Dynamics of micelles and vesicles

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The dynamic properties of spherical micelles and vesicles whose surfaces have an anomalously low surface tension are analyzed. Because of this low surface tension, curvature-dependent terms should be retained in the expansion of the surface energy in a description of the surfaces of these entities. Boundary conditions, which also depend on the curvature, at the interface between two liquids are formulated for this case. These (linearized) boundary conditions are used to analyze the natural modes of a spherical micelle. Among these modes there are some characteristic surface modes whose dispersion relation is determined by parameters of the surface energy. One of these modes is associated with distortions of the spherical shape of the micelle, but it differs from a capillary wave in that it is overdamped. Another surface mode is associated with a redistribution of molecules of a surface-active substance over the surface of the micelle. The frequency of this mode has real and imaginary parts which are comparable in order of magnitude. Binary dynamic correlation functions of surface properties are derived. This derivation requires first eliminating volume variables from the effective action. The expressions for the correlation functions found as a result are determined by the corresponding dispersion relations and satisfy the fluctuation–dissipation theorem.

1. INTRODUCTION

Microemulsion physics has recently attracted much interest. Microemulsions form in mixtures of two mutually insoluble liquids (as a rule, water and an oil) when a surface-active substance is added to the mixture. From the macroscopic standpoint, a microemulsion is a homogeneous phase. It may coexist with the liquids from which it is formed. The volume of a microemulsion phase is proportional to the amount of surface-active substance which has been added to the mixture. It thus becomes possible to dissolve in water liquids (oils) which are ordinarily insoluble in it and to control the process by controlling the dose of surface-active substance—an extremely important capability for applications.

The literature on microemulsions is of formidable size. The reviews by Bellocq *et al.*[1] and Safran and Clark[2] provide an introduction to the physical properties of microemulsions. Those reviews contain the basic experimental facts and their interpretation.

The following physical picture of the formation of microemulsions is now generally accepted. The surface-active molecules settle primarily at the interface between the liquids. At a certain critical concentration of the surface-active substance, the formation of an interface with a certain spontaneous curvature becomes preferable to a plane interface. The result is the formation of micelles—droplets of one liquid in the other, with boundaries saturated with surface-active molecules. A microemulsion is a solution of micelles containing one liquid in the other liquid.

Microemulsions which are weak solutions of micelles can be described in the gas approximation, in which the micelles are treated as weakly interacting. In this case one can deal with the properties of some individual micelle. It is this problem that we will be discussing below.

Another entity in this discussion is a vesicle. Vesicles are formed in solutions of molecules which have a tendency to form bilayer membranes. In such solutions a membrane often forms a closed structure, which is called a "vesicle." We are interested in spherical vesicles here.

We will examine micelles and vesicles at a phenomenological level. In other words, the interface between the liquids is assumed to be infinitely thin, and the energy of the interface is assumed to be determined by such parameters as its area, its curvature, and the concentration of surface-active molecules at it. At the phenomenological level, micelles and vesicles can be treated in parallel.

A necessary condition for taking the phenomenological approach is that the length scale of the problem be much larger than the molecular scale. This condition is clearly met by vesicles, which are of micron size. The situation regarding micelles is slightly more complicated. As a rule, the size of micelles in a microemulsion is on the order of 10^2 Å. The phenomenological approach to the description of such micelles is right at its applicability boundary. It is possible, however, to add to a microemulsion various substances which will increase the size of the micelles to 10^3 Å without disrupting their spherical shape. The phenomenological approach can be taken for such micelles without reservation, and it is in microemulsions with micelles of this sort that the theoretical conclusions should be tested.

We are interested in the dynamic properties of micelles and vesicles, primarily the spectra of surface modes associated with the interface. These modes can be seen experimentally in the inelastic scattering of light or neutrons by microemulsions. Observations of this sort might serve as a method for testing the characteristics of an interface.

The literature reveals that attempts have already been made to calculate the dispersion relation for a mode associated with the relaxation of the surface of a micelle or vesicle to a spherical shape.[3,4] Those studies, however, have used the incorrect assumption that the area of the interface remains constant (this constancy should reflect the presence of the surface-active substance at the interface, in the opinion of the authors). A correct derivation requires a joint consideration of the dynamic equations for the displacement vector of the interface and the concentration of surface-active mole-

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cules at it. Along this path we find, in addition to the mode associated with the surface shape relaxation, yet another characteristic surface mode, which might be called a "concentration mode."

As was first pointed out by de Gennes and Taupin,[5] thermal fluctuations of the interface play an important role in a micelle or vesicle, leading to a logarithmic renormalization of the constants of the theory. In real microemulsions, however, fluctuation effects can be ignored.

This paper is organized in the following way. In the second section we present a phenomenological theory which describes the static properties of micelles and vesicles. The third section deals with the stability of a droplet with respect to slight shape distortions, and the conclusions concerning the role of thermal fluctuations are summarized. Nonlinear equations describing the dynamics of a micelle are derived in the fourth section. The spectrum of surface modes is analyzed in the linear approximation in the fifth section. The dynamic correlation functions of surface properties are derived in the sixth section, and the component of the inelastic scattering associated with their fluctuations is calculated. The final section discusses the range of applicability of the results.

2. THE HELFRICH THEORY

When a surface-active substance is added to a mixture of mutually insoluble liquids, the surface tension α at the interface of the liquids decreases sharply, usually by two orders of magnitude. The microemulsion then begins to form. An anomalously low surface tension α is the fundamental fact underlying the phenomenological theory of the interface between liquids, which explains the formation of micelles.

In the phenomenological approach the interface is treated as infinitely thin. A convenient way to describe its properties is in terms of the thermodynamic potential Ω, which is a function of the temperature, the velocity, and the chemical potentials, since these properties are continuous at the interface (while the mass density, for example, is discontinuous). The interface contribution to the potential Ω is written as the surface integral

$$\Omega_s=\int ds\,\omega_s, \tag{1}$$

which is evaluated over the interface.

Generally speaking, the quantity ω_s in (1) depends on the curvature of the surface. This dependence is usually inconsequential, and in such cases ω_s may be treated as a function of the temperature and the chemical potentials. It is this quantity which is called the "surface tension" α. At small values of α, however, the dependence of ω_s on the surface curvature must be taken into account. Helfrich[6] was the first to grasp this point. He showed that by taking this path one finds that a new scale, associated with the size of a micelle, arises in a natural way.

When the first two terms of an expansion in the curvature are taken into account, the quantity ω_s in (1) is written

$$\omega_s=\alpha-\beta\left(\frac{1}{R_1}+\frac{1}{R_1}\right)+\frac{\varkappa}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2+\frac{\bar\varkappa}{R_1R_2}. \tag{2}$$

Here R_1 and R_2 are the local radii of curvature of the interface. Expression (2) contains the so-called average curvature $(1/2)(1/R_1+1/R_2)$ and the Gaussian curvature $1/R_1R_2$, which constitute all of the first- and second-order invariants.

The coefficient α in (2) determines the tension of a plane interface, and it is this quantity which would naturally be called the "surface tension." We will be assuming $\beta>0$ below; this condition can always be met by measuring the radius of curvature from the appropriate side of the interface. If expansion (2) is to be meaningful, the following conditions must hold:

$$\varkappa>0,\qquad 2\varkappa+\bar\varkappa>0. \tag{3}$$

In the opposite case, surface energy (1) will not be positive-definite for micelles with small radii of curvature; i.e., an instability which cannot be described on the basis of expansion (2) will arise.

The term in (2) which contains the coefficient β and which changes sign upon a change in the sign of the curvature radii reflects the fact that the liquids separated by the micelle boundary are different. For this reason, the directions out of and into a micelle are not equivalent. Outside and inside a vesicle, in contrast, we are dealing with the same liquid, which is divided by a bilayer membrane, so these directions are equivalent. In studying a vesicle we should thus set $\beta=0$.

From the constants in (2) we can construct a quantity with the dimensionality of a length:

$$R_s=2\varkappa/\beta. \tag{4}$$

This quantity determines the typical size of a micelle (R_s^{-1} is usually called the "spontaneous curvature"). As we have already mentioned, a necessary condition for the validity of the phenomenological approach is that the size of the micelle be much greater than molecular sizes. According to (4), this condition means that the constant β in (2) must be sufficiently small. Since we have $\beta\equiv0$ for vesicles, this condition is no problem for them.

We now consider a spherical micelle of radius R. Its surface energy is

$$\Omega_R=4\pi(\alpha R^2-2\beta R+2\varkappa+\bar\varkappa). \tag{5}$$

Conditions (3) guarantee that energy (5) will be positive-definite at small values of R. With a decrease in α, surface energy (5) vanishes first at

$$\alpha=\beta^2/(2\varkappa+\bar\varkappa). \tag{6}$$

The radius at which this vanishing occurs is

$$R_m=\beta/\alpha=(2\varkappa+\bar\varkappa)/\beta. \tag{7}$$

From inequlities (3) and $\beta>0$ we find $R_m>0$; i.e., the radii of curvature in (2) should be measured from inside the micelle.

A phenomenological analysis thus draws the following picture of the formation of a microemulsion: When a surface-active substance is added to a mixture of two mutually insoluble liquids, the surface tension α decreases. When it reaches the value given by (6), micelles with radii (7) begin to form in the mixture. We wish to point out that the relation $\alpha>0$ holds here; i.e., a plane interface remains stable with respect to small perturbations.

This picture is valid if the distribution of micelles with respect to radii has a sharp maximum near $R = R_m$. Comparing the energies of micelles with different radii, we find that this condition is met if

$$T/8\pi(2\varkappa+\bar{\varkappa}) \ll 1, \tag{8}$$

where T is the temperature. Experimental evidence that condition (8) is satisfied would be a change in slope on a plot of the surface tension α versus the concentration of the surface-active substance,[2] which would imply the abrupt beginning of micelle formation when critical value (6) is reached.

3. FLUCTUATIONS IN SURFACE SHAPE

In general, for an arbitrary value of α, a microemulsion will contain micelles with various radii. Let us examine deviations of the surface of a micelle of radius R from a spherical shape. We will first calculate the energy associated with such deviations, and then we will discuss the role played by thermal fluctuations of the surface.

We assume that the interface is described by the condition $\Phi(\mathbf{r}) = 0$ and that we have $\Phi < 0$ inside the micelle and $\Phi > 0$ outside. In this case the quantity

$$\mathbf{l}=\nabla\Phi/|\nabla\Phi| \tag{9}$$

is a unit vector along the outward normal to the micelle surface. We rewrite the energy expressions (1) and (2) in the form

$$\Omega_s = \int d^3r\,\delta(\Phi)\,|\nabla\Phi|\,\omega_s, \tag{10}$$

$$\omega_s=\alpha-\beta\nabla_i l_i+{}^1/_2\varkappa(\nabla_i l_i)^2+{}^1/_2\bar{\varkappa}[(\nabla_i l_i)^2-\nabla_i l_k\nabla_k l_i]. \tag{11}$$

In (10) the energy is written as a functional of $\Phi(\mathbf{r})$. On the other hand, this energy should depend on only the surface characteristics, not on the particular method by which it is parametrized. The energy should therefore be invariant under the transformation

$$\Phi\to f(\Phi), \quad f(0)=0, \quad f'(0)>0, \tag{12}$$

where f is some arbitrary function which satisfies only the conditions specified in (12). The invariance of energy (10) under transformation (12) can easily be tested directly.

The surface integral of the Gaussian curvature,

$$\int ds(R_1R_2)^{-1} = \frac{1}{2}\int d^3r\,\delta(\Phi)\,|\nabla\Phi|\,[(\nabla_i l_i)^2-\nabla_i l_k\nabla_k l_i],$$

is a topological invariant which does not depend on the surface shape (for a surface having the topology of a sphere, this integral has the value 4π). Consequently, the variation of this integral upon changes in surface shape which do not affect the topology of the surface is zero. In studying the stability of a micelle with respect to small perturbations, we can thus omit the term with the coefficient $\bar{\varkappa}$ from (11).

In a study of micelles whose shape differs only slightly from spherical, it is convenient to chose the function $\Phi(\mathbf{r})$ in the form

$$\Phi(\mathbf{r})=r-R-u(\theta,\varphi). \tag{13}$$

Here r, θ,φ are spherical coordinates, and R is the equilibrium radius of the micelle. The shape of the micelle is specified by the condition $\Phi(\mathbf{r}) = 0$, so u has the meaning of the radial displacement of the micelle surface. In an analysis of variations in the shape of a micelle, the liquid within the micelle should be treated as incompressible; we accordingly have the auxillary condition

$$\int do[(R+u)^3-R^3]=0. \tag{14}$$

We consider the second variation of energy (10) with respect to the displacement vector u, which should be calculated under auxilliary condition (14). Substituting expression (13) into (9)–(11), expanding energy (10) to second order, and using (14), we find

$$\Omega_s^{(2)}=\sum_{l,m}\frac{\alpha_l}{2}(l-1)(l+2)|u_{lm}|^2. \tag{15}$$

Expression (15) is a sum of the displacement vector u in spherical harmonics, which are introduced in accordance with the definition

$$u(\theta,\varphi)=\sum_{l,m}u_{lm}Y_{lm}(\theta,\varphi), \tag{16}$$

where $Y_{lm}(\theta,\varphi)$ are the spherical harmonics. In (15) we have introduced the definition

$$\alpha_l=\alpha-2\beta/R+\varkappa(l^2+l)/R^2. \tag{17}$$

In accordance with the point discussed above, there is no term with the coefficient $\bar{\varkappa}$ in (17).

The summation over l in (16) begins at $l = 1$, since the term with $l = 0$ corresponds to a uniform expansion of the droplet, which would contradict condition (14). Note that the term with $l = 1$ in (15) is zero. This is a natural result, since this term corresponds to a displacement of the droplet as a whole, in the course of which the energy of the droplet cannot change. The summation in (16) thus begins with $l = 2$.

The condition for the stability of a spherical micelle with respect to small perturbations is $\alpha_l > 0$. Since $\varkappa > 0$, it is sufficient to test this condition for $l = 2$. Micelles which are unstable with respect to small perturbations arise first at $\alpha < \beta^2/6\varkappa$. These micelles have radii in the interval

$$\frac{\beta-(\beta^2-6\alpha\varkappa)^{1/2}}{6\varkappa}<R<\frac{\beta+(\beta^2-6\alpha\varkappa)^{1/2}}{6\varkappa}. \tag{18}$$

The condition for the stability of a micelle of radius (7) with surface tension (6) gives us the inequality $\bar{\varkappa} < 4\varkappa$, which is a necessary condition if this analysis is to be meaningful.

As de Gennes and Taupin showed,[5] thermal fluctuations of the surface shape play a major role at a small value of β. These fluctuations give rise to logarithmic corrections to α, β, $\varkappa$, and $\bar{\varkappa}$. To study the behavior of the system in this situation we should use the renormalization-group method.[7] Energy (1) with density (2) is renormalizable; it is therefore possible to formulate a closed system of renormalization-group equations for α,β,$\varkappa$, $\bar{\varkappa}$.

Helfrich[8] was the first to attempt to do this. Correct equations for $\varkappa$ in the single-loop approximation were found in Refs. 9–11. Kleinert[12] found renormalization-group equations for β and $\bar{\varkappa}$ in the same approximation. We will reproduce these renormalization-group equations here, supplementing them with the single-loop equation for the surface tension:

$$d\ln\alpha/dL=T/4\pi\varkappa,\qquad d\ln\beta/dL=T/4\pi\varkappa,$$
$$d\varkappa/dL=-3T/4\pi,\qquad d\bar{\varkappa}/dL=5T/6\pi. \tag{19}$$

Here T is the temperature, and $L=\ln(\Lambda r)$, where Λ is a cutoff parameter and r a length scale. Equations (19) are to be integrated from $L=0$ to $L=\ln(\Lambda R)$.

It follows from Eqs. (19) that the role of an invariant charge is played by the quantity

$$g=3T/4\pi\varkappa, \tag{20}$$

which must be small if a perturbation theory is to be valid and thus if Eqs. (19) are to be valid. By virtue of Eq. (19) for $\varkappa$ and Eq. (20), we find

$$g=g_0/(1-g_0L). \tag{21}$$

In other words, g increases with increasing scale; i.e., we are dealing with a situation of asymptotic freedom.

At scales at which g is on the order of unity, perturbation theory begins to break down. It is difficult to say much about the state of the boundary in this case. de Gennes and Taupin[5] assumed that a "random" phase, characterized by a random state of the boundary, would arise in this case. We will assume here that the condition $g\ll 1$ holds; under this condition, fluctuation effects are weak. It is apparently only under this condition that one could meaningfully discuss an individual micelle. Note that the condition $g\ll 1$ is essentially the same as condition (8), which guarantees a narrow maximum near the equilibrium value in the distribution of micelles with respect to radius.

4. DYNAMIC EQUATIONS

We turn now to the dynamics of a micelle, whose surface is an interface between liquids. We are interested in dynamic characteristics associated with the presence of this interface. Our first problem is thus to study the boundary conditions for the hydrodynamic equations at the interface.

A method for constructing such boundary conditions was discussed by Kats and one of us in Ref. 13. We will summarize that derivation here, taking account of the specific features of the surface under consideration, whose energy [(1), (2)] contains curvature-related terms. Expression (2) refers to a liquid surface. In this paper we will not discuss effects associated with a possible crystalline or liquid-crystal structure of the surface (such effects were discussed in detail in Ref. 13 for the case of a plane film).

On the two sides of the interface (outside and inside the micelle) the dynamics of the liquid is described by the usual hydrodynamic equations

$$\frac{\partial\rho}{\partial t}=-\nabla\mathbf{j}, \tag{22}$$

$$\frac{\partial j_i}{\partial t}=-\nabla_k(P\delta_{ik}+v_kj_i+\Pi_{ik}). \tag{23}$$

Here ρ is the density of the liquid, $\mathbf{v}$ is the velocity, $\mathbf{j}=\rho\mathbf{v}$ is the momentum density, P is the pressure, and Π_{ik} is a dissipative stress tensor, given by

$$\Pi_{ik}=-\eta(\nabla_iv_k+\nabla_kv_i-{}^2/{}_3\delta_{ik}(\nabla v))-\zeta(\nabla\mathbf{v})\delta_{ik}. \tag{24}$$

We will use a subscript 1 to specify quantities associated with the liquid inside the micelle, and 2 for the liquid outside.

At the interface, in the leading approximation in the hydrodynamic parameter $(\Lambda R)^{-1}$, the temperature, the chemical potentials of the two liquids and of the surface-active substance, and the velocity component tangent to the surface are all continuous. It is for this reason that we used the thermodynamic potential Ω above, which is a function of these extensive variables. We wish to stress that the surface tension α and other coefficients in expansion (2) or (11) are functions of these variables.

To construct dissipationless dynamic equations it is convenient to use a Poisson-brackets method.[14,15] In this method, dynamic equations are found as Liouville equations with the thermodynamic energy E as the Hamiltonian. When there is an interface between liquids, the energy of the system is written in the form

$$E=\int d^3r(\varepsilon_1\theta(-\Phi)+\varepsilon_2\theta(\Phi)+\varepsilon_s|\nabla\Phi|\delta(\Phi)), \tag{25}$$

where θ is the unit step function. The quantities ε_1 and ε_2 in (25) are the energy densities of the liquids, and ε_s is the surface energy density.

The intensive quantities pertaining to this system, such as the energy density in (25), are written as sums of volume and surface parts. The momentum density, for example, is written

$$\mathbf{j}=\mathbf{j}_1\theta(-\Phi)+\mathbf{j}_2\theta(\Phi)+\mathbf{j}_s|\nabla\Phi|\delta(\Phi), \tag{26}$$

where $\mathbf{j}_s$ is the surface momentum density. Completely similar expressions are used for the mass density ρ, the entropy density s, the number density of surface-active molecules, etc. The dynamic equations are written for specifically these densities.

Dissipationless terms in the dynamic equations for these densities can be found by using the standard three-dimensional expressions for Poisson brackets.[14,15] These expressions need to be supplemented with only the brackets for the variable Φ, which describes the position of the interface. The structure of the only nonzero brackets which contain Φ is established by analogy with smectics[15,16].

$$\{\mathbf{j}(\mathbf{r}_1),\Phi(\mathbf{r}_2)\}=-\nabla\Phi\delta(\mathbf{r}_1-\mathbf{r}_2). \tag{27}$$

The idea is that the interface can be treated as a single smectic layer.

The Liouville equations for the volume current densities $\mathbf{j}_1$ and $\mathbf{j}_2$ in (26), which are found with the help of these expressions for the Poisson brackets, are of course the same as the standard dissipationless hydrodynamic equations. For surface densities of the $\mathbf{j}_s$ type in (26) the situation is slightly more complicated. To find equations for these quantities we need to introduce some parametrization of the interface and then find an expression for the Poisson brackets which contain the surface densities in this parametrization. We accomplish this through a reduction of the expressions for the three-dimensional Poisson brackets. We can then write Liouville equations for the surface quantities, which give us the dissipationless part of the dynamic equations.

This program was carried out in Ref. 13 (see also Ref. 17), where a surface parametrization of the $z=z(x,y)$ type was used. Since the resulting equations are local, a parametrization of this sort can also be regarded as local. As a result of the use of this parametrization, we find equations which can easily be rewritten in a form invariant with respect to the choice of a parametrization of the surface.

The only difference between our case and that discussed in Ref. 13 is that the dependence of the surface energy density on the curvature of the surface is taken into account. According to (9) and (11), we can write

$$\omega_s=\omega_s(\nabla\Phi,\ \nabla_i\nabla_k\Phi). \tag{28}$$

The expressions for the Poisson brackets for the surface quantities are the same as those found in Ref. 13.

Here is the final form of the dynamic equations for the surface quantities:

$$\partial\Phi/\partial t+\mathbf{v}_s\nabla\Phi=0, \tag{29}$$

$$\frac{\partial}{\partial t}(|\nabla\Phi|n_s)+\nabla(n_s\mathbf{v}_s|\nabla\Phi|)=0, \tag{30}$$

$$\frac{\partial}{\partial t}(|\nabla\Phi|j_{si})+\nabla_k(|\nabla\Phi|[\rho_s v_{si}v_{sk}+T_{sik}])=(P_1-P_2)\nabla_i\Phi$$
$$-(\mathbf{v}_s-\mathbf{v}_1)\nabla\Phi j_{1i}+(\mathbf{v}_s-\mathbf{v}_2)\nabla\Phi j_{2i}+(\Pi_{1ik}-\Pi_{2ik})\nabla_k\Phi. \tag{31}$$

Here $\mathbf{v}_s$ is the velocity of the interface, $\mathbf{j}_s=\rho_s\mathbf{v}_s$ is the surface momentum density, and n_s is the surface density of surface-active molecules. The surface stress tensor in (31) is

$$|\nabla\Phi|T_{sik}=-\omega_s|\nabla\Phi|\delta_{ik}+\frac{\partial(\omega_s|\nabla\Phi|)}{\partial\nabla_k\Phi}\nabla_i\Phi$$
$$+2\frac{\partial(\omega_s|\nabla\Phi|)}{\partial\nabla_n\nabla_k\Phi}\nabla_n\nabla_i\Phi$$
$$-\nabla_n\left(\frac{\partial(\omega_s|\nabla\Phi|)}{\partial\nabla_n\nabla_k\Phi}\nabla_i\Phi\right). \tag{32}$$

We first note that Eq. (29) is invariant under transformation (12); i.e., the surface dynamics described by this equation is independent of the particular method used to parametrize the surface, as it should be. Derivatives in all directions are formally present on the left sides of Eqs. (30) and (31), although there are quantities there which are defined only at the surface. Using (29), however, we can verify that equations (30) and (31) actually contain derivatives of the surface quantities exclusively along the surface. The surface quantities in these equations can thus be continued in an arbitrary fashion in the third dimension.

The stress tensor T_{sik} given by (32) is not symmetric. However, its divergence, which appears in Eq. (31), can be rewritten as a divergence of a symmetric tensor:

$$\nabla_k(|\nabla\Phi|T_{sik})=\nabla_k\Bigg[|\nabla\Phi|T_{sik}-\nabla_n\left(\frac{\partial(\omega_s|\nabla\Phi|)}{\partial\nabla_n\nabla_i\Phi}\nabla_k\Phi\right)$$
$$+\nabla_n\left(\frac{\partial(\omega_s|\nabla\Phi|)}{\partial\nabla_i\nabla_k\Phi}\nabla_n\Phi\right)\Bigg]. \tag{33}$$

The symmetry of the tensor on the right side of (33) follows from the identity

$$\varepsilon_{ikn}\left[\frac{\partial(\omega_s|\nabla\Phi|)}{\partial\nabla_k\Phi}\nabla_i\Phi+2\frac{\partial(\omega_s|\nabla\Phi|)}{\partial\nabla_k\nabla_m\Phi}\nabla_i\nabla_m\Phi\right]=0,$$

which is a consequence of the rotational invariance of ω_s. The angular-momentum conservation law can thus be formulated in the standard way.

The right side of Eq. (31) contains momentum fluxes to the surface from the adjacent liquids (both dissipationless and dissipative fluxes). Generally speaking, corresponding terms describing the flux of surface-active molecules to the surface should be added to the right side of Eq. (30). However, these terms are associated with some extremely slow processes involving the diffusion of surface-active molecules, so we will ignore them.

Surface kinetic terms have been omitted from Eqs. (30) and (31) [Eq. (29) is exact, and there are no corrections to it[13]]. It is a straightforward matter to verify that these surface terms lead to effects which are small, by a factor on the order of the hydrodynamic parameter $(\Lambda R)^{-1}$, so we are justified in ignoring them.

Finally, we write the explicit expression for the surface stress tensor which is found from (10) in accordance with (32):

$$T_{sik}=-[\alpha+\beta\nabla\mathbf{l}+{}^1/_2\varkappa(\nabla\mathbf{l})^2]\delta_{ik}^{\perp}+\tilde\beta\nabla_i^{\perp}l_k-l_i\nabla_k^{\perp}\tilde\beta. \tag{34}$$

Here we have used the notation

$$\tilde\beta=\beta+\varkappa(\nabla\mathbf{l}),\qquad \delta_{ik}^{\perp}=\delta_{ik}-l_il_k,\qquad \nabla_i^{\perp}=\delta_{ik}^{\perp}\nabla_k.$$

Expression (34) does not contain the coefficient $\bar\varkappa$, because the term with this coefficient in (10) is invariant with respect to small variations.

5. SPECTRUM OF NATURAL MODES OF A MICELLE

We turn now to the spectrum of micelle surface modes which are associated with the time variation of the quantities characterizing this surface. A variation of this sort is of course accompanied by a volume hydrodynamic motion of the liquid in the region adjacent to the surface of the micelle. It is this motion, as we mentioned above, that is the primary source of energy dissipation and thus of the damping of the surface modes.

In this section of the paper we analyze the spectrum of micelle modes in the linear approximation. Correspondingly, we assume that the shape of the micelle deviates only slightly from spherical. In this case it is convenient to introduce a spherical coordinate system and to describe the micelle surface shape by means of the radial displacement vector u, which we introduced in (12). All quantities which determine the state of the micelle surface are assumed to be functions of the angles θ and φ. In addition to the displacement vector u we will be using the surface velocity $\mathbf{v}_s$ and the deviation (n_s') from the equilibrium value of the surface density of surface-active molecules.

We must now linearize Eqs. (29)–(31) in terms of the variables $\mathbf{v}_s$, u, and n_s'. As a result we find

$$\partial u/\partial t=v_r{}^s, \tag{35}$$

$$\rho_s\frac{\partial v_r{}^s}{\partial t}-\left(\alpha+\frac{2\beta}{R}\right)\left(\nabla_\perp{}^2u+\frac{2u}{R^2}\right)+\varkappa\left(\nabla_\perp{}^4u+\frac{2\nabla_\perp{}^2u}{R^2}\right)$$
$$=P_1'-P_2'-2\eta_1\frac{\partial v_{r1}}{\partial r}+2\eta_2\frac{\partial v_{r2}}{\partial r}, \tag{36}$$

$$\rho_s\frac{\partial v_\theta{}^s}{\partial t}-\frac{1}{R}\frac{\partial\alpha}{\partial n_s}\frac{\partial n_s'}{\partial\theta}=-\eta_1\left(\frac{1}{R}\frac{\partial v_{r1}}{\partial\theta}+\frac{\partial v_{\theta1}}{\partial r}-\frac{v_{\theta1}}{R}\right)$$
$$+\eta_2\left(\frac{1}{R}\frac{\partial v_{r2}}{\partial\theta}+\frac{\partial v_{\theta2}}{\partial r}-\frac{v_{\theta2}}{R}\right), \tag{37}$$

$$\rho_s\frac{\partial v_\varphi{}^s}{\partial t}-\frac{1}{R\sin\theta}\frac{\partial\alpha}{\partial n_s}\frac{\partial n_s'}{\partial\varphi}=-\eta_1\left(\frac{1}{R\sin\theta}\frac{\partial v_{r1}}{\partial\varphi}+\frac{\partial v_{\varphi1}}{\partial r}-\frac{v_{\varphi1}}{R}\right)$$
$$+\eta_2\left(\frac{1}{R\sin\theta}\frac{\partial v_{r2}}{\partial\varphi}+\frac{\partial v_{\varphi2}}{\partial r}-\frac{v_{\varphi2}}{R}\right), \tag{38}$$

$$\frac{\partial n_s'}{\partial t}+\frac{n_s}{R}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta v_\theta{}^s)+\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}v_\varphi{}^s\right]=0. \quad (39)$$

We recall that the subscripts 1 and 2 refer to quantities inside and outside the micelle. The quantities P_1' and P_2' in (36) are the variable parts of the pressures. In the same equation we find the combination

$$\nabla_\perp{}^2=\frac{1}{R^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right), \quad (40)$$

whose meaning is the angular part of the Laplacian.

On the right sides of (36)–(38) there are viscous terms which contain derivatives of the volume velocities. The values of these derivatives should be taken at the interface. In writing these viscous terms we took account of the incompressibility condition $\operatorname{div}\mathbf{v}=0$, which is valid in a discussion of surface modes. The left sides of (37) and (38) contain derivatives of α but not of β or $\varkappa$ with respect to n_s. The reason is that, in contrast to α, the derivative $\partial\alpha/\partial n_s$ has no special small factor, so the terms with $\partial\beta/\partial n_s$ and $\partial\varkappa/\partial n_s$ are small quantities, by a factor on the order of the hydrodynamic parameter $(\Lambda R)^{-1}$, in comparison with the terms which have been retained.

The velocities of the liquids adjacent to the interface, $\mathbf{v}_1$ and $\mathbf{v}_2$, which are equal to $\mathbf{v}^s$ right at the interface, appear in Eqs. (36)–(38). The right sides of (36)–(38), however, contain not the velocities themselves but their derivatives $\partial v_1/\partial r$ and $\partial v_2/\partial r$, whose calculation requires knowledge of the volume distribution of the velocity inside and outside the micelle. A complete solution of the problem thus requires, in addition to (35)–(40), the well-known linear hydrodynamic equations, which can be found by linearizing (23), (24).

A velocity $\mathbf{v}$ can always be written in the form

$$\mathbf{v}=\nabla\psi+\operatorname{rot}(\mathbf{r}\zeta)+\operatorname{rot}(\mathbf{n}\chi), \quad (41)$$

where ψ, ζ, and χ are scalar functions, and $\mathbf{n}$ is a unit vector along the z axis. The radial component of the velocity is

$$v_r=\partial\psi/\partial r+r^{-1}\partial\chi/\partial\varphi. \quad (42)$$

The potential ψ determines the irrotational component of the velocity; in the leading approximation it is related to the pressure variation by

$$P'=-\rho\partial\psi/\partial t. \quad (43)$$

The surface modes in which we are interested are fairly low-frequency modes, so in analyzing them we assume that the liquids are incompressible. In other words, we asume that we can set $\operatorname{div}\mathbf{v}=0$, which is, by virtue of (41), equivalent to the equation

$$\nabla^2\psi=0. \quad (44)$$

For the quantity χ we have the equation

$$\rho\partial\chi/\partial t=\eta\nabla^2\chi. \quad (45)$$

We assume that all quantities are expanded in spherical harmonics as in (16) (the coefficients of the expansion of ψ, ζ, and χ in this series are of course functions of r). Since the linear approximation assumes that u is small in comparison with R, the boundary conditions on the velocities v_1 and v_2 should be imposed at $r=R$. It follows that the equations for the individual spherical harmonics can be separated. We will discuss the equation for the harmonic with angular indices l, m. We will also examine the Fourier time components with frequency ω; i.e., we assume that all quantities have a time dependence $\propto\exp(-i\omega t)$.

In this case a solution of Eq. (44) can be written in the form

$$\psi_1=\psi_{10}(r/R)^lY_{lm}(\theta,\varphi),\qquad \psi_2=\psi_{20}(R/r)^{l+1}Y_{lm}(\theta,\varphi). \quad (46)$$

In analyzing the surface modes, we can ignore the term with the time derivative in (39). Now using representation (41) for the velocity, we find the following boundary condition from (39):

$$l(l+1)\psi_{1,2}+\frac{\partial}{\partial r}(imr\chi_{1,2})=0. \quad (47)$$

After taking the derivative with respect to r we should set here $r=R$. We also rewrite boundary condition (36), omitting the term with $\partial v_r^s/\partial t$ from it and substituting in (43):

$$\frac{\alpha_l}{R^2}(l-1)(l+2)u=i\omega(\rho_1\psi_1-\rho_2\psi_2)-2\eta_1\frac{\partial v_{r1}}{\partial r}+2\eta_2\frac{\partial v_{r2}}{\partial r}. \quad (48)$$

The quantity α_l which appears here is given by (17).

We first consider the spectrum of capillary waves of a droplet, assuming that these waves are slightly damped. In this case the quantity χ, which is associated with the rotational component of the velocity, vanishes except in a narrow neighborhood of the interface, so we can write

$$\frac{\partial\chi}{\partial r}\gg\frac{1}{R}\frac{\partial\chi}{\partial\theta},\frac{1}{R}\frac{\partial\chi}{\partial\varphi}.$$

Consequently, we find from (45)

$$\chi_1=\chi_{10}\exp[2^{-1/2}(1-i)(\rho_1\omega/\eta_1)^{1/2}(r-R)]Y_{lm}(\theta,\varphi),$$
$$\chi_2=\chi_{20}\exp[2^{-1/2}(1-i)(\rho_2\omega/\eta_2)^{1/2}(R-r)]Y_{lm}(\theta,\varphi).$$

Boundary condition (47) can now be used to relate χ_{10} and χ_{20} to ψ_{10} and ψ_{20} which were introduced in (46).

Substituting the resulting expressions for χ_{10} and χ_{20} into (35) and (42), we find

$$-i\omega u=\frac{l}{R}\psi_{10}\left[1-\frac{l+1}{R}\frac{1+i}{2^{1/2}}\left(\frac{\eta_1}{\rho_1\omega}\right)^{1/2}\right]Y_{lm}(\theta,\varphi)$$
$$=-\frac{l+1}{R}\psi_{20}\left[1-\frac{l}{R}\frac{1+i}{2^{1/2}}\left(\frac{\eta_2}{\rho_2\omega}\right)^{1/2}\right]Y_{lm}(\theta,\varphi).$$

Expressing ψ_{10} and ψ_{20} in terms of u on the basis of this equation, and then substituting the result into (48), where we can omit the viscous term, we find the final expression for the dispersion relation:

$$\omega=\left[\frac{\alpha_l}{R^3}\frac{(l-1)l(l+1)(l+2)}{(l+1)\rho_1+l\rho_2}\right]^{1/2}$$
$$\times\left[1-\frac{i}{2R(2\omega)^{1/2}}\frac{(l+1)^2(\eta_1\rho_1)^{1/2}+l^2(\eta_2\rho_2)^{1/2}}{(l+1)\rho_1+l\rho_2}\right]. \quad (49)$$

This dispersion relation differs from that of an ordinary droplet by simply the replacement $\alpha\to\alpha_l$.

If a capillary wave is to be damped only slightly, we must, in accordance with (49), require $Q\gg1$, where

$$Q=\alpha\rho R/\eta^2. \tag{50}$$

The same condition guarantees the legitimacy of approximation (48). For spherical vesicles it would appear to be completely possible to satisfy the inequality $Q \gg 1$, but for micelles the opposite inequality would be more likely (see the Conclusion). We turn now to a calculation of the dispersion for the mode associated with distortions of the micelle shape, under the condition $Q \ll 1$.

As will be shown below, the frequency of this mode can be estimated from

$$\rho\omega R^2/\eta \sim Q \ll 1.$$

The term on the right side of (45) can thus be treated as a small correction to the equation $\eta\nabla^2\chi = 0$. Correspondingly, the solution of Eq. (45) can be sought by a perturbation theory in the small parameter $\rho\omega R^2/\eta$. The first two terms of the expansion are

$$\chi_1=\frac{il}{m}\psi_{10}\left(\frac{r}{R}\right)^l\left[1+\frac{i\rho_1\omega}{2\eta_1(2l+3)}\left(\frac{l+3}{l+1}R^2-r^2\right)\right]Y_{lm}(\theta,\varphi),$$

$$\chi_2=-\frac{i(l+1)}{m}\psi_{20}\left(\frac{R}{r}\right)^{l+1} \times\left[1-\frac{i\rho_2\omega}{2\eta_2(2l-1)}\left(\frac{l-2}{l}R^2-r^2\right)\right]Y_{lm}(\theta,\varphi). \tag{51}$$

In deriving (51) we used boundary condition (47) and expression (46). From (42) and (51) we find the following results for the radial component of the velocity:

$$v_{r1}=-\frac{il\rho_1\omega}{2\eta_1R(2l+3)}\psi_{10}\left(\frac{r}{R}\right)^{l-1}\left(\frac{l+3}{l+1}R^2-r^2\right)Y_{lm}(\theta,\varphi),$$

$$v_{r2}=-\frac{i(l+1)\rho_2\omega}{2\eta_2R(2l-1)}\psi_{20}\left(\frac{R}{r}\right)^{l+2}\left(\frac{l-2}{l}R^2-r^2\right)Y_{lm}(\theta,\varphi). \tag{52}$$

We can now use the relation

$$-i\omega u=v_{r1}(r=R)=v_{r2}(r=R)$$

to express ψ_{10} and ψ_{20} in terms of u. Substituting the result into (48), and replacing the derivatives with respect to r on the basis of (52), we finally find

$$\omega=-i\alpha_l(l-1)l(l+1)(l+2)/R[\eta_1(l+1)(2l^2+l+3) +\eta_2l(2l^2+3l+4)]. \tag{53}$$

This mode is of a purely relaxation nature.

We turn now to the mode associated with a redistribution of surface-active molecules over the surface of the micelle. This mode is more rigid than the mode with dispersion relation (53). Taking this circumstance into account, we find from Eqs. (35) and (36) that the potential component of the velocity near the surface can be ignored, while the solenoidal component depends on the radius in the same way as χ in (48). It is not difficult to see that as a result we have

$$\frac{\partial v}{\partial r}\gg\frac{1}{R}\frac{\partial v}{\partial\theta},\frac{1}{R}\frac{\partial v}{\partial\varphi},$$

so on the right sides of (37) and (38) we need retain only the terms with the derivative $\partial/\partial r$, and we can transform this derivative in accordance with functional dependence (48). Omitting also the terms with $\partial v/\partial t$, we find as a result

$$-\frac{1}{R}\frac{\partial\alpha}{\partial n_s}\frac{\partial n_s'}{\partial\theta}=\frac{1-i}{2^{1/2}}v_\theta{}^s[(\rho_1\eta_1\omega)^{1/2}+(\rho_2\eta_2\omega)^{1/2}],$$

$$-\frac{1}{R\sin\theta}\frac{\partial\alpha}{\partial n_s}\frac{\partial n_s'}{\partial\varphi}=\frac{1-i}{2^{1/2}}v_\varphi{}^s[(\rho_1\eta_1\omega)^{1/2}+(\rho_2\eta_2\omega)^{1/2}].$$

It is now a simple matter to find the dispersion relation for the mode of interest. We multiply the first of the equations written above by $(1/\sin\theta)\partial\sin\theta/\partial\theta$, multiply the second by $(1/\sin\theta)\partial/\partial\varphi$, and take the sum. Comparing the equation found as a result with (39), we find a closed equation for n_s', from which we find the dispersion relation

$$\omega=\frac{\pm3^{1/2}-i}{2}\left\{\frac{Bl(l+1)}{R^2[(\rho_1\eta_1)^{1/2}+(\rho_2\eta_2)^{1/2}]}\right\}^{2/3}, \tag{54}$$

where

$$B=-n_s\partial\alpha/\partial n_s. \tag{55}$$

The mode with dispersion relation (54) is completely analogous to the concentration mode which was analyzed in Ref. 13 for the case of a plane interface.

6. DYNAMIC CORRELATION FUNCTIONS

In this section of the paper we examine inelastic scattering by a microemulsion. We consider scattering with a small frequency transfer since the cross section for this type of scattering is determined by collective degrees of freedom. In this cross section we can distinguish two components, one stemming from the usual volume hydrodynamic modes and a second stemming from the surface modes which we discussed in the preceding section. This surface component of the cross section is a distinguishing feature of a microemulsion, so we will focus our attention on this component.

In practice, we would be talking about scattering of soft neutrons, x rays, or light by a microemulsion. The hope of observing a surface component of the scattering cross section is pinned on the large value of the total surface area of micelles in a microemulsion. We also note that the surface component of the cross section has an unusual frequency dependence, which might be of assistance in distinguishing it.

The cross section for inelastic scattering is determined by corresponding dynamic correlation functions. In analyzing inelastic scattering by a micelle we should, in accordance with the results of the preceding section, examine correlation functions

$$\langle u(t)u(0)\rangle,\quad\langle n_s'(t)n_s'(0)\rangle, \tag{56}$$

where u is the micelle surface displacement and n_s' is the change in the surface density of the surface-active substance. To calculate a correlation function of this type we should use Wyld's diagram technique,[18] which is set forth in Ma's monograph.[19] For the problem at hand, it is convenient to use the generating functional which generates this diagram technique; the corresponding formalism and the necessary references can be found in the monograph by Kats and Lebedev.[15]

Our immediate goal is to calculate the nucleating values of correlation functions (56) which correspond to linearized dynamic equations (35)–(39) discussed in the preceding section. The fluctuational corrections to the nucleating values will be small to the extent that interaction constant (20) is small. Calculating these corrections is a separate problem, whose solution goes beyond the scope of the present paper.

The calculation of nucleating values of correlation functions, which reduces to taking corresponding Gaussian integrals, usually presents no difficulty. In the case at hand the problem is complicated by the circumstance that we are interested in the correlation functions of surface quantities, while layers of liquid near the surface are also entrained in the motion associated with the surface modes. For this reason the procedure of calculating the nucleating values of correaltion functions (56) must include a joint analysis of the surface and volume degrees of freedom, and the latter must be effectively eliminated from consideration through an integration of this generating functional over them.

This generating functional is determined by a path integral which involves a factor of $\exp(iI)$, where I is an effective action which is determined by the dynamic equations of the system. The general recipe for constructing I is given in Ref. 15. For an individual micelle the effective action can be written as the sum

$$I=I_1+I_2+I_s, \tag{57}$$

where I_1 refers to the liquid within the micelle, I_2 to that outside the micelle, and I_s to the interface. The structure of I_1 and I_2 is determined by the volume hydrodynamic equations, while that of I_s is determined by the surface terms in boundary conditions (29)–(31).

The volume part of the effective action can be written in the form

$$I_{1,2}=\int dt\,d^3r\Big\{-\frac{\partial\mathbf{p}}{\partial t}\rho\mathbf{v}-P\nabla\mathbf{p}+\eta\nabla_k p_i(\nabla_i v_k+\nabla_k v_i)$$
$$+iT\eta\nabla_k p_i(\nabla_i p_k+\nabla_k p_i)\Big\}. \tag{58}$$

Here $\mathbf{p}$ is an auxiliary Bose field, I_1 is determined by an integral over the volume inside the micelle, and I_2 is determined by an integral over the volume outside the micelle. In writing (58) we omitted a term which is quadratic in the velocity and also some dissipative terms proportional to div $\mathbf{v}$. We will not need these terms below. The surface part of the action is

$$I_s=-\int dt\,ds\left(\nabla_k p_i{}^s T_{sik}+\frac{\partial p_i{}^s}{\partial t}\rho^s v_i\right). \tag{59}$$

Here T_{sik} is surface stress tensor (34), and $\mathbf{p}^s$ is the value of the field $\mathbf{p}$ on the surface.

To calculate the nucleating values of the correlation functions in action I it is sufficient to retain the term which is quadratic in the fields $\mathbf{p}$ and $\mathbf{v}$. The integration of $\exp(iI)$ over the volume components of $\mathbf{p}$ and $\mathbf{v}$ is then determined by Gaussian integrals; it reduces to the replacement of action I in the argument of the exponential function by its extremum over the fields $\mathbf{p}$ and $\mathbf{v}$. The conditions for an extremum,

$$\delta I/\delta\mathbf{v}=0,\qquad \delta I/\delta\mathbf{p}=0, \tag{60}$$

are conveniently written for components (41) and for components of the field $\mathbf{p}$ introduced in a corresponding way:

$$\mathbf{p}=\nabla\psi^p+\mathrm{rot}(\mathbf{r}\zeta^p)+\mathrm{rot}(\mathbf{n}\chi^p). \tag{61}$$

Conditions (60) lead to the equations

$$\partial^2\psi^p/\partial t^2-c^2\nabla^2\psi^p=0, \tag{62}$$

$$\rho\partial\chi^p/\partial t+\eta\nabla^2\chi^p=0, \tag{63}$$

$$\rho\partial\chi/\partial t-\eta\nabla^2\chi-2iT\eta\nabla^2\chi^p=0, \tag{64}$$

where $c^2=\partial P/\partial\rho$. For ζ^p and ζ there are equations completely analogous to equations (63), (64) for χ^p, χ. In deriving (62) we used the continuity equation

$$\partial\rho/\partial t=-\nabla(\rho\mathbf{v}), \tag{65}$$

and we omitted an inconsequential dissipative term. A corresponding dissipative term can be omitted in the equation for ψ; as a result, that equation reduces to relation (43), from which, along with (65), we find the standard equation

$$\partial^2\psi/\partial t^2-c^2\nabla^2\psi=0. \tag{66}$$

Integrating by parts, we can put the volume terms in (58) in the form

$$I_{1,2}=\int dt\,d^3r\Big\{\mathbf{p}\frac{\delta I_{1,2}}{\delta\mathbf{p}}-iT\mathbf{p}\frac{\delta I_{1,2}}{\delta\mathbf{v}}-iT\eta\rho\mathbf{p}\frac{\partial\mathbf{p}}{\partial t}$$
$$-iT\rho c^2\nabla\mathbf{p}\left(\frac{\partial}{\partial t}\right)^{-1}\nabla\mathbf{p}\Big\}+\ldots. \tag{67}$$

The ellipsis (...) in (67) represents surface terms. The first two terms in (67) vanish when the extremum of the action is taken, by virtue of (60); the third and fourth can be omitted since they are total time derivatives. When an extremum over the fields $\mathbf{p}$ and $\mathbf{v}$ is taken, the volume part of action (58) reduces to a surface term, for which the explicit expression is

$$I_{1,2}^{\mathrm{ext}}=\int dt\,ds_k\Big\{-p_kP+\eta p_i(\nabla_i v_k+\nabla_k v_i)$$
$$+iT\eta p_i(\nabla_i p_k+\nabla_k p_i)+iT\rho p_k\frac{\partial\psi^p}{\partial t}\Big\}. \tag{68}$$

The last term in (68) has been transformed with the help of Eq. (62).

In an analysis of a shperical micelle, the integral in (59), (68) should be understood as an integral over the surface of a sphere of radius R. Equations (36)–(38) are of course extrema of the action in this case:

$$I_\mathrm{I}=I_1{}^{ext}+I_2{}^{ext}+I_s. \tag{69}$$

Equations (35) and (39) should now be understood as additional conditions which relate u and n_s' with the dynamic variables $\mathbf{v}_s$. Expression (68) does not yet give us the purely surface action, since it contains derivatives $\partial\mathbf{v}/\partial r$ and $\partial\mathbf{p}/\partial r$, which should be determined from the volume equations for $\mathbf{v}$ and $\mathbf{p}$.

Since we are interested in correlation functions (56), it is convenient to eliminate the other variables which figure in (69) by integrating $\exp(iI_\mathrm{I})$ over them. Since the corresponding integrals are Gaussian, this integration reduces to the replacement of I_I by its extremum over the fields which are being eliminated. This procedure cannot be carried out in general form; we will do it separately for each type of surface mode.

We first consider the mode with dispersion relation (54), which is associated with a redistribution of the surface-active substance over the surface of the micelle. In this case it is meaningful to consider the correlation function $\langle n_s' n_s' \rangle$. As in the analysis of dispersion relation (54), in evaluating this correlation function we can assume

$$R\frac{\partial\chi}{\partial r} \gg \frac{\partial\chi}{\partial\theta}, \frac{\partial\chi}{\partial\varphi}. \tag{70}$$

Corresponding inequalities hold for ζ, χ^p, and ζ^p. In this situation, taking an extremum of (69) over ψ and ψ^p reduces in the leading order to simply the conditions $\psi = \psi^p = 0$.

Taking the extremum of action (69) with respect to ζ, we find the condition

$$\frac{\partial p_\theta}{\partial\varphi} - \frac{\partial}{\partial\theta}(\sin\theta p_\varphi) = 0. \tag{71}$$

Using (71) and $\psi = \psi^p = 0$ to transform action (69), we find, in the leading approximation,

$$I_{\rm I}^{ext} = R^2 \int dt\, do \left\{ \frac{\partial\alpha}{\partial n_s} Rp\nabla_\perp^2 n_s' + p\frac{\partial}{\partial\varphi}\left[\eta_1 \frac{\partial^2}{\partial r^2}(\chi_1 + iT\chi_1^p) - \eta_2 \frac{\partial^2}{\partial r^2}(\chi_2 + iT\chi_2^p)\right]\right\}. \tag{72}$$

Here we have introduced a field p such that we have

$$p_\theta = \partial p/\partial\theta. \tag{73}$$

It is not difficult to verify that the following equation holds when we use (71):

$$\frac{\partial^2\chi_1^p}{\partial\varphi\partial r} = \frac{\partial^2\chi_2^p}{\partial\varphi\partial r} = -R^2\nabla_\perp^2 p. \tag{74}$$

Writing an expression for the combination of velocities which figures in (39), we find, in the leading approximation,

$$\frac{\partial n_s'}{\partial t} = \frac{n_s}{R}\frac{\partial^2\chi_1}{\partial r\partial\varphi} = \frac{n_s}{R}\frac{\partial^2\chi_2}{\partial r\partial\varphi}. \tag{75}$$

By virtue of Eqs. (63) and (64), χ and χ^p are damped exponentially with distance from the surface. For the Fourier component with frequency ω inside the micelle, the following proportionality holds in the leading order:

$$\chi + iT\chi^p \propto \exp[-i(i\rho_1\omega/\eta_1)^{1/2}(r-R)]. \tag{76}$$

The argument of the exponential function has been chosen here in a form convenient for analytic continuation into the upper half-plane. A corresponding proportionality law holds outside the micelle. Expressing the second derivatives with respect to r in (72) in terms of the first derivatives on this basis, and using (74) and (75), we find

$$I_{\rm I}^{ext} = R^2 \int dt\, do\, Rp\left\{ -\frac{B}{n_s}\nabla_\perp^2 n_s' + \frac{x}{n_s}(1 - i\,\mathrm{sgn}\,\omega)|\omega|^{1/2}\frac{\partial n_s'}{\partial t} - iTRx|\omega|^{1/2}\nabla_\perp^2 p\right\}, \tag{77}$$

where

$$x = (\rho_1\eta_1/2)^{1/2} + (\rho_2\eta_2/2)^{1/2}. \tag{78}$$

We can now use the standard rules[20,21] to find an expression for the binary correlation function $\langle n_s' n_s' \rangle$. It is convenient to write the expression for the correlation functions of the coefficients of an expansion in spherical harmonics:

$$n_s'(\theta,\varphi) = n_s \sum_{lm} \nu_{lm} Y_{lm}(\theta,\varphi).$$

The Fourier component of the correlation function $\langle \nu_{lm}(t)\nu_{l-m}(0)\rangle$ is given by

$$\langle \nu_{lm}\nu_{l-m}\rangle_\omega = \frac{2T}{R^4}\frac{l(l+1)x|\omega|^{1/2}}{[(B/R^2)l(l+1) - x|\omega|^{3/2}]^2 + x^2|\omega|^3}. \tag{79}$$

The simultaneous correlation function $\langle \nu_{lm}(t)\nu_{l-m}(t)\rangle$ is given by

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\langle \nu_{lm}\nu_{l-m}\rangle_\omega = \frac{T}{BR^2}. \tag{80}$$

As expected, the right side of (80) is the same as the static correlation function, since we have

$$B = -n_s\frac{\partial\alpha}{\partial n_s} = n_s^2\frac{\partial^2\varepsilon_s}{\partial n_s^2}.$$

The correlation function

$$\langle \nu_{lm} p_{l-m}\rangle = [R^3 x\omega(2i\omega)^{1/2} - BRl(l+1)]^{-1}$$

has the meaning of a generalized susceptability[15] and is accordingly analytic in the upper half-plane. The dispersion relation for the natural modes of the system should be determined by singularities of the generalized susceptibility in the lower half-plane. At frequencies (54), this correlation function does indeed have poles.

We now consider the mode with dispersion relation (53), which is associated with distortions of the shape of the micelle surface. We will calculate the corresponding correlation function $\langle uu \rangle$. The condition for an extremum of action (69) with respect to n_s' leads to the relation

$$\frac{\partial}{\partial\theta}(\sin\theta p_\theta) + \frac{\partial}{\partial\varphi}p_\varphi = 0. \tag{81}$$

Yet another relation between p_θ and p_φ comes from the condition for an extremum of the action with respect to ζ. As a consequence of these two relations, we have $p_\theta = p_\varphi = 0$ on the surface.

Using this result, and omitting the term with $\rho^s \partial\mathbf{v}/\partial t$, we can write an effective action as follows:

$$I_{\rm II} = R^2\int dt\, do\, p_r\left\{ -\left(\alpha + \frac{2\beta}{R}\right)\left(\nabla_\perp^2 + \frac{2}{R^2}\right)u + \varkappa\left(\nabla_\perp^4 + \frac{2\nabla_\perp^2}{R^2}\right)u + \rho_1\left(\frac{\partial\psi_1}{\partial t} + iT\frac{\partial\psi_1^p}{\partial t}\right) - \rho_2\left(\frac{\partial\psi_2}{\partial t} + iT\frac{\partial\psi_2^p}{\partial t}\right) + 4\frac{\eta_2 - \eta_1}{R}(v_r + iTp_r)\right\}. \tag{82}$$

Here we are using relation (43) and also

$$\left(\frac{\partial p_{r\,1,2}}{\partial r}\right)_{r=R} = -\frac{2}{R}p_{r\,1,2}, \quad \left(\frac{\partial v_{r\,1,2}}{\partial r}\right)_{r=R} = -\frac{2}{R}v_{r\,1,2}.$$

These relations follow from the conditions div $\mathbf{v}$ = div

$\mathbf{p} = 0$ [which in turn follow from (62) and (65) in the low-frequency limit], Eq. (39) (in which we can omit $\partial n_s/\partial t$), and (81).

We now need to solve system (62)–(64), (66) for ψ, χ, ψ^p, and χ^p, taking account of the additional constraints imposed on these functions by conditions (39) and (81). The procedure for solving these equations is similar to that used in calculating (52). As a result, we find the following relations for functions with an angular dependence $\propto Y_{lm}(\theta,\varphi)$ in the leading approximation in ω:

$$v_r+iTp_r=\frac{\rho_1 Rl}{\eta_1(2l+3)(l+1)}\left(\frac{\partial\psi_1}{\partial t}+iT\frac{\partial\psi_1{}^p}{\partial t}\right)$$
$$=-\frac{\rho_2 R(l+1)}{\eta_2(2l-1)l}\left(\frac{\partial\psi_2}{\partial t}+iT\frac{\partial\psi_2{}^p}{\partial t}\right).$$

These relations are valid at $r = R$. They make it possible to express the integrand in (82) in terms of p_r and v_r.

Replacing v_r by $\partial u/\partial t$ in accordance with (35), we finally find

$$I_{\rm III}=\sum_{lm}\int dt\left\{\alpha_l(l-1)(l+2)p_{r\,l-m}u_{lm}+\Gamma_l p_{r\,l-m}\left(\frac{\partial u_{lm}}{\partial t}+iTp_{rlm}\right)\right\}. \qquad (83)$$

We have switched here from an integration over angles to a summation over spherical harmonics; α_l is determined by (17); and

$$\Gamma_l=R\left(\frac{2l^2+l+3}{l}\eta_1+\frac{2l^2+3l+4}{l+1}\eta_2\right). \qquad (84)$$

From the form of (83) for the effective action we find, working by the standard rules,[20,21] the following expression for the Fourier component of the binary correlation function $\langle u(t)u(0)\rangle$:

$$\langle u_{l-m}u_{lm}\rangle_\omega=\frac{2\Gamma_l T}{\alpha_l{}^2(l-1)^2(l+2)^2+(\Gamma_l\omega)^2}. \qquad (85)$$

The equal-time correlation function $\langle u(t)u(t)\rangle$ is

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\langle u_{l-m}u_{lm}\rangle_\omega=\frac{T}{\alpha_l(l-1)(l+2)}. \qquad (86)$$

This correlation function is of course the same as the static correlation function calculated from (15). Correlation function (85) has a pole at frequency (53).

We now consider the correlation function $\langle uu\rangle$ in the range of applicability of dispersion relation (49), which describes ordinary capillary waves. In this case, a functional dependence of the type in (76) holds. Now using conditions (39) (without $\partial n_s/\partial t$) and (81), we find, on the surface,

$$\frac{\partial}{\partial\varphi}(\chi_1+iT\chi_1{}^p)=iR\left(\frac{\eta_1}{i\rho_1\omega}\right)^{1/2}\nabla_\perp{}^2(\psi_1+iT\psi_1{}^p),$$
$$\frac{\partial}{\partial\varphi}(\chi_2+iT\chi_2{}^p)=-iR\left(\frac{\eta_2}{i\rho_2\omega}\right)^{1/2}\nabla_\perp{}^2(\psi_2+iT\psi_2{}^p).$$

For the component proportional to $Y_{lm}(\theta,\varphi)$ we then find

$$v_r+iTp_r=\frac{l}{R}\left[1-i\left(\frac{\eta_1}{i\rho_1\omega}\right)^{1/2}\frac{l+1}{R}\right](\psi_1+iT\psi_1{}^p)$$
$$=-\frac{l+1}{R}\left[1-i\left(\frac{\eta_2}{i\rho_2\omega}\right)^{1/2}\frac{l}{R}\right](\psi_2+iT\psi_2{}^p).$$

Expressing $\psi_1+iT\psi_1^p$ and $\psi_2+iT\psi_2^p$ in terms of v_r+iTp_r on the basis of these equations, and substituting the results into (82), we find the action $I_{\rm IV}$, in which there are only surface quantities. The last term in the integrand in (82) can be omitted here.

Replacing v_r by $\partial u/\partial t$ in accordance with (35), and switching from an integration over angles to a summation over spherical harmonics, we finally find

$$I_{\rm IV}=\sum_{lm}\int dt\left\{\alpha_l(l-1)(l+2)p_{rl-m}u_{lm}+R^3\rho_l p_{rl-m}\frac{\partial^2 u_{lm}}{\partial t^2}+R^2x_l|\omega|^{1/2}\left(\frac{\partial u_{lm}}{\partial t}+iTp_{rlm}\right)\right\}. \qquad (87)$$

Here

$$\rho_l=\frac{\rho_1}{l}+\frac{\rho_2}{l+1},\qquad x_l=\frac{l+1}{l}\left(\frac{\rho_1\eta_1}{2}\right)^{1/2}+\frac{l}{l+1}\left(\frac{\rho_2\eta_2}{2}\right)^{1/2}. \qquad (88)$$

In deriving (87) we discarded small terms on the order of the parameter Q^{-1} everywhere, where Q is given by (50) (a small value of Q^{-1} guarantees that the damping of the capillary wave is slight).

Using explicit expression (87), and working by the standard rules,[20,21] we find Fourier component of the correlation function $\langle u(t)u(0)\rangle$:

$$\langle u_{lm}u_{l-m}\rangle_\omega=\frac{2Tx_lR^2|\omega|^{1/2}}{[R^3\rho_l\omega^2-\alpha_l(l-1)(l+2)]^2+R^4x_l{}^2|\omega|^3}. \qquad (89)$$

It is not difficult to verify that relation (86) is valid for correlation function (89) in the leading approximation in Q^{-1}. We can thus reproduce the static limit. Note that correlation function (89) has a pole at frequency (49).

The inelastic scattering is actually determined by correlation functions averaged over the distribution of micelles. For the scattering of neutrons, for example, we should speak in terms of a density correlation function, in the scattering of light we should speak in terms of a correlation function of the dielectric susceptibility, and so forth. For a single micelle all such quantities can be written as a sum of the type in (26). For definiteness we will discuss the mass density:

$$\rho=\rho_1\theta(-\Phi)+\rho_2\theta(\Phi)+\rho_s|\nabla\Phi|\delta(\Phi). \qquad (90)$$

In the leading approximation, ρ_1 and ρ_2 can be treated as constants, and ρ_s as depending on n_s. A fluctuation of the density can then be written in the form

$$\rho'(\mathbf{r})=\left[(\rho_1-\rho_2)u+\frac{\partial\rho_s}{\partial n_s}n_s'\right]\delta(|\mathbf{r}-\boldsymbol{\xi}|-R),$$

where $\boldsymbol{\xi}$ is the radius vector of the center of a micelle, of radius R.

We can now express the correlation function $\langle\rho'\rho'\rangle$ in terms of the correlation functions $\langle uu\rangle$ and $\langle n_s'n_s'\rangle$. Averaging the result over the position of the micelles, and transforming to the Fourier component with the wave vector k, we find

$$\langle\rho'(t)\rho'(0)\rangle_k=NR^4\int do_1\,do_2\exp[-ikR(\cos\theta_1-\cos\theta_2)]$$
$$\times\Big[(\rho_1-\rho_2)^2\langle u(t\theta_1\varphi_1)\,u(0\theta_2\varphi_2)\rangle$$
$$+\left(\frac{\partial\rho_s}{\partial n_s}\right)^2\langle n_s(t\theta_1\varphi_1)\,n_s(0\theta_2\varphi_2)\rangle\Big].$$

Here N is the number of micelles per unit volume, and the integration is over the surface of a micelle.

Transforming to the Fourier time component, and integrating over the angles, we finally find

$$\langle\rho'\rho'\rangle_{\omega k}=4\pi NR^4\sum_l(-1)^l(2l+1)$$
$$\times\left[\left(\frac{R}{k}\right)^l\left(\frac{1}{R}\frac{d}{dR}\right)^l\frac{\sin kR}{kR}\right]^2$$
$$\times\left[(\rho_1-\rho_2)^2\langle u_{lm}u_{l-m}\rangle_\omega+\left(\frac{\partial\rho_s}{\partial\ln n_s}\right)^2\langle v_{lm}v_{l-m}\rangle_\omega\right].\tag{91}$$

Here the summation pertaining to the correlation function $\langle uu\rangle$ begins with $l=2$, while that pertaining to $\langle vv\rangle$ begins with $l=1$. If $kR\ll 1$, we should retain only the first terms in sum (91); as a result we find

$$\langle\rho'\rho'\rangle_{\omega k}\approx\frac{4\pi}{3}NR^4(kR)^2\Big[\frac{(kR)^2}{15}(\rho_1-\rho_2)^2\langle u_{lm}u_{l-m}\rangle_\omega$$
$$-\left(\frac{\partial\rho_s}{\partial\ln n_s}\right)^2\langle v_{lm}v_{l-m}\rangle_\omega\Big].\tag{92}$$

We recall that expressions (91) and (92) are not specific to the density correlation function. Corresponding expressions could be written for any local quantity which can be represented as in (90). To estimate the cross section for the scattering of light, for example, we should use the permittivity. The correlation functions which figure in (91) and (92) are given by expressions (79) and (85) or (89). The integrated scattering cross section can be estimated from (80) and (86).

7. CONCLUSION

We have examined the dynamic properties of a liquid droplet on whose surface there is a film which is a membrane in the case of a vesicle or a monolayer of surface-active molecules in the case of a micelle. It turns out that for a droplet of this type there are at least two characteristic surface modes. One is associated with a time variation in the shape of the droplet surface. In the case of a plane interface (a droplet of large radius) this mode converts into an ordinary capillary wave. The other mode is associated with a change in the density of the surface film.

The latter mode has an extremely unusual dispersion relation, which is given by (54). This expression involves the quantity B, given in (55), which is a positive-definite quantity since the surface tension at a water-oil interface decreases with increasing concentration of the surface-active substance at this interface. In contrast with the surface tension α itself, which is anomalously small for a micelle, the derivative $\partial\alpha/\partial n_s$ has no special small factor. We would thus expect B to have a value on the order of an ordinary surface tension, i.e., $\sim 10\ \mathrm{erg/cm^2}$. This is thus a fairly high-frequency mode, and the derivative which determines B should be regarded as adiabatic (and isobaric).

The mode associated with a change in the shape of the micelle surface, on the other hand, is no different from ordinary capillary waves for vesicles of micron size. For micelles, however, this is not the case, because of the anomalously small surface tension α. For a micelle, this mode is overdamped, and its dispersion relation is (53). In deriving this dispersion relation we used the condition $\delta^{\perp}_{ik}\nabla_k V^s_i=0$ which follows from (39) and which presupposes a fairly high concentration of surface-active molecules at the interface.

Using $\alpha\sim\beta^2/\varkappa$, we can rewrite the condition for the applicability of dispersion relation (53) in the form

$$R_m\gg R_v,$$

where R_m is the micelle radius from (7), and $R_v=\rho\varkappa/\eta^2$ is on the order of a molecular size. The condition for the applicability of dispersion relation (53) is thus essentially the same as the condition which ensures the validity of a macroscopic description of a micelle.

The inequality written just above clearly holds as $\beta\to 0$. In the formalism which we have been using here, this inequality means that we are approaching a so-called lamellar phase.[2] The latter consists of alternating layers of water and oil, which would correspond to an infinite radius of curvature of the interface, i.e., $\beta=0$ (a lamellar phase actually exists not only at $\beta=0$ but also in some neighborhood of this point, because there is no interaction of the layers in our formalism). The growth of the micelle radius near the transition to the lamellar phase leads to an increase in the intensity of inelastic scattering by the micelle. According to (6) and (17), this mode softens. A lamellar phase can be controlled only if the external parameters (the pressure and the temperature) are chosen in a certain way, while for a vesicle the condition $\beta=0$ would always hold.

These surface modes of a droplet are analogous to the modes of a plane water-oil interface at which there is a surface-active substance. The dynamics of the latter case was analyzed by Kats and Lebedev in Ref. 13. There is a complete analogy for the case of a liquid interface. This is a natural situation, since the interface discussed above was essentially treated as a liquid surface. As a result, terms (including some which depend on the curvature) which are invariant with respect to the choice of coordinate system appear in the expansion of the energy.

As was pointed out in Ref. 13, when an order (crystalline or liquid-crystal) is produced in the film some new low-frequency surface modes arise. They stem from a spontaneous violation of the symmetry of the surface. The modes characteristic of the liquid film persist even in an ordered film; their dispersion relation turns out to be insensitive to the symmetry of the film. A corresponding assertion apparently holds for the surface of a micelle or vesicle.

As we mentioned earlier, thermal fluctuations lead to a logarithmic renormalization of the constants of the theory. It would clearly be of methodological interest to examine the role played by thermal fluctuations in the micelle surface dynamics. Dynamic fluctuational contributions would be determined by the same interaction constant, g in (20), as in the static case. The role of dynamic fluctuations would accordingly be significant at sufficiently large values of g and would be governing in a "random" de Gennes-Taupin phase, with $g\gtrsim 1$.

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