\delta\rho+\rho\nabla\cdot\mathbf{v}=0\ , \tag{1}$$

$$\rho\frac{\partial v_l}{\partial t}=-c^2\nabla_l\delta\rho-\eta(\nabla\times\nabla\times\mathbf{v})_l+\left[\frac{4\eta}{3}+\zeta\right]\nabla_l\nabla\cdot\mathbf{v}+\nabla_n\sigma_{ln}\ . \tag{2}$$

Here, η and ζ are the viscosity coefficients, $\delta\rho$ is the deviation from the equilibrium mass density ρ, $\mathbf{v}$ is the fluid velocity, and c is the velocity of sound. The temperature T is assumed to be constant throughout the system. The variable part of the pressure is $\delta p=c^2\delta\rho$. In what follows, the indices $i=1$ and 2 will refer the quantities to the regions interior and exterior to the droplet. The small radial displacements of the droplet shape from the sphere can be expanded in spherical harmonics,

$$R(\theta,\varphi,t)=R_0\left[1+\sum_{lm}u_{lm}(t)Y_{lm}(\theta,\varphi)\right]\ , \tag{3}$$

where R_0 is the equilibrium radius of the droplet. The index m runs from $-l$ to l, and l changes from $l=2$ to some $l_{\max}\sim\pi R_0/d$ determined by the mean interatomic distance d [7]. The mode $l=1$ is excluded since it corresponds to motion of the center of mass of the droplet. The mode $l=0$ is connected with the uniform dilation of the droplet.

In our phenomenological description, the interface has a negligible thickness and is characterized by the surface density ω^s of the thermodynamic potential [9]. It can be represented using the expansion in the local curvature radii of the interface, R_1 and R_2, as follows:

$$\omega^s=\alpha-\beta\left[\frac{1}{R_1}+\frac{1}{R_2}\right]+\kappa\left[\frac{1}{R_1}+\frac{1}{R_2}\right]^2+\frac{\bar{\kappa}}{R_1R_2}\ . \tag{4}$$

Here, ω^s is expanded to the second order using the invariants $(R_1+R_2)/2$ and $1/R_1R_2$ (the mean and Gaussian curvature, respectively). The quantity $\beta/2\kappa$ is the so-called spontaneous curvature. The expansion coefficients α, β, κ, and $\bar{\kappa}$ have been discussed in Refs. [8,9]. We only note that α is the usual surface tension coefficient in the case of the planar interface, $\beta=0$ for vesicles and $\beta>0$ for micelles (if the curvature radii are measured from the interior to the exterior of the micelle). The conditions $\kappa>0$ and $2\kappa+\bar{\kappa}>0$ must be fulfilled to make the function (4) positively defined. The stability of the spherical micelle with respect to small perturbations is ensured by the condition

$$\alpha_l=\alpha-\frac{2\beta}{R_0}+\frac{\kappa l(l+1)}{R_0^2}>0\ , \tag{5}$$

and the micelle distribution in radii has a sharp maximum at the radius R_0 if $k_BT/8\pi(2\kappa+\bar{\kappa})\ll 1$, where k_B is the Boltzmann constant and T is the temperature. This condition allows us also to neglect a renormalization of the parameters α, β, κ, and $\bar{\kappa}$ that is due to thermal fluctuations [9].

In the presence of surface-active molecules, the energy density parameters depend on the surface concentration of the surfactants. Small deviations δn^s from the equilibrium value of the surfactant density n^s can be expanded analogously to Eq. (3),

$$\delta n^s=n^s\left[1+\sum_{lm}\nu_{lm}Y_{lm}(\theta,\varphi)\right]\ . \tag{6}$$

Here, the minimum value of l is also 2. Using the assumption that there is no change in the total amount of surfactant material in the surface layer, it is easy to find that ν_{00} is of the second order in the small quantities u and ν. The terms with ν_{1m} are also excluded since the $l=1$ mode corresponds to the translational motion of the undeformed droplet. In this case, there is no motion in the surface layer and the droplet moves like a hard sphere [21].

The excess energy of the surface,

$$E^s=\int d^3r\delta(r-R)|\nabla(r-R)|\epsilon^s , \tag{7}$$

can be found expanding ϵ^s, the δ function, and grad$(r-R)$ in the small quantities δn^s and u. In ϵ^s, we have $\alpha=\alpha(n^s+\delta n^s)$. The dependence on δn^s for the other coefficients can be neglected [9]. Using the above discussed conservation of the total amount of surfactants in the layer, the result of evaluation to the second order in the small quantities reads

$$\begin{gathered} E^s=\tfrac{1}{2}R_0^2\sum_{lm}[\alpha_l(l-1)(l+2)|u_{lm}|^2+B|v_{lm}|^2] , \\ B=(n^s)^2\frac{\partial^2\epsilon^s}{\partial(n^s)^2}=-n^s\frac{\partial\alpha(n^s)}{\partial n^s}>0 . \end{gathered} \tag{8}$$

An analogous expression [with $l\geq 1$ in the second term of Eq. (8)] has been already used in Ref. [9].

The adsorbed surfactant layer can essentially affect hydrodynamic properties of the droplet. The changes of the droplet shape that are connected with the motion of the liquids lead to stretches and compressions of the layer and, consequently, to the changes of the surfactant concentration. Corresponding additional forces must be then taken into account in the boundary conditions at the interface [21]. For the hydrodynamic fields described by Eqs. (1) and (2), these conditions are supplemented with terms depending on the surface velocity $\mathbf{v}^s$ (the surface momentum density $\rho^s\mathbf{v}^s$). For the case of incompressible bulk fluids, the linearized boundary conditions that take into account the dependence on the curvature have been discussed in detail in Ref. [9]. We will write these conditions for compressible fluids inside and outside the droplet and supplement them with the radial and tangential forces at the interface that are determined by the difference of the random volume stresses $f_i^s=\sigma_{ir}^{(2)}-\sigma_{ir}^{(1)}$.

If such a description the boundary conditions describing the dynamics of the interface are as follows:

$$v_r^s=\dot{R} , \quad \mathbf{v}_1=\mathbf{v}_2 , \tag{9}$$

$$\begin{aligned} \rho^s\dot{v}_r^s-\delta p_1&+\left[\zeta_1-\frac{2\eta_1}{3}\right]\nabla\cdot\mathbf{v}_1+2\eta_1\frac{\partial v_{1r}}{\partial r} \\ &+\sum_{lm}\left[\frac{\alpha_l}{R_0}\right](l-1)(l+2)u_{lm}Y_{lm} \\ &=-\delta p_2+\left[\zeta_2-\frac{2\eta_2}{3}\right]\nabla\cdot\mathbf{v}_2+2\eta_2\frac{\partial v_{2r}}{\partial r}+f_r^s , \end{aligned} \tag{10}$$

$$\begin{aligned} \rho^s\dot{v}_t^s-\left[\frac{\partial\alpha}{\partial n^s}\right]&\nabla_t\delta n^s+\nabla_t(\eta_1v_{1r}-\eta_2v_{2r}) \\ &+\left[\frac{\partial}{\partial r}-\frac{1}{r}\right](\eta_1v_{1t}-\eta_2v_{2t})=f_t^s , \end{aligned} \tag{11}$$

$$\frac{\partial\delta n^s}{\partial t}+n^s\nabla_tv_t^s=0 . \tag{12}$$

These equations generalize the usual conditions for the tangential and normal components of the viscous stress tensor, and for the continuity of normal and tangential velocity components. In agreement with the preceding discussion, the continuity equation (12) for the surfactant material in the layer is used. The indices r and t denote the radial and tangential components of the vectors in the spherical coordinate system with the origin located at the center of the equilibrium droplet.

In these equations, the very slow diffusion of the surface-active molecules between the layer and the bulk fluids is neglected [9]. This approximation is good for the surfactants which are insoluble in the liquids. The used boundary conditions imply also that there is no flow of mass from one side of the interface to the other side. This assumption is commonly accepted for micelles where the bulk fluids outside and inside the micelle are different, and often used for vesicles [7,9]. For vesicles, however, both fluids are more or less the same and the use of stick boundary conditions is then not necessarily appropriate. This shortcoming limits our phenomenological theory to model fluid droplets with impenetrable surfaces.

In the linear approach, the amplitudes u_{lm} of the surface displacement expansion (3) are small compared to unity. For this reason, the boundary conditions are taken on the surface of the undistorted spheres ($r=R_0$).

It is convenient to write all equations in the Fourier transformed form. We will use the same notation for the quantities of interest and their Fourier components replacing the differentiation in time $\partial/\partial t$ by $-i\omega$.

The spectral densities of the fluctuating hydrodynamic fields will be obtained using the fluctuation-dissipation theorem (FDT). To make this (see, e.g., Ref. [22]), one must find a system of linear stochastic equations for the spectral amplitudes of the parameters, say, $\xi_i(t)$, and the corresponding generalized forces $F_i(t)$,

$$\xi_j(\omega)=\sum_k\alpha_{jk}(i\omega)F_k(\omega) , \tag{13}$$

where $\{\alpha_{jk}\}$ is the matrix of generalized susceptibility. Then the correlation matrix of the spectral amplitudes $\xi_j(\omega)$ [for the stationary processes $\xi_j(t)$ and $F_j(t)$] is

$$\langle\xi_j(\omega)\xi_k^*(\omega')\rangle=\langle\xi_j\xi_k^*\rangle\delta(\omega-\omega') , \tag{14}$$

and the FDT in the classical limit reads

$$\langle\xi_j\xi_k^*\rangle_\omega=\frac{ik_BT}{2\pi\omega}(\alpha_{jk}-\alpha_{kj}^*) . \tag{15}$$

The Fourier transformation of this spectral density matrix determines the time correlation functions $\langle\xi_j(t)\xi_k^*(0)\rangle$. The correspondence between the generalized forces and coordinates can be found from the expression for energy dissipation in the system under the action of the generalized forces F_j. In our case, we must know the expression for the power Q dissipated in the system due to the random sources [20]. Using the well-known hydrodynamic formula for the dissipation of energy [21], we obtain

$$Q=Q^{(1)}+Q^{(2)}+Q^{(s)} , \tag{16}$$

with

$$Q^{(i)} = -\int_{(V_i)} d^3r\,\mathbf{v}_i \cdot \mathbf{f}^{(i)}\,, \quad Q^{(s)} = -\int_{(S)} dS\,\mathbf{f}^s \cdot \mathbf{v}^s\,,$$
$$f_l^{(i)} = \nabla_k \sigma_{lk}^{(i)}, \quad i = 1,2\,. \tag{17}$$

In Eq. (17), V_1 and V_2 denote the volume of the droplet and outer fluid, respectively, and S is the droplet surface.

Owing to the linearity of the hydrodynamic and boundary equations, the total solution of the boundary-value problem for the inhomogeneous equations can be represented as a sum of two contributions. The first one will satisfy the inhomogeneous equations in both regions with the flow velocities vanishing at the interface. The second one is determined by the homogeneous equations without random forces but with the hydrodynamic fields being subjected to the boundary conditions (9)–(12). Thus, the total spectral densities of the hydrodynamic correlation fields split into two independent contributions corresponding to the spectral densities of the fields excited by the random volume stresses and by the random forces f^s distributed on the interface S.

III. SPECTRAL HYDRODYNAMIC FLUCTUATIONS WITHIN A SPHERICAL CAVITY

For the thermal flow with the velocity vanishing at the interface, the interior problem fully separates from the exterior one. Here, we will consider the thermodynamic fluctuations inside the sphere with the radius R_0. This section is as a whole based on the results obtained for the first time in Ref. [23] (see also Ref. [19]).

The Euler velocity field inside the droplet can be represented using the basis functions for the vector Helmholtz equation (in this section, the index 1 referring to the interior of the droplet is omitted),

$$\nabla(\nabla \cdot \mathbf{L}) = -k^2\mathbf{L}, \nabla \times (\nabla \times \mathbf{M}) = k^2\mathbf{M}\,,$$
$$\nabla \times (\nabla \times \mathbf{N}) = k^2\mathbf{N}\,. \tag{18}$$

Three sets of solutions (finite at $r=0$) are determined as follows [24]:

$$\mathbf{L}_{lm} = \frac{1}{k}\nabla[Y_{lm}(\theta,\varphi)j_l(kr)]\,.$$
$$\mathbf{M}_{lm} = \nabla \times (\mathbf{r}Y_{lm}j_l), \quad \mathbf{N}_{lm} = \frac{1}{k}\nabla \times \mathbf{M}_{lm}\,. \tag{19}$$

Here, $j_l(kr)$ are the spherical Bessel functions. The velocity expansion is then

$$\mathbf{v}(\mathbf{r},\omega) = \sum_{\lambda, A} u_\lambda^A(\omega)\,\tilde{\mathbf{A}}_\lambda(\mathbf{r}), \quad A = L,M,N\,, \tag{20}$$

where we have introduced the normalized functions

$$\tilde{\mathbf{A}} = \mathbf{A} \Big/ \left[\int d^3r\,\mathbf{A}(\mathbf{r}) \cdot \mathbf{A}^*(\mathbf{r})\right]^{1/2}\,. \tag{21}$$

From the boundary conditions, we obtain transcendental equations for the proper values k_λ,

$$j_l(\beta_{ln}) = 0, \quad k_\lambda = \beta_{ln}/R_0\,,$$
$$\gamma_{ln}j_l'(\gamma_{ln}) + \mu j_l(\gamma_{ln}) = 0, \quad \mu = -l, l+1\,, \tag{22}$$
$$k_\lambda = \gamma_{ln}/R_0\,.$$

The first equation determines the proper values k_λ for the function $\mathbf{M}$, and the second pair of equations gives k_λ for the function $\mathbf{L}$ and $\mathbf{N}$. The prime denotes the differentiation with respect to argument and n is a root number. The cumulative index λ from Eq. (20) is thus a set of the summation indices l, m, and n. The normalizing coefficients in (21) can be easily calculated but we shall not use them.

We expand the volume densities of the forces $\mathbf{f}(\mathbf{r},\omega)$ into the series as in Eq. (20) with expansion coefficients $f_\lambda^A(\omega)$. Using the orthogonality of the proper functions, we find from the hydrodynamic equations (1) and (2) in their spectral form, the following relations between the flow velocity amplitudes and the amplitudes of random forces:

$$u_\lambda^{M,N}(\omega) = \frac{1}{\rho}\frac{f_\lambda^{M,N}(\omega)}{-i\omega + \nu k_\lambda^2}\,,$$
$$u_\lambda^L(\omega) = \frac{1}{\rho}\frac{-i\omega f_\lambda^L}{-\omega^2 + c^2k_\lambda^2 - i\omega\nu_\parallel k_\lambda^2}\,, \tag{23}$$
$$\nu = \eta/\rho, \quad \nu_\parallel = (\zeta + 4\eta/3)/\rho\,.$$

For a periodic force with the frequency ω,

$$\Phi(\mathbf{r},t) = \tfrac{1}{2}[\Phi(\mathbf{r},\omega)e^{-i\omega t} + \Phi^*(\mathbf{r},\omega)e^{i\omega t}]\,, \tag{24}$$

the energy absorbed in the system per unit time is obtained after the time averaging in the form

$$Q = -\tfrac{1}{2}\,\mathrm{Re}\sum_{A\lambda} u_\lambda^A \Phi_\lambda^{A*}(\omega)\,. \tag{25}$$

The total dissipation of the power (17) is obtained to be

$$Q(t) = -\sum_{A\lambda} u_\lambda^A(t) f_\lambda^{A*}(t)\,. \tag{26}$$

As has been mentioned above, Eqs. (25) and (26) allow one to choose the energetically conjugated generalized coordinates and forces and to write down the susceptibility matrix $\alpha_{\lambda\lambda'}^A(i\omega)$. If the coordinates are $u_\lambda^A(t)$, then the forces are $F_\lambda^A(t)$ and $f_\lambda^A = dF_\lambda^A/dt$ with the Fourier components $f_\lambda^A(\omega) = -i\omega F_\lambda^A(\omega)$. Then the application of the FDT is straightforward [22] and results in the following spectral density matrices:

$$\langle u_\lambda^L u_{\lambda'}^{L*} \rangle_\omega = \frac{k_B T \delta_{\lambda\lambda'}}{\pi\rho}\,\mathrm{Re}\frac{-i\omega}{-\omega^2 + c^2k_\lambda^2 + i\omega\nu_\parallel k_\lambda^2}\,,$$
$$\langle u_\lambda^B u_{\lambda'}^{B*} \rangle_\omega = \frac{k_B T \delta_{\lambda\lambda'}}{\pi\rho}\,\mathrm{Re}\frac{1}{-i\omega + \nu k_\lambda^2}, \quad B = M,N\,. \tag{27}$$

The spectral densities differ from those known for an unbounded homogeneous liquid only by a discrete character of the wave numbers.

As an illustration, we give also an expression for the mean power dissipated in the system, $\langle Q \rangle$. In this case, the FDT is to be used in the form

$$\langle u_\lambda F_\lambda^* \rangle_\omega = \frac{ik_B T}{2\pi\omega}\left[\sum_{Am} \alpha_{\lambda m}^A [\alpha_{\lambda m}^{A*}]^{-1} - 1\right]\,. \tag{28}$$

Substituting $u_\lambda^A(t)$ and $f_\lambda^A(t)$ into Eq. (26) as their

Fourier integrals of $u_\lambda^A(\omega)$ and $f_\lambda^A(\omega)$, averaging it and applying the FDT, the formula for $\langle Q \rangle$ becomes especially simple:

$$\langle Q \rangle = -\frac{k_B T}{R_0^2} \sum_\lambda [\nu(\beta_\lambda^2+\gamma_\lambda^2)+\nu_\parallel \gamma_\lambda^2] \,. \tag{29}$$

Finally, the spectral density of the velocity correlation function is easily written from Eqs. (20) and (23) as follows:

$$\langle \mathbf{v}(\mathbf{r},t)\cdot\mathbf{v}(\mathbf{r}',t') \rangle_\omega = \sum_{\lambda A} \langle |u_\lambda^A|^2 \rangle_\omega \tilde{\mathbf{A}}_\lambda(\mathbf{r})\cdot \tilde{\mathbf{A}}_\lambda^*(\mathbf{r}') \,, \quad A=M,N,L \,. \tag{30}$$

The spectrum of the mass density fluctuations can be found using Eq. (30) and the continuity equation,

$$\langle \delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r}',t') \rangle_\omega = \sum_\lambda \langle |u_\lambda^L|^2 \rangle_\omega \left[\frac{\rho k_\lambda}{\omega} \right]^2 \tilde{\mathbf{L}}_\lambda(\mathbf{r})\cdot \tilde{\mathbf{L}}_\lambda^*(\mathbf{r}') \,. \tag{31}$$

One can analogously find the spectral densities of the Euler field in the region exterior to the droplet.

IV. FLUCTUATIONS EXCITED BY SURFACE RANDOM SOURCES

In this case, we have to obtain the solutions of homogeneous Navier-Stokes equations in the regions interior and exterior to the droplet. The random sources are now located on the droplet surface. It is convenient to search for the solution expanding the velocity fields in the series of the spherical vector functions [24] **P**, **B**, and **C**. For example, the velocity inside the sphere is

$$\mathbf{v}_1(\mathbf{r},\omega) = \sum_\lambda [\mathbf{P}_\lambda(\theta,\varphi)F_{1\lambda}(r,\omega)+\mathbf{B}_\lambda(\theta,\varphi)G_{1\lambda}(r,\omega) + \mathbf{C}_\lambda(\theta,\varphi)H_{1\lambda}(r,\omega)], \quad \lambda=l,m \,. \tag{32}$$

One can easily find from the Navier-Stokes equations a set of equations for the scalar functions F, G, and H. The interior solutions finite at $r=0$ have the following form:

$$\begin{aligned} F_1 &= C_1^L j_l'(k_{1\parallel}r) + C_1^N \frac{l(l+1)}{k_{1\perp}r} \,, \\ G_1 &= [l(l+1)]^{1/2} \left[C_1^L \frac{j_l(k_{1\parallel}r)}{k_{1\parallel}r} + C_1^N \left[j_l'(k_{1\perp}r) + \frac{j_l(k_{1\perp}r)}{k_{1\perp}r} \right] \right] , \\ H_1 &= [l(l+1)]^{1/2} C_1^M j_l(k_{1\perp}r) \,. \end{aligned} \tag{33}$$

Here, we have introduced the notation

$$\begin{aligned} k_{1\perp} &= (i\omega\rho_1/\eta_1)^{1/2} \,, \\ k_{1\parallel} &= [(c_1/\omega)^2(1-i\omega\nu_{1\parallel}/c_1^2)]^{-1/2} \,. \end{aligned} \tag{34}$$

The superscripts in the integration constants C_l have the same sense as above and the indices of spherical harmonics are omitted. Changing the indices 1 for 2 and substituting the spherical Hankel functions of the first kind, $h_l^{(1)}$, instead of the spherical Bessel functions j_l, we obtain the exterior solutions. They correspond to longitudinal and transverse damped waves. Note that the general exterior solutions must contain both $h_l^{(1)}$ and the Hankel function of the second kind. To exclude the exponential divergency as $r \rightarrow \infty$, we must use $h_l^{(1)}$ if its argument has a positive imaginary part, and $h_l^{(2)}$ in the opposite case. However, in what follows, these functions enter the equations only in such combinations that are invariant with respect to replacement of the indices 1 and 2.

The unknown integration constants $C_{1,2}^A$ will be determined from the boundary conditions (9)–(12). The velocity of the interface and the random forces at the surface can be expressed using the expansions analogous to Eq. (32),

$$\begin{aligned} \mathbf{v}^s(\theta,\varphi) &= \sum_{lm} (F_{lm}^s \mathbf{P}_{lm} + G_{lm}^s \mathbf{B}_{lm} + H_{lm}^s \mathbf{C}_{lm}) \,, \\ \mathbf{f}^s(\theta,\varphi) &= \sum_{lm} (f_{lm}^s \mathbf{P}_{lm} + g_{lm}^s \mathbf{B}_{lm} + h_{lm}^s \mathbf{C}_{lm}) \,. \end{aligned} \tag{35}$$

Equation (12) and the conditions of the continuity of the tangential velocity components lead to the following expression:

$$-i\omega R_0 v_{lm} = [l(l+1)]^{1/2} G_{lm}^s = [l(l+1)]^{1/2} G_{1lm}(R) \,. \tag{36}$$

Using it, we find a system of linear inhomogeneous algebraic equations for the coefficients C and the displacement amplitudes u_{lm} for all l and m (below, the indices of the spherical harmonics will be omitted),

$$\tilde{C}_1^L Q(x_1) + \tilde{C}_1^N l(l+1) = R_0 \dot{u} \,, \tag{37}$$

$$\tilde{C}_2^L H(x_2) + \tilde{C}_2^N l(l+1) = R_0 \dot{u} \,, \tag{38}$$

$$\tilde{C}_1^L + \tilde{C}_1^N [Q(y_1)+1] = \tilde{C}_2^L + \tilde{C}_2^N [H(y_2)+1] \,, \tag{39}$$

$$u[\alpha_1(l+2)(l-1)-\rho^s\omega^2R_0^2]-\tilde{C}_1^L\eta_1[y_1^2+4Q(x_1)-2l(l+1)]$$
$$+\tilde{C}_1^N 2l(l+1)\eta_1[Q(y_1)-1]+\tilde{C}_2^L\eta_2[y_2^2+4H(x_2)-2l(l+1)]-\tilde{C}_2^N 2l(l+1)\eta_2[H(y_2)-1]=R_0f^s, \tag{40}$$

$$[-i\omega\rho^sR_0^2-Bl(l+1)/i\omega]\{\tilde{C}_1^L+\tilde{C}_1^N[Q(y_1)+1]\}+2\eta_1\{\tilde{C}_1^L[Q(x_1)-1]-\tilde{C}_1^N[Q(y_1)+1-l(l+1)+y_1^2/2]\}$$
$$-2\eta_2\{\tilde{C}_2^L[H(x_2)-1]-\tilde{C}_2^N[H(y_2)+1-l(l+1)+y_2^2/2]\}=R_0g^s/\sqrt{l(l+1)}\ . \tag{41}$$

Here, in addition, we have introduced the notation

$$Q(x)=\frac{xj_l'(x)}{j_l(x)},\quad H(x)=\frac{xh_l^{(1)\prime}(x)}{h_l^{(1)}(x)}\ ,$$
$$x_i=k_{i\|}R_0,\quad y_i=k_{i\perp}R_0\ , \tag{42}$$
$$\tilde{C}_1^A=C_1^A\frac{j_l(\xi_1)}{\xi_1},\quad \tilde{C}_2^A=C_2^A\frac{h_l^{(1)}(\xi_2)}{\xi_2},\quad \xi\equiv x\delta_{LA}+y\delta_{NA}\ .$$

The equations determining the coefficients $C_{1,2}^M$ are independent from the above given equation and result in

$$C_1^M=A^Mh^s\ ,$$
$$A^m=\frac{R_0}{\sqrt{l(l+1)}j_l(y_1)}\{-i\omega\rho^sR_0+\eta_1[Q(y_1)-1]$$
$$+\eta_2[H(y_2)-1]\}^{-1}\ . \tag{43}$$

Using the Kramer's rule, the coefficients C can be easily found from the linear equations (37)–(41) through the amplitudes of the random forces. For example, the solution for the interior of the droplet can be written as follows:

$$C_1^L=A^{Lf}f^s+A^{Lg}g^s,\quad C_1^N=A^{Nf}f^s+A^{Ng}g^s\ . \tag{44}$$

Explicit expressions for the matrices A have a very bulky form and we do not write them here. These matrices determine the frequency-dependent generalized susceptibilities for the random expansion amplitudes of the hydrodynamic fields. Analogously, as in the preceding section, the energy dissipation $Q^{(s)}$ from Eq. (17) allows us to determine the correspondence between the Fourier amplitudes of the generalized coordinates and forces and to find the susceptibility matrix. The mean power absorbed by the system, in the case of a harmonic force $\mathbf{f}^s(t)=(\frac{1}{2})[\mathbf{f}^s(\omega)\exp(-i\omega t)+\mathbf{f}^{s*}(\omega)\exp(i\omega t)]$, is

$$Q^s=-\left(\frac{R_0^2}{2}\right)\mathrm{Re}\sum_{lm}(F_{lm}^sf_{lm}^{s*}+G_{lm}^sg_{lm}^{s*}+H_{lm}^sh_{lm}^{s*})\ , \tag{45}$$

where we have also used the expansions (35). Then the spectral densities of the fluctuating expansion amplitudes are found by using the FDT. To make this, we write the linear relations between the surface velocity amplitudes and the coefficients C_1 [see Eqs. (33), (44), and (45)],

$$F^s=\tilde{C}_1^LQ(x_1)+\tilde{C}_1^Nl(l+1)\ ,$$
$$G^s=\sqrt{l(l+1)}\{\tilde{C}_1^L+\tilde{C}_1^N[Q(y_1)+1]\}\ , \tag{46}$$
$$H^s=\sqrt{l(l+1)}j_l(y_1)C_1^M\ .$$

Then, using Eqs. (43) and (44), we have

$$F^s=\alpha^{Ff}f^s+\alpha^{Fg}g^s,\quad G^s=\alpha^{Gf}f^s+\alpha^{Gg}g^s,\quad H^s=\alpha^{Hh}h^s\ . \tag{47}$$

The new matrices α are determined by the relations

$$\begin{vmatrix}\alpha^{Ff} & \alpha^{Fg}\\ \alpha^{Gf} & \alpha^{Gg}\end{vmatrix}=\begin{vmatrix}Q(x_1) & l(l+1)\\ \sqrt{l(l+1)} & \sqrt{l(l+1)}[Q(y_1)+1]\end{vmatrix}$$
$$\times\begin{vmatrix}A^{Lf} & A^{Lg}\\ A^{Nf} & A^{Ng}\end{vmatrix}\ , \tag{48}$$
$$\alpha^{Hh}=\sqrt{l(l+1)}j_l(y_1)A^M\ .$$

Application of the FDT to Eqs. (45) and (47) leads to the following spectral densities of the fluctuating velocity amplitudes:

$$\langle F_\lambda^SF_{\lambda'}^{S*}\rangle_\omega=\delta_{\lambda\lambda'}\frac{k_BT}{\pi R_0^2}\mathrm{Re}\alpha_{\lambda\lambda}^{Ff}\ ,$$
$$\langle G_\lambda^SG_{\lambda'}^{S*}\rangle_\omega=\delta_{\lambda\lambda'}\frac{k_BT}{\pi R_0^2}\mathrm{Re}\alpha_{\lambda\lambda}^{Gg}\ , \tag{49}$$
$$\langle F_\lambda^SG_{\lambda'}^{S*}\rangle_\omega=\delta_{\lambda\lambda'}\frac{k_BT}{2\pi R_0^2}(\alpha_{\lambda\lambda}^{Gf}+\alpha_{\lambda\lambda}^{Gf*}),\quad \lambda=\{l,m\}\ .$$

These results allow us to find the spectral densities of any bilinear combinations of the hydrodynamic fields. For example, the spectral density for the amplitude C_1^L (the amplitude determining the fluctuations of density) is, using Eqs. (49) and (46),

$$\langle|\tilde{C}_{1lm}^L|^2\rangle_\omega=\frac{k_BT}{\pi R_0^2}\mathrm{Re}\frac{A_l^{Lf}[1+Q_l^*(y_1)]-\sqrt{l(l+1)}A_l^{Lg}}{[1+Q_l^*(y_1)]Q_l^*(x_1)-l(l+1)}\ . \tag{50}$$

The roots of the determinant of Eqs. (37)–(41) correspond to all kinds of the collective excitations of micelles or vesicles in the used viscous blob model.

V. APPROXIMATE RESULTS FOR THE SHAPE AND SURFACTANT FLUCTUATIONS OF MICELLES AND VESICLES

The spectral amplitudes $u_{lm}(\omega)$ can be obtained from the boundary condition (9) and the expression for the velocity expanded in the vector functions (19),

$$-i\omega R_0u_{lm}(\omega)=C_{1lm}^Nl(l+1)\frac{j_l(y_1)}{y_1}+C_{1lm}^Lj_l'(x_1)\ . \tag{51}$$

Hence, the spectral density of fluctuations of the droplet surface displacement is [see Eq. (46)]

$$\langle |u_{lm}|^2\rangle_\omega = \langle |F_{lm}^s|^2\rangle_\omega/(R_0\omega)^2 = \frac{k_BT}{\pi R_0^4}\,\mathrm{Re}[l(l+1)A_{lm}^{Nf}+Q_l(x_1)A_{lm}^{Lf}] \; . \tag{52}$$

The character of the collective excitations of micelles and vesicles is determined by the relations between their sizes, the penetration depth of the corresponding viscous waves, and the sound wavelength. Typical sizes of micelles are of the order 10^2-10^3 Å ("good microemulsions" from the point of view of the phenomenology are those with typical sizes of the droplets significantly exceeding a molecular size; the phenomenological theories would be compared with experiments on the systems of droplets with large radii such as 10^3 Å), therefore $\omega R_0/c$ is small compared to unity for the studied low-frequency acoustic excitations. If, moreover, the penetration depth of the shear wave is much larger than the micelle radius, then $R_0(\omega/\nu)^{1/2} \ll 1$ and the shape oscillations are damped. The stretching forces acting on the surfactant layer are small and the surface layer can be considered to be incompressible. These conditions can be used for significant simplifications of the analytical form of the spectral density function (52). It must be taken into account in such calculations that the results depend on the order in which $x_{1,2}$ and $y_{1,2}$ reach their small or large values.

(1) Let the effects of compressibility be small so that the conditions $|x_{1,2}| \ll |y_{1,2}| \ll 1$ are satisfied. In this case, restricting ourselves to the dominant terms in $|y_{1,2}|$, we find [19]

$$\langle |u_{lm}|^2\rangle_\omega = \frac{k_BT}{\pi R_0^2}[\alpha_l(l-1)(l+2)\tau_{\alpha 1}]^{-1} \times \left[\omega^2 + \left[\frac{1}{\tau_{\alpha 1}} - \omega^2\tau_1\right]^2\right]^{-1} . \tag{53}$$

Here,

$$\frac{1}{\tau_{\alpha 1}} = \alpha_l(l-1)l(l+1)(l+2)(2l+1)\frac{\eta_1+\eta_2}{R_0q_lp_l} ,$$
$$\rho_l = \frac{\rho_1}{l} + \frac{\rho_2}{l+1} ,$$
$$q_l = 2(l^2-1)\eta_1 + (2l^2+1)\eta_2 ,$$
$$p_l = (2l^2+4l+3)\eta_1 + 2l(l+2)\eta_2 , \tag{54}$$
$$\tau_1 = \frac{R_0^2}{q_lp_l}\left[\rho_l l(l+1)(2l+1)(\eta_1+\eta_2) + 2(\eta_1-\eta_2)\left[\frac{\rho_1 q_l l(l+2)}{\eta_1(2l+3)(2l+5)} - \frac{\rho_2 p_1(l^2-1)}{\eta_2(2l-3)(2l-1)}\right]\right] .$$

These results correspond to Ref. [18] where the poles of the spectral densities of the surface displacement have been analyzed in more detail for incompressible fluids. Due to the condition $\omega\tau_1 \ll 1$, the spectrum (53) consists of the peaks close to Lorentzians with the widths determined by Eq. (54). It corresponds to an overdamped mode of the shape vibrations. The static correlation function of the amplitudes $u_{lm}(t)$ is

$$\langle u_{lm}(t)u_{lm}^*(t)\rangle = \int \langle |u_{lm}|^2\rangle_\omega d\omega = \frac{k_BT}{R_0^2\alpha_l(l-1)(l+2)}\left[1-\frac{\tau_1}{\tau_{\alpha 1}}\right]^{-1/2} . \tag{55}$$

In the considered example, the effects of compressibility lead to additional (linear with respect to $\eta/c^2\rho$) contributions to the relaxation time τ_1, so that τ_1 becomes $\tau_1+\gamma_1\eta_1/c_1^2\rho_1+\gamma_2\eta_2/c_2^2\rho_2$ with dimensionless coefficients γ_1 and γ_2. The influence of these terms on the form of the spectrum is small. The result (55) differs from the stationary one [following from the surface energy (8)] only by a factor close to unity.

(2) Consider the case when $|y_{1,2}| \ll |x_{1,2}| \ll 1$ (e.g., large values of the viscosities η_1 and η_2). The spectral density of the displacement fluctuations is again a Lorentzian [19],

$$\langle |u_{lm}|^2\rangle_\omega = \frac{k_BT}{\pi R_0^2\alpha_l(l+2)(l-1)}\frac{\tau_{\alpha 2}}{1+(\omega\tau_{\alpha 2})^2} ,$$
$$\tau_{\alpha 2} = 2R_0\frac{(l-1)\eta_1+2\eta_2}{\alpha_l(l-1)} , \tag{56}$$

but its width has a different parametrical dependence on the viscosities.

(3) In the opposite case when the penetration depth of the shear wave is small, $|y_{1,2}| \gg 1$, the spectral density of the shape fluctuations correspond to the capillary waves. Taking into account $|x_{1,2}| \ll 1$, we find [19]

$$\langle |u_{lm}|^2\rangle_\omega = \frac{k_BT}{\pi R_0^5\rho_l}\frac{\sqrt{\omega_1\omega/2}}{(\omega^2-\omega_0^2)^2+\omega_1\omega^3}, \quad \omega > 0 , \tag{57}$$

where

$$\omega_0^2 = \frac{\alpha_l(l-1)(l+2)}{R_0^3\rho_l} ,$$
$$\omega_1 = \left[\frac{(2l+1)\sqrt{\eta_1\eta_2}\rho_2(\rho_1-\rho_2)}{l(l+1)(\sqrt{\rho_1\eta_1}+\sqrt{\rho_2\eta_2})R_0\rho_l\sqrt{\rho_1\rho_2}}\right]^2 . \tag{58}$$

Equation (57) is applicable for not too small frequencies and the result is correct for small ω_1/ω_0. In this case, the viscosities are small and it is not necessary to take into account the presence of the surfactants in the layer. The capillary wave is low damped when $\eta^2/\alpha R_0\rho \ll 1$. This holds for vesicles while for micelles, as a rule, the opposite inequality takes place [9].

Using $\omega_1/\omega_0 \ll 1$, the spectrum (57) can be expressed as

$$\langle |u_{lm}|^2\rangle_\omega = \frac{k_BT}{\pi\rho_l R_0^5\sqrt{2\omega_0\omega_1}}\left[\omega^2+\frac{\omega^2-\omega_0^2}{\omega_0\omega_1}\right]^{-1} . \tag{59}$$

This leads to a static correlator with the main contribution from Eq. (55),

$$\langle |u_{lm}|^2\rangle_\omega = \frac{k_B T}{\rho_l R_0^5 \omega_0^5}\left[1+O\left[\frac{\omega_1}{\omega_0}\right]\right] . \tag{60}$$

(4) We will give one more result [19] corresponding to the conditions $|y_{1,2}| > |x_{1,2}| \gg 1$:

$$\langle |u_{lm}|^2\rangle_\omega = \frac{k_B T}{4\pi(\eta_1+\eta_2)R_0^3}\,\mathrm{Re}\left[i\omega\left[-i\omega+\frac{1}{\tau_4}\right.\right.$$
$$\left.\left. -i\omega\sqrt{-i\omega\tau_5}\right]^{-1}\right] ,$$
$$\frac{1}{\tau_4} = \frac{\alpha_l(l-1)(l+2)}{4R_0(\eta_1+\eta_2)} , \tag{61}$$
$$\tau_5 = \frac{R_0^2}{16(\eta_1+\eta_2)^2}(\rho_1\sqrt{\nu_{1\|}}+\rho_2\sqrt{\nu_{2\|}})^2 .$$

Here, the viscosities are small again, $\tau_5 \gg \tau_4$, and the influence of the surfactants is negligible.

(5) The inhomogeneity of the surfactant concentration on the droplet surface leads to an additional contribution to the spectral densities of the hydrodynamic fields. The corresponding concentration mode has a specific dependence on the frequency and viscosity [9,18]. This dependence displays best of all in the spectrum of fluctuations of the concentration amplitudes (6),

$$\langle |\nu_{lm}|^2\rangle_\omega = \frac{l(l+1)}{(\omega R_0)^2}\langle |G_{lm}^s|^2\rangle_\omega = \frac{k_B T l(l+1)}{\pi\omega^2 R_0^4}\,\mathrm{Re}\,\alpha_{lm,lm}^{Gg} . \tag{62}$$

Let the penetration depth of the shear wave be small as before, $|y_{1,2}| \gg 1$, and the vibration frequencies at small viscosities are much larger than those for the capillary waves from Eq. (58), that is, $\omega \gg \omega_0$. If, moreover, $\rho^s \ll R_0\rho_1$, and $|x_{1,2}| \ll 1$, we obtain the following simplification of Eq. (62) that coincides with the results found in Refs. [9,18]:

$$\langle |\nu_{lm}|^2\rangle_\omega \simeq \frac{3l(l+1)k_B T}{\pi R_0^4 B(\sqrt{2\rho_1\eta_1}+\sqrt{2\rho_2\eta_2})}$$
$$\times\mathrm{Re}\left[i\omega\left[\frac{Bl(l+1)}{R_0^2(\sqrt{\rho_1\eta_1}+\sqrt{\rho_2\eta_2})}\right.\right.$$
$$\left.\left.+(-i\omega)^{3/2}\right]\right]^{-1} . \tag{63}$$

Integrating this expression over all frequencies, we obtain

$$\langle |\nu_{lm}(t)|^2\rangle = \frac{k_B T}{R_0^2 B} , \tag{64}$$

in agreement with the static correlator obtained from the Boltzmann distribution with the energy (8).

The spectral densities of the amplitudes (49) determine the correlation functions of the velocity inside the micelle. In the approximation $|x_{1,2}| \ll |y_{1,2}| \ll 1$, they have the same frequency dependence as in Eq. (52). In this approximation, we have calculated the spectrum of the micelle or vesicle mass density fluctuations. The spectrum is determined by the fluctuations of the amplitudes C_1^L. Using the properties of spherical functions, it can be expressed in the form

$$\langle \delta\rho_1(\mathbf{r},t)\delta\rho_1(\mathbf{r}',t')\rangle_\omega$$
$$= \frac{k_B T\rho_1\eta_1}{4\pi^2 c_1^4(\eta_1+\eta_2)}\,\frac{\omega^2}{1+(\omega\nu_{1\|}/c_1^2)^2}$$
$$\times\sum_{l>1} P_l(\cos(\mathbf{r},\mathbf{r}'))\left[\frac{rr'}{R_0^2}\right]^l$$
$$\times\frac{(l+1)(2l+1)(2l+3)q_l}{\alpha_l l(l-1)(l+2)[1+(\omega\tau_{1\alpha})^2]} . \tag{65}$$

The above given equations allow one to write the spectra of the hydrodynamic correlation functions corresponding to the surface collective modes. The complete results for the correlation functions of hydrodynamic fields are the sums of contributions from both the surface mode and the bulk modes (30), (31).

VI. DYNAMIC STRUCTURE FACTOR OF MICROEMULSIONS

The effects of compressibility and consistent calculations of the density fluctuation spectra are of considerable interest in various applications. For example, the fluctuations of density determine the spectra of inelastic scattering from the solutions of micelles and vesicles. The collective excitations have an effect on the scattering cross section with small energy transfers as in the slow neutron and visible light scattering. The obtained spectrum of the mass density fluctuations can be used to determine this cross section and to interpret the neutron spin-echo experiments on such systems [25]. In our recent paper [26] we considered microemulsions of incompressible bulk fluids also taking into account the redistribution of the surfactant density at the micelle surface. The dynamic structure factor (DSF) of the inelastic scattering of neutrons has been found there. In the region of frequencies much larger than the frequency of capillary waves, it predicts the existence of satellite peaks (with respect to the central peak of the DSF) which are determined mainly by the dynamics of surfactants. The central peak is connected with the fluctuations in the droplet shape. Comparing the obtained analytical formulas with the experiment we have, in particular, estimated a bending elasticity coefficient to be about three times smaller than its value found in Ref. [25]. Smaller bending elasticity was reported also from experiments based on Kerr-effect measurements [27] (for more references and discussion about the confrontation of the theoretical ideas with experimental results see Refs. [28] and [29]; the latter work presents also a simple phenomenological approach describing the formation of thermodynamically stable spherical microemulsion droplets in a dilute suspension). In the present paper, we give a more general result concerning

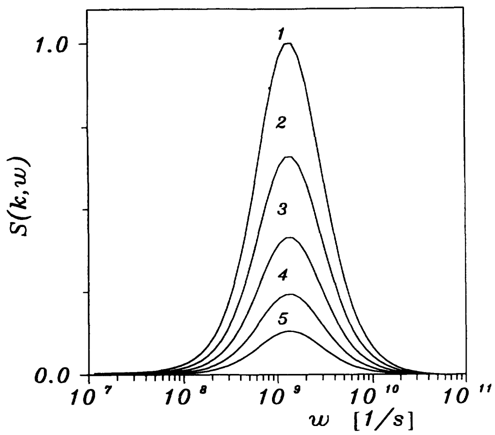

FIG. 1. Dynamic structure factor of an oil microemulsion droplet (with the parameters of castor oil) in water. The droplet radius is $R_0=400$ Å, and $kR_0=0.5$ (curve 1), 0.45 (2), 0.4 (3), 0.35 (4), and 0.3 (5). Surfactant fluctuations are not considered.

the DSF of microemulsions that takes into account the compressibility of the bulk fluids. Based on the density-density correlation function from Eq. (31) and the results of Sec. IV, one can determine the DSF as a Fourier transform in space

$$S(\mathbf{k},\omega)=\int\int d\mathbf{r}\,d\mathbf{r}'\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')]\times\langle\delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r}',t')\rangle_\omega\,. \tag{66}$$

The result of integrating for the DSF of a micelle is

$$S_1(k,\omega)\propto\left[\frac{\rho_1R_0^3}{c_1}\right]^2\frac{\omega^2}{1+(\omega\nu_{1\parallel}/c_1^2)^2}\times\sum_l(2l+1)\left|j_l(kR_0)\frac{Q(kR_0)-Q(x_1)}{(kR_0)^2-x_1^2}\right|^2\times\langle|C_{1l}^L|^2\rangle_\omega\,. \tag{67}$$

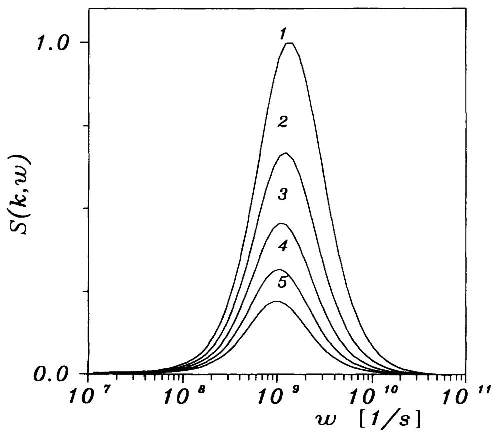

FIG. 2. Dynamic structure factor of the same oil droplet as in Fig. 1, with $R_0=400$ Å, $kR_0=0.2$, and various solvent viscosities: $\eta_2=0.001$ (curve 1), 0.1 (2), 0.2 (3), 0.3 (4), and 0.4 (5) kg/(m s). Surfactant fluctuations are not considered.

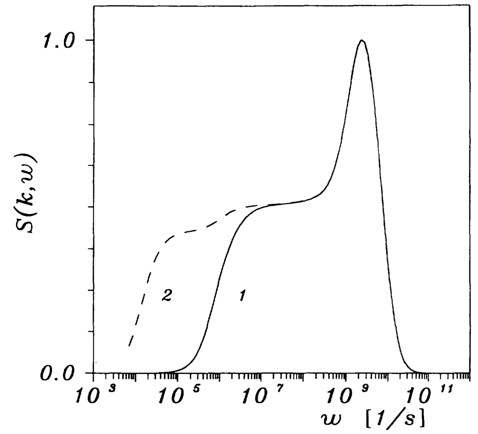

FIG. 3. Dynamic structure factor of a microemulsion droplet in the low-frequency region for two surface moduli B [Eq. (8)]: $B=0.05$ (curve 1) and $B=0.008$ J/m^2 (curve 2). Other parameters are as follows: $kR_0=0.3$, $R_0=400$ Å, $\rho_1=900$; $\rho_2=1000$ kg/m^3, $\eta_1=1$; $\eta_2=0.2$ kg/m s, $\zeta=0.75\eta$, $c_1=1400$; $c_2=1500$ m/s, $\alpha_{l=2}=10^{-4}$ J/m^2; $\rho_s=4.5\times10^{-7}$ kg/m^2.

The structure factor for the micelle environment, $S_2(k,\omega)$, can be found analogously. The results is the same as given by Eq. (67) if the index 1 is replaced by 2 and $Q(x_1)$ by $H(x_2)$.

The numerical calculations of the DSF for an individual microemulsion droplet, $S_1(k,\omega)$, are represented here by Figs. 1–4. Figure 1 illustrates the dependence of the DSF on kR_0 for the oil droplet (with the parameters of castor oil) in water. Figure 2 shows the DSF of the same oil droplet but for constant kR_0 and various solvent viscosities. In both the cases, the surfactant is not taken into account. The DSF in the presence of surfactant is given by Figs. 3–4. The dependence on various surface

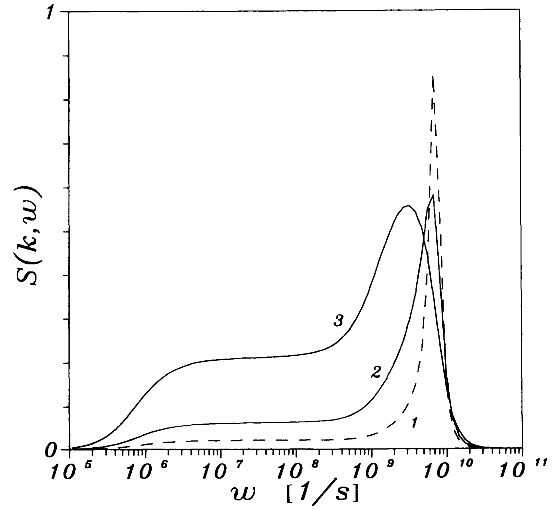

FIG. 4. Dynamic structure factor of a microemulsion droplet for various solvent viscosities η_2: 0.05 (curve 1), 0.1 (2), and 0.2 kg/m s (curve 3). The droplet radius is $R_0=400$ Å, $kR_0=0.2$, and $B=0.05$ J/m^2. Other parameters are the same as in Fig. 3.

moduli B [see Eq. (8)] is considered in Fig. 2, while Fig. 4 illustrates the change of the DSF when the solvent viscosity coefficient η_2 changes.

These figures can be supplemented by the following note. The numerical analysis that we carried out showed that the form of the DSF is weakly sensitive to the value of the surface tension coefficient. Besides this, the contribution to the DSF that is due to the random sources distributed in the volume of the droplet (i.e., not at the surface) is small for $l > 1$ and $kR_0 < 0.5$, and can be neglected. For the values of parameters that have been used in our calculations, the main contribution is given by the nearest surroundings to the interface. The contribution of the fluctuating surroundings rapidly disappeared with the distance from the droplet surface. This allows us to conclude that the DSF of the microemulsion in our approximation consists, in fact, of additive contributions given by the dynamic structure factors of independent droplets and is simply proportional to their concentration. At the same time, the effect on the DSF given by the nearest surroundings exhibits itself through the solvent viscosity as is demonstrated by the presented numerical calculations.

VII. CONCLUSIONS

We have investigated the thermal surface and bulk hydrodynamic fluctuations of fluid droplets (micelles and vesicles) coated with a thin film and immersed in a fluid medium. There are two equivalent ways of finding the equilibrium correlation functions for such systems. In the first method, 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 time-dependent correlation functions can be found if the static correlation functions, which determine the amplitudes of the fluctuations, are known. Such a method was used by us in Ref. [26], where a more simple case of incompressible fluids was considered. Here, we have used the second method based on a solution of hydrodynamic and boundary equations including Langevin forces (fluctuating stress tensor). According to Ref. [7], this method is inappropriate for problems such as we have here in which the stresses must satisfy conditions on the boundary. However, dividing the solution to the contributions corresponding to the fields excited by the random volume stresses and the fields excited by the surface sources, the application of the fluctuation-dissipation theorem allowed us to find the spectral densities of the hydrodynamic correlation functions of interest in a quite simple way. The approach based on the FDT has been already used in Ref. [15] to study the shape fluctuations of micelles assuming the bulk fluids inside and outside the micelle being incompressible. In that work, only the radial components of random forces on the surface have been taken into account. This means that only the so-called poloidal velocity fields [30] are studied and the toroidal mode is neglected ($C_{1,2}^{M}=0$ in our notation). This is true in the case of incompressible bulk fluids [18], however, for compressible fluids both the poloidal and toroidal modes exist. Moreover, the tangential random forces also lead to contributions to the fluctuating poloidal fields. Our approach includes both the radial and tangential random stresses acting at the interface. The liquids are considered to be compressible. We have also taken into account the redistribution of the surfactant molecules on the micelle surface. The surface energy density depends on the curvature which may be significant for micelles with small surface tension. It is worth mentioning that in our approach, we have assumed the surfactant to be insoluble in both the volume liquids (inside and outside the microemulsion droplet). Other possible situations which are necessary to consider in a more general theory are well described in Ref. [29]. In some cases our approximation (when the flow of surfactants into the bulk phase is neglected) will be no longer valid.

The contribution to the spectral densities for the bulk hydrodynamic fields of the fluctuating droplet differs from that for a homogeneous unbounded liquid by a discrete character of the wave numbers. The surface excitations strongly depend on the relation between the droplet radius, the penetration depth of viscous wave and the sound wavelength. We have considered a few special cases of such excitations. For micelles, in the case when the presence of surfactants on the droplet surface is negligible (incompressible surface layer), these excitations are overdamped and the spectrum is nearly a Lorentzian with the relaxation time $\tau_{\alpha 1}$ from Eq. (54). For model (impenetrable) vesicles, the condition $(\omega_1/\omega_0)^2 \sim \eta^2/\alpha R_0 \ll 1$ from Eq. (58) is satisfied. This corresponds to the low-damped capillary wave for the droplets with large radii. We have also obtained the spectrum of fluctuations of the surfactant concentration amplitudes that coincides with the previously found redistribution mode [9]. In this paper, we presented an illustrative numerical analysis which shows the dependence of the DSF on various parameters of the system. For the detailed comparison of the theory with experiment, the obtained DSF has to be averaged over the equilibrium distribution in the droplet radii. We assumed that such an averaging leads to small corrections that is true if the polydispersity of the droplets is small compared to unity. This is not always an experimental situation. Thus, the precise analysis requires explicit calculations of the relevant thermodynamic parameters based on a rigorous treatment of the thermodynamics of microemulsion systems [29].

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[1] L. M. Prince, *Microemulsions. Theory and Practice,* (Academic, New York, 1977).

[2] *Physics of Complex and Supramolecular Fluids,* edited by S. A. Safran and N. A. Clark (Wiley, New York, 1987).

[3] *Surfactants in Solution,* edited by K. Mittal and B. Lindman (Plenum, New York, 1984 and 1987).

[4] *Physics of Amphiphilic Layers,* edited by J. Meunier, D. Langevin, and N. Boccara (Springer, New York, 1987).

[5] R. Lipowsky, Nature (London) **349**, 475 (1991).

[6] S. A. Safran, in *Strcuture and Dynamics of Supramolecular Aggregates,* edited by S. H. Chen, J. S. Huang, and P. Tartaglia (Kluwer Academic, Dordrecht, 1991).

[7] L. C. Sparling and J. E. Sedlak, Phys. Rev. A **39**, 1351 (1989).

[8] W. Helfrich, Z. Naturforsch. Teil B **103**, 67 (1975).

[9] V. V. Lebedev and A. R. Muratov, Zh. Eksp. Teor. Fiz. **95**, 1751 (1989) [Sov. Phys. JETP **95**, 1751 (1989)].

[10] F. Szoka, Jr. and D. Papahadjopoulos, Annu. Rev. Biophys. Bioeng. **9**, 467 (1980).

[11] P. Meleard, M. Mitov, J. F. Faucon, and P. Bothorel, Europhys. Lett. **11**, 355 (1990).

[12] M. B. Schneider, J. T. Jenkins, and W. W. Webb, J. Phys. (Paris) **45**, 1457 (1984).

[13] S. T. Milner and S. A. Safran, Phys. Rev. A **36**, 4371 (1987).

[14] G. A. Levachova, E. A. Manykin, and P. P. Poluektov, Mech. Fluids Gases (Moscow) **2**, 17 (1985).

[15] S. Ljunggren and J. Ch. Eriksson, J. Chem. Soc., Faraday Trans. 2, **85**, 1553 (1989).

[16] E. van der Linden, D. Bedeaux, and M. Borkovec, Physica A **162**, 99 (1989).

[17] J. Melema, C. Blom, and J. Beekwilder, Rheol. Acta **26**, 418 (1987).

[18] V. Lisy, Phys. Lett. A **150**, 105 (1990).

[19] V. Lisy, A. V. Zatovsky, and A. V. Zvelindovsky, Physica A **183**, 262 (1992).

[20] L. D. Landau and E. M. Lifshitz, Zh. Eksp. Teor. Fiz. **32**, 618 (1957) [Sov. Phys. JETP **32**, 618 (1957)].

[21] L. D. Landau and E. M. Lifshitz, *Hydrodynamics* (Nauka, Moscow, 1986).

[22] S. M. Rytov, *Introduction to Statistical Radiophysics* (Nauka, Moscow, 1966).

[23] A. V. Zatovsky and A. V. Zvelindovsky, J. Tech. Phys. (St. Peterburg) **60**, 129 (1990).

[24] P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Vol. 2.

[25] J. S. Huang, S. T. Milner, B. Farago, and D. Richter, Phys. Rev. Lett. **59**, 2600 (1987).

[26] V. Lisy and A. V. Zatovsky, Phys. Lett. A **166**, 253 (1992).

[27] M. Borkovec and H.-F. Eicke, Chem. Phys. Lett. **157**, 457 (1989).

[28] B. Farago, D. Richter, J. S. Huang, S. A. Safran, and S. T. Milner, Phys. Rev. Lett. **65**, 3348 (1990).

[29] M. Borkovec, Adv. Colloid. Interface Sci. **37**, 195 (1992).

[30] S. Chandrasekhar, *Hydrodynamics and Hydrodynamic Stability* (Clarendon, Oxford, 1968).