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Fluctuations of compressible droplets: the role of surface excitations

A. V. Zvelindovsky and A. V. Zatovsky

Department of Theoretical Physics and Research Institute for Physica, I. I. Mechnikov Odessa State University, Petra Velikogo 2, Odessa 270100, Ukraine

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Abstract. — The thermal fluctuations of nearly spherical micelles are considered. The viscosity and compressibility of the surfactant layer and of the bulk fluids are taken into account as well as the bending energy. The dynamical equations for surface and bulk variables are the linearized hydrodynamic equations with random sources of stresses. Employing the fluctuation-dissipation theorem the spectral densities of fluctuations related with surface excitations were derived. The behaviour of the dynamical structure factor $S(k, \omega)$ is discussed for various droplet parameters.

1. Introduction.

The existence of so-called amphiphilic molecules is the origin of local constraints which lead to spontaneous aggregation into microemulsions. The microemulsion is a dispersion of micelles which are liquid droplets stabilised by a monolayer of tensioactive molecules in aqueous or apolar solvent. The nature and dynamics of interface play a great role for a wide variety of physical and chemical phenomena in microemulsions [1-3]. The surface is an important factor in many industrial applications such as oil-displacement mechanisms in enhanced oil recovery, coalescence of fluid droplets, rheology of emulsions, etc. [4, 5]. Fluctuations of micelles are intensively studied by experimental techniques, for instance, by spin-echo neutron scattering [6] or video microscopy [7].

Already Rayleigh and Lamb have studied theoretically the behaviour of fluctuating droplets in terms of the phenomenological parameters such as surface tension and densities of liquids [8]. In order to consider the dissipation effects the oscillations of viscous droplets immersed in viscous fluid have been investigated by a number of authors [9-12]. Sparling and Sedlak have developed the viscous droplet model taking also into account the viscosity and compressibility of surface film [13].

A description of microemulsion droplets requires additional physical concepts because the coefficient of the micelle surface tension is zero or practically zero, and the dependence of the surface energy on the curvature should be taken into consideration. Such approach has been put
forward by Helfrich [14]. then it has been developed and used in many works (see, for example, [7, 15-20]). In Helfrich’s theory the surface energy density is given by the expression

$$g = \alpha - \beta \left( \frac{1}{R_1} + \frac{1}{R_2} \right) + \frac{\kappa}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)^2 + \frac{\kappa}{R_1 R_2},$$

(1)

where $\kappa$ and $\bar{\kappa}$ are the elastic constants for cylindrical bending and saddle bending, respectively, $(1/R_1 + 1/R_2)/2$ and $1/R_1 R_2$ are the mean and Gaussian curvature. $\alpha$ determines the usual surface tension of the planar interface, $\beta/2 \kappa$ is so-called spontaneous curvature. The last term of (1) is in general omitted as the integral of Gaussian curvature over the surface is topological invariant. (It is $4 \pi \bar{\kappa}$ for spheres, ideal or deformed.) The most general development of Helfrich’s approach has been carried out in reference [17] where the surfactant redistribution mode was studied in addition to the deformations of micelle form. However, the authors of the papers [7, 14-19] disregarded the viscosity of surface layer.

Moreover, in all the above papers the bulk fluids were assumed to be incompressible and only the fluctuations of quantities that are closely associated with the deviations of the droplet shape from spherical have been studied. For this reason the approximate expression for the spectrum of the density fluctuations, which is solely determined by the shape fluctuations and the redistribution of surfactant at the micelle surface, has been obtained. However, as was noticed long ago in reference [21], the neglect of the bulk compressibility is inappropriate approximation in case when the scattering with small energy transfers is examined. Recently we have already studied the hydrodynamic fluctuations of a compressible droplet immersed in a compressible liquid [22-24]. In these articles, however, the interface is described by only one phenomenological parameter, the constant surface tension $\alpha$ [22, 23] or effective surface tension $\alpha_f$ [24], and only the radial components of random forces on the droplet surface are considered. This means that surfactant fluctuations are negligible and only the shape fluctuations occur.

In this paper we present the most general approach to the study of the thermal fluctuations of nearly spherical micelles. We regard the micelles as an ideal gas, assuming rather dilute micelle dispersions. So, we can focus our attention on the study of the dynamic properties of a separate micelle. The viscosity and compressibility of the surface film and the bulk fluids inside and outside the droplet are taken into account as well as the curvature energy (1) and the redistribution of the surfactant on the interface. Low-frequency collective excitations of the microemulsions are described in the framework of two- and three-dimensional hydrodynamics. The spectral densities of the correlation functions for hydrodynamic variables are found based on the fluctuation-dissipation theorem. The obtained results can also be helpful for the investigation of the excitations of vesicles and biological cell solutions.

2. Theory.

2.1 THE PHENOMENOLOGICAL MODEL. — The micelles are modelled by fluid drops immersed in a fluid with different properties and coated with an infinitely thin film. The fluctuating velocities $\mathbf{v}$ and densities of the interior and exterior fluids are solutions to the linearized continuity equation and the Navier-Stokes equation containing random stresses $\sigma_{ln}$

$$\frac{\partial}{\partial t} \delta \rho + \rho \div \mathbf{v} = 0,$$

$$\rho \frac{\partial \mathbf{v}_l}{\partial t} = -c^2 \nabla_t \delta \rho - \eta \mathbf{rot}_t \mathbf{rot} \mathbf{v} + \left( \frac{4}{3} \eta + \xi \right) \nabla_t \div \mathbf{v} + \nabla_n \sigma_{ln}.$$  

(2)
Here, \( \eta \) and \( \zeta \) are the shear and bulk viscosities, \( \delta \rho \) is the deviation from the equilibrium mass density \( \rho \), \( c \) is the sound velocity. For the sake of simplicity we neglect the fluctuations of temperature. In what follows, quantities referring to the interior (exterior) fluids will be labelled with \( 1(2) \).

Using spherical polar coordinates \( (r, \theta, \varphi) \), with origin at the centre of the droplet, we can describe a slightly deformed spherical micelle by the series of spherical harmonics

\[
R(\theta, \varphi, t) = R_0 \left( 1 + \sum_{\ell m} u_{\ell m}(t) Y_{\ell m}(\theta, \varphi) \right), \quad \ell \gg 2.
\]

where \( R_0 \) is the equilibrium radius of the droplet, \( -\ell \leq m \leq \ell \), and the maximum mode number will be of order \( \ell_{\text{max}} \sim \pi R_0/d \), where \( d \sim 5 \, \text{Å} \) is a typical molecular diameter [13]. The redistribution of the surfactant on the interface can be described analogously to (3)

\[
n^\delta(\theta, \varphi, t) = n^\delta + \delta n^\delta = n^\delta \left( 1 + \sum_{\ell m} v_{\ell m}(t) Y_{\ell m}(\theta, \varphi) \right), \quad \ell \gg 1,
\]

where \( \delta n^\delta \) is a small deviation of surfactant density from the equilibrium value \( n^\delta \). The surface tension depends on the surfactant concentration \( (4) \) [25], and we define the elastic modulus of interface film as \( B = -n^\delta \partial \alpha (n^\delta)/\partial n^\delta > 0 \). The dependence on \( n^\delta \) for the other coefficients of expansion \( (1) \) can be neglected [17]. We assume that the infinitely thin surface layer behaves as a compressible Newtonian surface fluid described by two viscosities \( \eta_s \) and \( \zeta_s \). Besides, the surface layer is chosen to be insoluble in the surrounding liquids. Then the boundary conditions derived from the surface momentum balance are

\[
\rho_s \frac{\partial v_s^r}{\partial t} + \sum_{\ell m} \alpha_\ell \frac{\partial}{\partial \theta} \left( \ell (\ell + 1) - 2 \right) u_{\ell m} Y_{\ell m} = \delta p_1 - \delta p_2 + \sigma^{(2)}_{\tau\tau} - \sigma^{(1)}_{\tau\tau} +
\]

\[
+ f_s - \eta_s \text{rot}_r \text{rot} v^s + \left( \frac{4}{3} \eta_s + \zeta_s \right) \nabla_r \text{div} v^s,
\]

\[
\rho_s \frac{\partial v_s^t}{\partial t} = (\sigma^{(2)}_{\tau t} n^t_k) - (\sigma^{(1)}_{\tau t} n^t_k) + \frac{\partial \alpha}{\partial n^\delta} \nabla_t \delta n^\delta + f_t -
\]

\[
- \eta_s \text{rot}_t \text{rot} v^s + \left( \frac{4}{3} \eta_s + \zeta_s \right) \nabla_t \text{div} v^s,
\]

providing that there is no flow of mass through the surface film. Here the indices \( r \) and \( t \) denote the radial and tangential components of the vectors in the spherical coordinate system, \( n \) is the normal to the interface (here and below, \( n \) is directed outside the sphere), \( \rho_s \) \( v^s \) is the surface momentum density, \( p_1 = \delta p_1 + p_0 + 2 \alpha/R_0 \), \( p_2 = \delta p_2 + p_0 \), \( p_0 \) is the pressure at \( r = \infty \), and \( \delta p_1 = c_1^2 \delta \rho_j \). \( f \) is the random surface forces. The components of the viscous stress tensor \( \sigma^{(i)}_{\tau t} \) are [26]

\[
\sigma^{(i)}_{\tau t} = 2 \eta_j \frac{\partial v_{jr}}{\partial r} + \left( \zeta_j - \frac{2}{3} \eta_j \right) \text{div} v_j,
\]

\[
(\sigma^{(1)}_{\tau t} n^t_k) = \eta_j \left( \frac{\partial}{\partial r} - \frac{1}{r} \right) v_{jt} + \eta_j \nabla_t v_{jr},
\]

since the bulk fluids are compressible. The second term of (5) has the form of the fluctuating part of Laplace pressure. Parameter \( \alpha_\ell \) is determined by the coefficients of (1)

\[
\alpha_\ell = \alpha - \frac{2 \beta}{R_0} + \frac{\kappa (\ell + 1)}{R_0^2},
\]
it must be positive lest the micelle is instable with respect to small perturbations. The surface density can be expressed in terms of the velocities by using the surface-continuity equation

$$\frac{\partial \delta n^r}{\partial t} + n^r \text{div} \mathbf{v}^r = 0.$$  \hfill (9)

In addition to (5), (6), (9), the velocity must be continuous across the interface and equal to the velocity of surfactant motion

$$v_1 = v_2 = v^r, \quad v^r = \dot{r}.$$  \hfill (10)

In the linear approach all the boundary conditions (5), (6), (9), (10) may be taken on the surface of the undeformed sphere \(r = R_0\).

It is convenient to rewrite all equations in a Fourier transform retaining the same notation for the Fourier components of the quantities and replacing the differentiation in time by \(-i\omega\).

Owing to the linearity of the hydrodynamic and boundary equations the total solution of the boundary-value problem can be represented as a sum of two contributions. The first one is the solution of Dirichlet problem for the velocity which satisfies the inhomogeneous equations (2). The second one is determined by the inhomogeneous boundary conditions (5), (6), (9), (10) and by equations (2) without random bulk forces \(\nabla_v \sigma^r_{l m}\). Thus, the total spectral densities of the hydrodynamic correlation functions split into two independent contributions corresponding to the random volume stresses \(\sigma^r_{l m}\) in (2) and to the random surface forces \(f^r\). The first term was earlier found in [27] where we also took into account fluctuations of the temperature. It turns out that the first contribution to the dynamic structure factor is small compared to the second one when the energy transfer is small and the sizes of micelles are of the order of \(10^2 - 10^3 \text{Å} [23]\). For this reason we shall investigate only the hydrodynamic fluctuations excited by the surface random sources.

2.2 THE SPECTRAL DENSITIES OF THE FLUCTUATIONS. — The solutions of the Navier-Stokes equation in the spherical coordinate system can be found in two different ways using the following expansions :

$$v_1(r, \omega) = \sum_\lambda \left[ P_\lambda(\theta, \varphi) F_\lambda(r, \omega) + B_\lambda(\theta, \varphi) G_\lambda(r, \omega) + C_\lambda(\theta, \varphi) H_\lambda(r, \omega) \right], \quad \lambda = \ell, m, \hfill (11)$$

or

$$v_1(r, \omega) = \sum_\lambda \left[ C^L_\lambda(\omega) L_\lambda(k_{1\parallel} r) + C^N_\lambda(\omega) N_\lambda(k_{1\perp} r) + C^M_\lambda(\omega) M_\lambda(k_{1\perp} r) \right], \hfill (12)$$

where \(P, B\), and \(C\) are spherical vector functions, \(L, N, M\) are basic functions for the vector Helmholtz equations. They are [28]

$$P_{\ell m} = \frac{r}{\ell} Y_{\ell m}(\theta, \varphi), \quad B_{\ell m} = \frac{r}{\sqrt{\ell (\ell + 1)}} \nabla Y_{\ell m}, \quad C_{\ell m} = \frac{\text{rot} (r Y_{\ell m})}{\sqrt{\ell (\ell + 1)}},$$

$$L_{\ell m} = \frac{1}{k_{1\parallel}} \nabla [Y_{\ell m} \times (k_{1\parallel} r)], \quad M_{\ell m} = \frac{\text{rot} (r Y_{\ell m} \times (k_{1\perp} r))}{k_{1\perp}}, \quad N_{\ell m} = \frac{1}{k_{1\perp}} \text{rot} M_{\ell m}.$$  \hfill (13)
Here, $f(t(kr))$ are the spherical Bessel functions. From equations (2) without inhomogeneous terms one can easily find the relations of the coefficients of expansions $F_\lambda$, $G_\lambda$, $H_\lambda$ to $C_\lambda$ (below, the indices of the spherical harmonics, $\lambda = \ell, m$, will be omitted):

$$F_\ell = C_1^\ell f(k_1 r) + C_1^N \frac{\ell(\ell + 1)}{k_1 r} f(k_1 r),$$

$$G_\ell = \sqrt{\ell(\ell + 1)} \left[ C_1^\ell f(k_1 r) + C_1^N \left( f(k_1 r) + \frac{j_\ell(k_1 r)}{k_1 r} \right) \right],$$

$$H_\ell = \sqrt{\ell(\ell + 1)} C_1^M f(k_1 r),$$

where $j_\ell(x) = \frac{\partial j_\ell(x)}{\partial x}$, and we have used the notation

$$k_1 \left( \frac{i \omega \rho_1}{\eta_1} \right)^{1/2}, \quad k_{1\parallel} = \frac{\omega}{c_1} \left( 1 - \frac{i \omega \nu_{11}}{c_1^2} \right)^{-1/2}, \quad \nu_{11} = \left( \xi + \frac{4}{3} \eta \right)i \rho .$$

Substituting the spherical Hankel functions of the first kind, $h_\ell^{(1)}$, for the spherical Bessel functions $j_\ell$ and the indices $l$ for $2$ we obtain the exterior solutions. They correspond to diverging longitudinal and transverse damped waves. Note that the quantities $k_{1\perp}$ and $k_{1\parallel}$ have two complex conjugate values. To exclude the exponential divergence of the solutions as $\ell \rightarrow \infty$ we use the values which have positive imaginary parts.

From the boundary conditions (5), (6), (9), (10) and the solutions (15) we obtain the inhomogeneous algebraic equations for the integration constants $C_{\ell}'$. The equations determining the coefficients $C_{\ell,2}$ are the simplest, they are independent from the other ones. For example,

$$C_1^M = A_1^M h_1 .$$

$$A_1^M = \frac{R_0}{j_\ell(y_1) \sqrt{\ell(\ell + 1)}} \left\{ - i \omega \rho_1 R_0 + \eta_1 (\mathcal{Q}(y_1) - 1) - \eta_2 (\mathcal{X}(y_2) - 1) + \eta_3 \frac{\ell(\ell + 1)}{R_0} \right\} .$$

The coefficients $C_{1,2}^{L,N}$ are determined by the following set of six equations

$$C_1^c \ell(\ell + 1) - 2 \mathcal{X}(x_2) + C_1^N \ell(\ell + 1) (\mathcal{X}(y_2) - 1) = - i \omega R_0 \nu_{1m} ,$$

$$C_1^c \ell(\ell + 1) - 2 \mathcal{Q}(x_1) + C_1^N \ell(\ell + 1) (\mathcal{Q}(y_1) - 1) = - i \omega R_0 \nu_{1m} ,$$

$$C_1^c \mathcal{Q}(x_1) + C_1^N \ell(\ell + 1) = - i \omega R_0 u_{1m} ,$$

$$C_2^c \mathcal{X}(x_2) + C_2^N \ell(\ell + 1) = - i \omega R_0 u_{1m} ,$$

$$u_{1m} \left[ \alpha_f (\ell + 2) (\ell - 1) - \rho_s \omega^2 R_0^2 \right]-$$

$$- C_1^c \left\{ \eta_1 y_1^2 + 4 \mathcal{Q}(x_1) - 2 \ell(\ell + 1) + \eta_3 \frac{\ell(\ell + 1)}{R_0} (1 - \mathcal{Q}(x_1)) \right\} +$$

$$+ C_1^N \ell(\ell + 1) \left\{ 2 \eta_1 (\mathcal{Q}(y_1) - 1) + \eta_3 \frac{\ell(\ell + 1) - \mathcal{Q}(y_1) - 1}{R_0} \right\} +$$

$$+ C_2^c \eta_2 y_2^2 + 4 \mathcal{X}(x_2) - 2 \ell(\ell + 1) - C_2^N \ell(\ell + 1) 2 \eta_2 (\mathcal{X}(y_2) - 1) +$$

$$+ i \omega \nu_{1m} \left( \frac{4}{3} \eta_s + \xi_s \right) = R_0 f^c , \quad (19)$$
\[ \nu_{\ell m} \left[ B - \frac{\rho \omega^2 R_0^2}{\ell (\ell + 1)} - i \omega \left( \frac{4}{3} \eta_\ast + \xi_\ast \right) \right] + u_{\ell m} \frac{2 \rho \omega^2 R_0^2}{\ell (\ell + 1)} = \\
+ 2 \eta_1 \left\{ \tilde{C}_i^L (\mathcal{Q} (x_1) - 1) - \tilde{C}_i^N \left[ \mathcal{Q} (y_1) + 1 - \ell (\ell + 1) + \frac{1}{2} y_1^2 \right] \right\} = \\
- 2 \eta_2 \left\{ \tilde{C}_i^L (\mathcal{J} (x_2) - 1) - \tilde{C}_i^N \left[ \mathcal{J} (y_2) + 1 - \ell (\ell + 1) + \frac{1}{2} y_2^2 \right] \right\} = g \frac{R_0}{\sqrt{\ell (\ell + 1)}}, \]

where, in addition, we have introduced the notation

\[ \tilde{C}_i^L = C_i^L u_i (x_i) y_i, \quad \tilde{C}_i^N = C_i^N u_i (y_i) \; \quad u_i = \begin{cases} j \nu, & i = 1 \\ h_\ell^{(1)}, & i = 2 \end{cases}, \]

\[ \mathcal{Q} (z) = z \frac{\partial}{\partial z} \ln j_\ell (z), \quad \mathcal{J} (z) = z \frac{\partial}{\partial z} \ln h_\ell^{(1)} (z), \quad z = \{ x_i, y_i \}, \] (20)

\[ x_{1, 2} = k_{1, 2 \perp} R_0, \quad y_{1, 2} = k_{1, 2 \perp} R_0, \]

and \( f^*, g^*, h^* \) are the amplitudes of the random force \( f \) expanded in the series of the spherical vector functions \( P, B \) and \( C \) (cf. (11)). As above, the index \( s \) denotes the quantities related to the surface. The roots of the determinant of the set of (17) and (19) correspond to all kinds of the collective excitations of micelles in our model. Equations (19) can be transformed into the form that is analogous to equation (17):

\[ \tilde{C}_j^L = A_j^{(L)} f^* + A_j^{(N)} g^*, \quad \tilde{C}_j^N = A_j^{(L)} f^* + A_j^{(N)} g^*, \quad j = 1, 2. \] (21)

The explicit expressions for \( A_j^{(K)} (\ell = \{ L, M \} ; K = \{ L_f, L_g, N_f, N_g \}) \) can be easily found by using Kramer's rule. As they have a very bulky form, we do not write them here. Note, that we shall set \( A_j^{(L), (N)} \big|_{\ell = 1} = 0 \) because \( u_{1, m} = 0 \).

To employ the fluctuation-dissipation theorem we must know the expression for energy dissipation in the system under the action of the random sources [29]. In our case, the dissipation is caused by both the bulk viscous forces and the surface ones. Therefore the random surface sources can be represented as a sum of two terms, \( f = f^{(\sigma)} + f^{(\nu \sigma)} \). The first one is determined by the difference of the bulk spontaneous stresses of (2) at the interface, \( f^{(\sigma)} = (\sigma_{1k}^{(2)} - \sigma_{1k}^{(1)}) n_{1k} \). The second one is the random surface sources proper \( f^{(\nu \sigma)} = \nabla \sigma_{ik} \).

Applying Gauss theorem to the well-known hydrodynamic formula for the dissipation of energy [26], we obtain the expression for the power absorbed in the bulk fluid due to random surface sources,

\[ Q^{(\sigma)} = - \oint ds \left[ v_i^{(1)} \sigma_{ik}^{(1)} n_k - v_i^{(2)} \sigma_{ik}^{(2)} n_k \right] = \oint ds \; v_i^{(\sigma)} f_i^{(\sigma)} \] (22)

where \( \oint ds \) denotes the integration over the droplet surface \( S \). Analogously, we find the energy dissipated in the two-dimensional surface fluid

\[ Q^{(\nu \sigma)} = - \oint ds \left( \sigma_{ik} n_i \nabla v_i \right) = \oint ds (v_i \; \nabla \sigma_{ik}) = \oint ds v_i^{(\sigma)} f_i^{(\nu \sigma)}. \] (23)

Averaging the sum of (22) and (23) over time and inserting (11) yield

\[ Q = \text{Re} \; R_0^2 \sum_{\lambda} \left( F_{\lambda}^{\ast} f_{\lambda}^{\ast} + G_{\lambda}^{\ast} g_{\lambda}^{\ast} + H_{\lambda}^{\ast} h_{\lambda}^{\ast} \right), \] (24)
and, via (10) and (15),

$$Q = \text{Re} R_0^2 \sum \alpha (C_{1,1} f_{1,1}^* + C_{N,1} f_{N,1}^* + j_1(y_1) \sqrt{\ell(L + 1)} C_{1,1}^M h_{1}^*),$$

where $f_{L,N}$ are the new conjugate generalized forces for the generalized coordinates $C_{L,N}^*$:

$$f_L = Q^*(x_1) f^* + \sqrt{\ell(L + 1)} g^*,
\quad f_N = \ell(L + 1) f^* + \sqrt{\ell(L + 1)} (Q^* (y_1) + 1) g^*.$$  \hspace{1cm} (26)

Application of the fluctuation-dissipation theorem to equations (17), (21) and (25) leads to the following spectral densities of the fluctuating velocity amplitudes

$$\langle |\tilde{C}_{1,1}^L|^2 \rangle_\omega = \frac{k_B T}{\pi R_0^2} \text{Re} \frac{A_{1,1}^L (1 + Q^* (y_1)) - \sqrt{\ell(L + 1)} A_{1,1}^a}{(1 + Q^* (y_1)) Q^*(x_1) - \ell(L + 1)},$$

$$\langle |\tilde{C}_{1,1}^N|^2 \rangle_\omega = \frac{k_B T}{\pi R_0^2} \text{Re} \frac{A_{1,1}^N Q^*(x_1) \sqrt{\ell(L + 1)} - A_{1,1}^f}{(1 + Q^*(y_1)) Q^*(x_1) - \ell(L + 1)},$$

$$\langle |\tilde{C}_{1,1}^M|^2 \rangle_\omega = \frac{k_B T}{\pi R_0^2} \text{Re} \frac{A_{1,1}^M}{j^* (y_1) \sqrt{\ell(L + 1)}},$$

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature and the asterisk denotes complex conjugation. Note that the spectral densities do not depend on $m$. The spectral densities for the amplitudes of the exterior velocity have an analogous form, for example,

$$\langle |\tilde{C}_{2,1}^L|^2 \rangle_\omega = \frac{k_B T}{\pi R_0^2} \text{Re} \frac{A_{2,1}^L (1 + \mathcal{K}^* (y_2)) - \sqrt{\ell(L + 1)} A_{2,1}^a}{(1 + \mathcal{K}^* (y_2)) \mathcal{K}^* (x_2) - \ell(L + 1)}.$$  \hspace{1cm} (30)

The formulae obtained, equations (27-30), essentially differ from what was found in our preceding articles [22-24], where we neglected the tangential components of spontaneous surface sources of stresses, $g^*$ and $h^*$. Those results correspond to the fluctuations of a compressible droplet in the absence of surface concentration modes at the fluid-fluid interface is described by the surface tension alone. In this case, the spectral density for the amplitude $C_{1,1}^L$, for example, is (cf. (27))

$$\langle \tilde{C}_{1,1}^L \tilde{C}_{1,1}^{L,*} \rangle_\omega = \frac{k_B T}{\pi R_0^2} \text{Re} \frac{A_{1,1}^L \delta_{\lambda,\lambda'}}{Q^* (x_1)},$$

where $A_{1,1}^L$ is determined by the equations derived from the proper boundary conditions [22, 24],

Finally, the spectral densities (27-30) allow us to write the Euler velocity correlation function,

$$\langle v_1(r, t) v_1(r', t') \rangle_\omega = \sum_{\lambda} \langle |C_{1,1}^\Phi|^2 \rangle_\omega \Phi (r) \Phi^* (r'), \quad \Phi = \{L, N, M\}.$$  \hspace{1cm} (32)

and the density correlation function, by means of continuity equation,

$$\langle \delta \rho_1(r, t) \delta \rho_1(r', t') \rangle_\omega = \sum_{\ell m} \left\langle |C_{1,1}^\ell m|^2 \right\rangle_\omega \frac{\rho_1(k_{1,1})^2}{\omega^2} j_t(k_{1,1} r) j^*_t (k_{1,1} r') \times
\hspace{3cm} \times Y_{\ell m} (\theta, \varphi) Y_{\ell m}^* (\theta', \varphi').$$  \hspace{1cm} (33)
To obtain such correlation functions for the outer fluid one must use the suitable spectral densities of amplitudes (e.g. (30)) and the Hankel functions instead of the Bessel ones.

3. Results and discussion.

3.1 Surface fluctuations of micelles. — In spite of cumbersome form of the final results they can be simplified considerably in limiting cases when some parameters are taken to be small. Let us demonstrate this for two main surface variables. The spectral density of fluctuations of the displacement of a droplet surface is easily recovered from equation (19) and fluctuation-dissipation theorem

$$\langle |u_{m\alpha}^2| \rangle_{\omega} = \frac{1}{(\omega R_0)^2} \left[ \ell^2 (\ell + 1)^2 \langle |\tilde{C}_{\ell\lambda}\rangle^2 \rangle_{\omega} + |\Theta(x_1)|^2 \langle |\tilde{C}_{\ell\lambda}|^2 \rangle_{\omega} \right]. \quad (34)$$

The character of the collective excitations depends on the relationships among the dimensions of the droplet, the penetration depth of the viscous wave and the acoustic wavelength. Since a typical micelle size is of the order $10^2$-10$^3$ Å, one has $\omega R_0/c \ll 1$ for low-frequency acoustic excitations. If the penetration depth of the shear wave is large compared to the micelle radius, then $\omega R_0/v \ll 1$, and the oscillations will be hindered — one is dealing only with shape distortions. Suppose likewise that the effects of compressibility are insignificant, so that the conditions $|x_{1,2}| \ll |y_{1,2}| \ll 1$ hold. Neglecting all surface parameters except $\alpha_\ell$ and keeping only the leading terms in powers of $|y|$, we find from (34) and (27-28)

$$\langle |u_{m\alpha}^2| \rangle_{\omega} = \frac{k_B T}{\pi R_0^2} \left[ \frac{\omega^2 + (\tau_{\alpha}^{-1} - \omega^2 \tau_1)^2 - 1}{\alpha_\ell (\ell + 2)(\ell - 1) \tau_{\alpha}} \right], \quad (35)$$

where

$$\tau_{\alpha}^{-1} = \alpha_\ell (\ell + 2)(\ell + 1) \frac{\eta_1 + \eta_2}{R_0 q_\ell p_\ell}, \quad q_\ell = 2(\ell^2 - 1) \eta_1 + (2 \ell^2 + 1) \eta_2, \quad p_\ell = (2 \ell^2 + 4 \ell + 3) \eta_1 + 2 (\ell + 2) \eta_2, \quad (36)$$

$$\tau_1 = \frac{R_0^2}{q_\ell p_\ell} \left[ \frac{\rho_1 \ell (\ell + 1)(2 \ell + 1)(\eta_1 + \eta_2) + 2(\eta_1 - \eta_2)}{\eta_1(2 \ell^2 + 3)(2 \ell + 5) - \rho_2(2 \ell^2 - 1)(2 \ell - 1)} \right], \quad \rho_{\tau} = \rho_{\epsilon}/\ell + \rho_{\epsilon}/(\ell + 1).$$

This result agrees with that obtained in reference [19], where a dispersion relation was studied for micelles and vesicles formed in incompressible liquids. Since $\omega \tau_1 \ll 1$, the spectrum (35) is close to Lorentzian, with a width determined by (36), and corresponds to an overdamped mode of surface oscillations. The single-time correlation function of the surface displacements is determined by integrating (35) over all frequencies:

$$\langle u_{m\alpha}(t) u_{m\alpha}^*(t) \rangle = \frac{k_B T}{R_0^2 \alpha_\ell (\ell - 1)(\ell + 2) \left( 1 - \frac{\tau_1}{\tau_{\alpha}} \right)^{-1/2}} \quad (37)$$

As the square-root factor in (37) is close to unity, the main term of (37) coincides with the expression obtained previously by Milner and Safran [16].
Then compression effects are taken into account, the relaxation time $\tau_1$ acquires contributions linear in $\eta/c^2 \rho$, so that $\tau_1 \to \tau_1 + \gamma_1/\eta_1/c_1^2 \rho_1 + \gamma_2 \eta/c_2^2 \rho_2$ with dimensionless coefficients $\gamma_1, \gamma_2$.

Analogously to (34) we can write the correlator for surfactant concentration (4):

$$\langle \left| \nu_{l m} \right|^2 \rangle = \frac{\ell^2 (\ell + 1)^2}{(\omega R_0)^2} \left[ 1 - \frac{2 Q(x_1)}{\ell (\ell + 1)} \right]^2 \left[ \left| \tilde{C}_{1 A}^L \right|^2 \right] + \left[ Q(x_1) - 1 \right]^2 \left[ \left| \tilde{C}_{1 A}^N \right|^2 \right] \omega \right], \quad \text{(38)}$$

Let the penetration depth of the shear wave be small, $|y_{1, 2}| \gg 1$, and the vibration frequencies at small viscosities are large compared to those for the capillary waves. If $|x_{1, 2}| \ll 1$ as before and $\rho_1 \ll R_0 \rho_1$, we obtain the following simplification of (38) neglecting surface film viscosities:

$$\langle \left| \nu_{l m} \right|^2 \rangle = \frac{3 \ell (\ell + 1) k_B T}{\pi R_0^2 B (\sqrt{2} \xi_1 + \sqrt{2} \xi_2)} \Re \left[ \frac{i \omega B \ell (\ell + 1)}{R_0^2 (\sqrt{\xi_1} + \sqrt{\xi_2})} - (- i \omega)^{5/2} \right]^{-1}, \quad \text{(39)}$$

The zero of the denominator of (39) fully coincides with solution of dispersion relation obtained earlier in [17, 19]. The static correlator has the simple form

$$\langle \nu_{l m}(t) \nu_{l m}^*(t') \rangle = \frac{k_B T}{R_0^2 B}, \quad \text{(40)}$$

which is the same as is obtained from the Boltzmann distribution with the surface energy [17].

3.2 THE DYNAMICAL STRUCTURE FACTOR. — In this subsection we shall study the behaviour of the dynamical structure factor (DSF) that is of concern for the fluctuation theory. The structure factor is determined by the density-density correlation function:

$$S(k, \omega) = \int \int d\mathbf{r} \, d\mathbf{r}' \, e^{i \mathbf{k}(\mathbf{r} - \mathbf{r}')} \langle \delta \rho(\mathbf{r}, t) \delta \rho(\mathbf{r}', t') \rangle \omega \right), \quad \text{(41)}$$

where $\int \int d\mathbf{r}$ denotes integration over volume. The structure factor, $S(k, \omega)$, can be calculated by the way of reference [30], where we have examined the density fluctuations of compressible liquid within the rigid spherical cavity. Substitution of (33) reduces equation (41) to the expression that contains square of volume integral. Using the decomposition

$$e^{i \mathbf{k} \mathbf{r}} = \sum_{m} i^n (2 \nu + 1) (2 - \delta_{\mu 0}) (\nu + \mu)! (\nu - \mu)! j_n(kr) Y_{\nu \mu}(\theta, \varphi) Y_{\nu \mu}^*(\theta, \varphi) \right), \quad \text{(42)}$$

then leads, after summation over $\nu, \mu, m$ and integration over $\theta, \varphi$ and $r (0 \leq r \leq R_0)$, to the final result for the DSF of a micelle

$$S_1(k, \omega) \propto \left( \frac{\rho_1 R_0^3}{c_1^2} \right)^2 \frac{\omega^2}{1 + (\omega c_1^2 \rho_1)^2} \times \sum T (2 \ell + 1) \left| j_\ell(kR_0) \frac{Q(kR_0) - Q(x_1)}{(kR_0)^2 - x_1^2} \right|^2 \left( \left| C_{1 A}^L \right|^2 \right)_\omega \quad \text{(43)}$$
The structure factor for the micelle environment \((R_0 \leq r \leq \infty)\) is found analogously

\[ S_2(k, \omega) \propto \left( \frac{\rho_2 R_0^3}{c_2} \right)^2 \frac{\omega^2}{1 + (\omega v_2/c_2)^2} \times \]

\[ \times \sum_l (2l + 1) \left| j_l(kR_0) \frac{\mathcal{Q}(kR_0) - x_l(x_2)}{(kR_0)^2 - x_2} \right|^2 \langle |C_{2l}|^2 \rangle_{\omega} \quad (44) \]

Numerical analysis of the density fluctuations excited by surface sources in the surrounding liquid shows that they decay rapidly when moving away from the micelle. Already when the distance is comparable with micelle radius they are practically zero. Consequently, the environment overlap contributions for different droplets are negligible. For this reason the sum of the contributions (43) and (44) is a good approximation for the structure factor of dilute dispersions of micelles which do not interact with each other. In the hydrodynamic approach the expressions derived for DSF, (43) and (44), are strict in contrast to the simplified results found by the other authors \([6, 13, 16]\) who approximated the density-density correlator by the correlation function of surface displacements.

The spectral densities of fluctuations have a complicated dependence on frequency owing to the presence of the Bessel function combinations. Figure 1 shows the frequency dependency of the DSF of fluid droplet when only the normal components of surface random forces are taken

![Fig. 1.](image)

![Fig. 2.](image)

Fig. 1. — Dynamical structure factor of emulsion droplet in the absence of surface concentration modes for \(k R_0 = 0.2 \) \((R_0 = 400 \text{ Å})\) \(v_2 = 1.4 \text{ 400 m s}^{-1} \rho_2 = 10^3 \text{ kg m}^{-3} \). \(\zeta_2 = 0.75 \eta_i\) and various solvent viscosities \(\eta_2 \text{ [kg m}^{-1} \text{s}^{-1}]\): 0.001 (1), 0.1 (2), 0.2 (3), 0.3 (4), 0.4 (5). The inner liquid parameters correspond to castor oil at standard conditions.

Fig. 2. — Dynamical structure factor of microemulsion for two values of surface elastic modulus \(B : 5 \times 10^{-2} (1), 10^{-1} (2) \text{[J m}^{-2}]\); and \(k R_0 = 0.3 \text{(}R_0 = 400 \text{ Å})\); \(\rho_1 = 900, \rho_2 = 10^1 \text{ kg m}^{-3}; \eta_1 = 1, \eta_2 = 0.2 \text{ kg m}^{-1} \text{s}^{-1} \). \(\zeta_1 = 0.75 \eta_i\), \(c_1 = 1.4 \text{ 400}, c_\gamma = 1.5 \text{ 500 m s}^{-1}\), \(\alpha_{l=2} \sim 10^{-3} \text{ J m}^{-2}\) \(\rho_\gamma = 4.5 \times 10^{-7} \text{ kg m}^{-2}\).
into account (see Eq. (31)). The viscosity is found to have a profound influence on the DSF. As the solvent viscosity increases both frequency of DSF maximum and DSF height decrease, while the increase of \( kR_0 \) leads to the increase of maximum of the spectrum without frequency shift [23].

The tangential components of the random surface forces engender the surface concentration modes, which modify considerably the structure factor. As shown in figure 2 the new step-like low-frequency contribution appears. It depends essentially on the elasticity of surface film, the low-frequency wing of DSF increases with decreasing elasticity modulus. The curves are the result of numerical calculation of equations (43), (44), (27), (30). The low-frequency contribution of DSF increases with the solvent viscosity (see Fig. 3) in contrast to the peak that decreases similarly to the case in the absence of the concentration modes (Fig. 1), whereas the dependence of the maximum position on the viscosity of liquid differs appreciably from that shown in figure 1. It should be observed that the spectrum is sensitive also to the bulk viscosity \( \zeta \) (Fig. 3, dashed line). The spectrum parameters are easily measured as a function of wave number \( k \). Such functions for the peak and low-frequency plateau heights are presented in figure 4, in which, besides, the great effect of the liquid viscosity on the wave number dependencies is shown. Figure 5 illustrates changing DSF when viscosity of surface fluid increases. It is remarkable that the influence of the surface viscosity on DSF differs utterly from the influence of the viscosities of the bulk fluids. In this case all the contributions increase or decrease together. As is expected, the surface fluctuations are larger when the elasticity and

![Fig. 3.](image)

**Fig. 3.** — Dynamical structure factor of microemulsion for \( kR_0 = 0.2 \) (\( R_0 = 400 \) Å), \( B = 0.05 \) J m\(^{-2}\) and various solvent viscosities \( \eta_2 \): 0.05 (1), 0.2 (2) [kg m\(^{-1}\) s\(^{-1}\)]. The rest parameters are the same as those described for figure 2. The dashed line differs from the solid line 2 only by the value of the bulk viscosity of inner liquid \( \zeta_i = 1.5 \eta_1 \).

![Fig. 4.](image)

**Fig. 4.** — The heights of the peaks and plateaux of the dynamical structure factor of emulsion as a function of wave number \( k \) for two viscosities of droplet fluid. Lines 1 and 3 correspond to the peak and plateau heights respectively when \( \eta_1 = 0.1 \) kg m\(^{-1}\) s\(^{-1}\), and lines 2 and 4 — when \( \eta_1 = 1 \) kg m\(^{-1}\) s\(^{-1}\). The rest parameters are the same as those for line 1 in figure 3.
viscosity of the droplet film are smaller. As it is evident from equations (35-37) the height and width of spectrum of the surface displacement correlation function depend on the parameter $\alpha_\ell$ and therefore on the coefficients of Helfrich's expansion (1). For micelles the term $\alpha$ in $\alpha_\ell$ is anomalously low (of the order $10^{-4}$ J m$^{-2}$ or smaller). Taking into account that $\alpha \sim \beta^2/\kappa$ [17], where $\beta/2 \kappa = R_0^{-1}$ is the spontaneous curvature (for vesicles $\beta = 0$), one can easily see that the term $\kappa \ell (\ell + 1) R_0^{-2}$ in $\alpha_\ell$ becomes predominant for small droplet radii. In figure 6 we show the influence of combined parameter $\alpha_\ell$, that contains Helfrich's coefficients $\alpha$, $\beta$, $\kappa$, on the shape of the dynamical structure factor. Unlike correlator (35) the dynamical structure factor includes all excitation modes, so this influence is significant in the low-frequency range.

Our main attention has been paid to the construction of a correlation theory of thermal fluctuation of nearly spherical micelles or vesicles modelled by the compressible viscous droplets. We have studied consistently the collective hydrodynamical excitations of interface taking into account the thermal bulk flows inside and outside the droplet as well as the dynamical properties of insoluble surfactant. The spectral densities of fluctuating hydrodynamical fields have a parametric dependence on the thermodynamical and kinetic properties of all three mediums, and, in this sense, they are universal. The poles of the fluctuation spectra contain both bulk and surface modes. The analysis carried out shows that in limiting cases the obtained correlators coincide with the known results of other authors [16, 17, 19]. The main contribution to the spectral densities of shape fluctuations has been found when the excitations decay strongly due to viscosity effect (Eq. (35)). The surfactant concentration mode has a

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**Fig. 5.** — Dynamical structure factor of microemulsion for $kR_0 = 0.2$ ($R_0 = 400 \text{ Å}$), $B = 0.05$ J m$^{-2}$, $\rho_s = 4.5 \times 10^{-7}$ kg m$^{-2}$, $\eta_1 = 1$, $\eta_2 = 0.1$ kg m$^{-1}$ s$^{-1}$ and various surface viscosities $\eta_s = \xi_s : 10^{-7}$ (1), $2.5 \times 10^{-7}$ (2), $10^{-6}$ (3) [kg s$^{-1}$].

**Fig. 6.** — Dynamical structure factor of microemulsion for various values of $\alpha_\ell = \alpha - 2 \beta/\kappa + \kappa \ell (\ell + 1)/R_0^2$ [J m$^{-2}$]: $5 \times 10^{-5}$ (solid line), $5 \times 10^{-4}$ (dotted line), $5 \times 10^{-3}$ (dashed line). The rest parameters are the same as those described for line 1 in figure 2.
specific fractional power dependence on the frequency and viscosity when the vibration frequencies are larger than those for the capillary waves (Eq. (39)).

In our approach the spectra of mass density and velocity fluctuations are found by using a common scheme. On this reason the dynamic structure factor, determined by twofold Fourier transform of density-density correlator, is specific and differs from the fluctuation spectra of other scalar densities of thermodynamic variables.

The numerical analysis of presented expressions showed that the surfactant dynamics leads to the considerable contribution to the structure factor in low-frequency range. The time correlation functions have essentially nonexponential form. These results can be verified by experiments on elastic scattering of thermal neutrons and dynamical Brillouin light scattering. The small angle neutron scattering and the dynamic light scattering experiments on micellar solutions, microemulsions, small proteins and large colloid particles are already known [31-33], where the main attention was focused on structure aspects and concentration dependence of spectra. We propose the details of spectrum shape to be examined. The spectra are expected to be sensitive to the surface collective excitations as it takes place for the flat liquid-vapour interface [34]. Neutron spin echo experiments [6] and dielectric relaxation [35, 36] also show that dynamic structure factor strongly depends on interface fluctuation in microemulsions. In article [37] the internal viscosity of micelle was studied by using the measurement of fluorescence intensity. Our results provide the possibility of extracting the complete information about viscosity dependence. Note that in our approach the solution of problem of diffusion motion inside confined region can be easily expressed in terms of velocity correlation functions obtained. This should be important in model studies of solute diffusion in cells or vesicles [38].


So, we have investigated the hydrodynamical fluctuations of fluid droplets (micelles) coated with a thin film and immersed in a fluid medium. In the present theoretical study the compressibility and viscosity of the surface and bulk fluids have been explicitly taken into account. The surface energy is considered to depend on curvature. The thermal fluctuations excited by the surface random sources are primary for the micelles with diameter of order $10^2-10^3$ Å. The frequency spectra of the fluctuations are found to depend strongly on the values of the phenomenological parameters.

The effect of compressibility is of considerable interest in various applications. For instance, the fluctuations of density determine the spectra of inelastic scattering from microemulsions. The collective excitations of micelles have an effect on the cross-section of scattering with small energy transfer (e.g. slow neutron scattering). We hope that the results obtained, in particular those concerning the structure of the DSF line shape, will stimulate additional experimental studies of the dynamical behaviour of micelle solutions.

References