Dynamics of Langmuir films

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A study is made of the dynamics of monomolecular Langmuir films formed by molecules of a surface-active substance at an interface between a liquid and a gas. All possible homogeneous phases of a Langmuir film permitted by the symmetry are considered: liquid, nematic, smectic, and crystalline. The boundary conditions are derived for the liquid-gas interface in the presence of a Langmuir film. The attention is concentrated on low-frequency surface modes the spectrum of which reflects directly the film symmetry. An important role of thermal fluctuations in the dynamics of smectic and nematic films is pointed out. The effects associated with the dipole interaction are considered.

INTRODUCTION

There is considerable interest in Langmuir films formed on the surfaces of water by molecules of a surface-active substance (surfactant). This interest is related mainly to the possibility of transfer of a Langmuir film to a solid substrate. Repeated application of such a procedure produces multilayer films on a solid with a given order of layers. Such "molecular architecture" makes it possible to create materials very promising from the point of view of their applications.[1]

However, Langmuir films are of interest for their own sake. For example, a change in the concentration of a surfactant in a Langmuir film results in numerous phase transformations the nature of which is still unclear. This is related primarily to the difficulties encountered in experimental investigations of such films. Such a situation reduces opportunities for molecular architecture, because the structure of the film transferred to the solid substrate is not clear.

We shall begin an analysis of a phase diagram of a Langmuir film from the classification of the phases which may be formed. From the symmetry point of view we can distinguish the following possibilities: a liquid or a gas, nematic, smectic, crystalline. Some of these phases may exhibit a spontaneous dipole moment in the plane of the film. The associated effects are discussed briefly at the end of the paper.

We shall assume that this symmetry classification applies only to homogeneous films. Several recent experimental investigations[2] have demonstrated that some phases of a Langmuir film correspond to an inhomogeneous state of the emulsion type. Such a situation requires a special analysis and will not be considered here.

Our task is to provide a dynamic criterion for the classification of surface phases in accordance with their symmetry. With this in mind we shall consider the surface dynamics of a liquid in the presence of a Langmuir film. Surface dynamic effects in a liquid are among the classical objects of interest in hydrodynamics. Basic information about these effects can be found in monographs.[3,4] In particular, these monographs give the spectrum of surface waves and the characteristics of damping of these waves in the presence of a surface film. However, such a spectrum is not very sensitive to the film symmetry. Therefore, we shall concentrate our attention on other low-frequency surface modes the spectrum of which reflects directly the film symmetry.

In studies of these modes we have to use the boundary conditions at a liquid-gas interface in the presence of a Langmuir film. Derivation of these boundary conditions allowing for the film symmetry is not a trivial task. It should be pointed out that when discussing surface dynamics of smectic and nematic films it is necessary to allow for the role of thermal fluctuations.

THERMODYNAMICS OF A FILM

We shall begin with an investigation of thermodynamics of a liquid--gas system in the presence of a Langmuir film at the interface. All the parameters representing a gas will be identified by a prime and the parameters of the interface will be labeled by an index s. It will be convenient to regard these as functions of all three spatial variables. Naturally, all the physical quantities can be expressed solely in terms of the values of these parameters on the surface.

The position of the interface in space will be described by the equation $\Phi = 0$, where Φ is a certain function of the radius vector. We shall assume that $\Phi > 0$ in the part of the space occupied by the gas and $\Phi < 0$ in that part which is occupied by the liquid. Then, a unit vector

$$l_i = \nabla_i \Phi / |\nabla \Phi| \tag{1}$$

is perpendicular to the surface and directed toward the gas.

In the spirit of a local equilibrium we can expect a macroscopic state of a system of this kind to be governed by a locally defined set of parameters. These parameters are extensive quantities that do not have δ-like singularities at the interface. In this case the thermodynamic state of a system is described by the thermodynamic potential Ω (Ref. 5).

It is convenient to represent Ω by an integral over the whole space, separating integration over the surface and over the liquid and gas regions, and introducing in the integrand both δ functions and step θ functions of Φ:

$$\Omega = \int d^3r[-\theta(-\Phi)P + |\nabla\Phi|\delta(\Phi)\alpha - \theta(\Phi)P']. \tag{2}$$

Here, P is the pressure in the liquid, P' is the pressure in the gas, and α is the surface tension. As expected, Eq. (2) is invariant under the transformation

$$\Phi \to f(\Phi), \quad f(0) = 0, \tag{3}$$

where f is an arbitrary function which satisfies the only second condition of Eq. (3).

The pressure P in Eq. (2) is a function of the temperature of the system T, chemical potential μ, and velocity $\mathbf{v}$. The thermodynamic identity for the pressure is

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$$dP=\rho d\mu+sdT+\mathbf{j}d\mathbf{v}. \tag{4}$$

Here, ρ is the mass density, s is the entropy density, and j is the density of the momentum. It follows from the Gallilean invariance that P depends only on the combination $\mu+\mathbf{v}^2/2$, which guarantees that $j=\rho\mathbf{v}$. A relationship similar to Eq. (4) applies also to a gas.

In general, we must allow also for the dependence of α on the chemical potential of surfactant molecules. Generalization of our procedure to this case presents no difficulty. However, we shall assume that practically all the surfactant molecules are concentrated on the surface (which corresponds to real experimental situations), so that the dependence mentioned above can be ignored.

The set of variables which govern the surface tension α is determined by the film symmetry. In the case of a liquid film the surface tension α is a function of the surface temperature T_s, chemical potential μ_s, velocity $\mathbf{v}_s$, and chemical potential of the surfactant ν_s. The thermodynamic identity for α is

$$d\alpha=-s_sdT_s-\rho_sd\mu_s-\mathbf{j}_sd\mathbf{v}_s-n_sd\nu_s. \tag{5}$$

Here s_s, ρ_s, j_s, and n_s are the surface densities of the entropy, mass, momentum, and number of surfactant molecules. We note that the surface mass density appears in the identity (5). It vanishes only when α is independent of μ_s, which is true, for example, in the case of an equilibrium between a liquid and its own vapor. However, in our case there is no justification for such an assumption. In view of the Gallilean invariance, we have

$$\mathbf{j}_s=\rho_s\mathbf{v}_s. \tag{6}$$

In the case of a crystalline film we have to allow for the dependence of the surface tension α on the strain tensor, which is equivalent to a dependence on ∇W_β, where the index β assumes two values and the meaning of the functions W_β is that they are (independent) phases of the density modulation, i.e., the equations $W_\beta=$ const (taken separately) govern the positions of some of the atomic layers. We shall consider W_β as a function of a three-dimensional radius vector, whereas physically W_β is defined only at the interface. This means that α can depend only on a combination which is invariant under the substitution $W_\beta \to W_\beta + f_\beta(\Phi)$. Such a combination is $\nabla_i^1 W_\beta$, where

$$\nabla_i^{\perp}=\delta_{ik}^{\perp}\nabla_k, \quad \delta_{ik}^{\perp}=\delta_{ik}-l_il_k. \tag{7}$$

A unit vector $\mathbf{l}$ along the normal to the surface is defined by Eq. (1).

We shall assume that under equilibrium conditions the interface coincides with the $z=0$ plane. We can investigate the deviations of a crystalline film from an equilibrium position by selecting (for the sake of convenience) the function Φ in the form

$$\Phi=z-u_z(x,\ y). \tag{8}$$

Here, u_z represents the displacement vector of the film along the z axis. The quantity u_z in Eq. (8) is not generally assumed to be small.

Following Eq. (8), we can similarly represent the function W_α:

$$W_\alpha \propto r_\alpha - u_\alpha(x,y). \tag{9}$$

Here and later the Greek indices have the values x or y. The first term on the right-hand side of Eq. (9) gives the equilibrium value of W_α corresponding to the undeformed state of a two-dimensional crystal. The second term in Eq. (9) appears as a result of deformation (strain) and represents the displacement vector of the crystal lattice in the xy plane. In the case of small deviations from equilibrium the elastic energy of the film with the hexagonal symmetry can be represented by

$$\alpha_{el}={}^1/_2B_l(\nabla_\alpha u_\alpha)^2+{}^1/_2B_t(\varepsilon_{\alpha\beta}\nabla_\alpha u_\beta)^2. \tag{10}$$

Here, $\varepsilon_{\alpha\beta}$ is a two-dimensional antisymmetric tensor and $B_{l,t}$ are the elastic moduli. The number of such moduli decreases on reduction in the symmetry of a crystalline film.

A film with modulation of the density only along one of the directions can be assumed to exhibit smectic ordering. In this case there is only one density modulation phase which we shall denote by W. By definition, the equation $W=$ const specifies the position of a smectic layer on a film. In the case of a smectic film the surface tension α depends on $\nabla_i^1 W$. It is well known that in the case of a three-dimensional smectic the expression for the energy cannot be limited to the dependence on the first derivative ∇W because of the absence of the shear modulus of layers relative to one another. This is exactly the situation in the case of a two-dimensional smectic. Therefore, we have to allow also for the dependence on $\nabla^{12} W$.

The leading terms of the expansion of α in terms of the gradients of W can be described as follows:

$$\alpha_{sm}={}^1/_8B[q_0^{-2}(\nabla^{\perp}W)^2-1]^2+{}^1/_2Kq_0^{-2}(\nabla^{\perp 2}W)^2, \tag{11}$$

where B and K are the elastic moduli and the wave vector $q_0=q_0(\mu_sT_s\nu_s)$ determines the density modulation period. Under equilibrium conditions, we have $|V={}^1W|=q_0$; we shall assume that $W=q_0x$, i.e., that smectic layers are parallel to the y axis. In the case of deviation from equilibrium, we have

$$W=q_0(x-u_x(x,\ y)), \tag{12}$$

where u_x plays the role of a displacement of smectic layers along the x axis. In the quadratic approximation, we have

$$\alpha_{sm}={}^1/_2B(\nabla_xu_x)^2+{}^1/_2K(\nabla^{\perp 2}u_x)^2. \tag{13}$$

As is known, in the three-dimensional case we can expect fluctuations of the displacement of smectic layers to give rise to a logarithmic renormalization of the moduli B and K (Ref. 6). These fluctuations are manifested even more strongly by a film which is a two-dimensional system. Fluctuations of the displacement of the interface play no significant role, so that in studies of the fluctuation effects we can assume that the interface is plane. In this case we can apply anisotropic scaling. The indices of the moduli B and K can be estimated using the ε expansion[7] in three-dimensional space.

It follows from Ref. 6 that in the $3-\varepsilon$ space the moduli B and K have renormalization group equations, which in the single-loop approximation are

$$d\ln B/dL=-2g, \qquad d\ln K/dL=g. \tag{14}$$

Here, $L=\ln(\Lambda r_y)$, where Λ is the cutoff wave vector and r

is the characteristic scalar along the y axis. In the case of an invariant charge g, Eq. (14) yields the proportionality:

$$g \propto B^{1/2} r_y^{\varepsilon} / K^{3/2}. \tag{15}$$

It follows from Eqs. (14) and (15) that the following scaling laws apply at the point $g = 2\varepsilon/5$:

$$B \propto r_y^{-4\varepsilon/5},\ K \propto r_y^{2\varepsilon/5}. \tag{16}$$

Substitution of $\varepsilon = 1$ into Eq. (16) shows that the modulus B of a film decreases very rapidly, whereas the modulus K rises on increase in the scaling length.

Spontaneous breaking of the rotational symmetry of a film may result in structures with the symmetry D_2, D_4, and D_6. In the case of the symmetry D_6 it is natural to refer to a hexatic film, whereas for D_2 we are dealing with a two-dimensional nematic. This state is characterized by a director $\mathbf{n}$, which is tangential to the film: $\mathbf{n},\mathbf{l} = 0$. Inhomogeneous strains n can be described conveniently with the aid of a nonholonomic angle φ, the variation of which is found as follows

$$\delta\varphi = 2\,[\mathbf{nl}]\,\delta\mathbf{n}. \tag{17}$$

We can readily show that the commutation function of variations of the angle φ is of the form

$$(\delta_1\delta_2 - \delta_2\delta_1)\varphi = 2|\nabla\Phi|^{-2}\varepsilon_{ikn} l_i \nabla_k \delta_1\Phi \nabla_n \delta_2\Phi. \tag{18}$$

Similarly, we can define a nonholonomic angle φ which satisfies the commutation rule (18) and can be introduced also for phases with the D_4 and D_6 symmetry.

The angle φ is considered as a function of W_α and it is defined at the interface, so that α should depend only on the combination $\nabla^{\perp}\varphi$. In the case with the D_2 symmetry the leading term of the expansion of α in terms of the parameter $\nabla\varphi$ can be represented as follows:

$$\alpha_{or} = {}^1/_2 A (\nabla^{\perp}\varphi)^2 + {}^1/_2 A_1 [(\nabla^{\perp}\varphi)^2 - 2(\mathbf{n}\nabla\varphi)^2]. \tag{19}$$

Here, A and A_i are the orientation moduli. In the case of phases of the symmetry D_4 and D_6 the orientational energy has a form similar to Eq. (19) but with $A_i = 0$, i.e., it is basically isotropic.

In the case of a two-dimensional system containing a film of the kind described above it is found that fluctuations of the director n play an important role. In studies of the fluctuation effects associated with n it has been usual to assume that the film is plane. It is demonstrated in Ref. 8 that in this situation we could expect fluctuations to result in logarithmic renormalization of the orientational moduli A and A_1 in Eq. (19). In the one-loop approximations there are no corrections to the modulus A, whereas the modulus A_1 decreases in accordance with the following scaling law:

$$A_1 \propto r^{-\xi}, \quad \xi = T/4\pi A, \tag{20}$$

where r is the characteristic scaling length. This is also true of other terms of the expansion of α in terms of $\nabla\varphi$ for all the phases mentioned above when the rotational invariance breaks down.

It follows that an increase in the scaling length causes isotropization of the orientational energy. In other words, the phases exhibiting the "unrenormalized" symmetry D_2, D_4, and D_6 acquire an asymptotic symmetry D_∞. This does not exclude the possibility of experimental observation of the anisotropy of a nematic Langmuir film, since in the case of finite scaling lengths the modulus A_1 remains finite.

It follows from general thermodynamic relationships[5] that the potential Ω can be used to determine the energy E of the system under investigation. It follows from Eq. (2) that

$$E = \int d^3r[\varepsilon\theta(-\Phi) + \varepsilon_s\delta(\Phi)\,|\nabla\Phi| + \varepsilon'\theta(\Phi)]. \tag{21}$$

Here, we have the energy density ε in a liquid, deduced in accordance with the definition

$$\varepsilon = \mu\rho + Ts + \mathbf{vj} - P, \tag{22}$$

from which we obtain the following standard thermodynamic identity:

$$d\varepsilon = \mu d\rho + Tds + \mathbf{v}d\mathbf{j}. \tag{23}$$

This is also true of a gas. In the case of a film we derive an expression for the surface energy which is similar to Eq. (22):

$$\varepsilon_s = \mu_s\rho_s + T_s s_s + \mathbf{v}_s\mathbf{j}_s + v_s n_s + \alpha. \tag{24}$$

The explicit form of the surface energy differential depends on the film symmetry. For example, in the case of a crystalline film, we have

$$d\varepsilon_s = \mu_s\, d\rho_s + T_s\, ds_s + \mathbf{v}_s\, d\mathbf{j}_s + v_s\, dn_s + \frac{\partial\alpha}{\partial\nabla_i^{\perp}W_\alpha} d\nabla_i^{\perp}W_\alpha. \tag{25}$$

It should be noted that in the last differential we cannot simply transpose d and $\nabla_i^{\perp}W_\alpha$

DYNAMIC EQUATIONS

The hydrodynamic equations for a liquid are well known and have the following form[3]:

$$\frac{\partial\rho}{\partial t} = -\nabla\mathbf{j}, \quad \frac{\partial s}{\partial t} = -\nabla(s\mathbf{v}+\mathbf{q}) + \frac{2R}{T},$$
$$\frac{\partial j_i}{\partial t} = -\nabla_k(P\delta_{ik} + v_k j_i + \Pi_{ik}). \tag{26}$$

Here, we have the dissipative fluxes

$$\mathbf{q} = -\varkappa\nabla\ln T, \tag{27}$$

$$\Pi_{ik} = -\eta(\nabla_i v_k + \nabla_k v_i - {}^2/_3\delta_{ik}\nabla\mathbf{v}) - \zeta\nabla\mathbf{v}\delta_{ik}, \tag{28}$$

where $\varkappa$ is the thermal conductivity, whereas η and ξ are the first and second viscosities. The dissipative function R is given by

$$2R = \frac{\varkappa}{T}(\nabla T)^2 + \eta[{}^1/_2(\nabla_i v_k + \nabla_k v_i)^2 - {}^2/_3(\nabla\mathbf{v})^2] + \zeta(\nabla\mathbf{v})^2. \tag{29}$$

Exactly the same equations apply to a gas.

We now have to derive equations for the surface variables noting that some of these equations represent simply the boundary conditions for the three-dimensional problem. We shall divide this derivation into two stages: we shall first obtain the equations that ignore the liquid and gas adjoining a film and then add the terms induced by the bulk.

The nondissipative part of the hydrodynamic equations is best found by the Poisson bracket method.[9] In view of the time inversion invariance the only brackets which are not equal are those containing the momentum density. Therefore, in the derivation of the nondissipative equations for the dynamics of a film we need to know the Poisson brackets which contain the surface density of momentum $\mathbf{j}_s$. The explicit form of these brackets can be found using the expressions for the brackets containing the three-dimensional momentum density $\mathbf{j}$.

With this in mind we shall find it convenient to use the representation (8) for the function Φ and to regard $\mathbf{j}_s$ as function of x and y. In this case the following representation is valid:

$$\mathbf{j}_s|\nabla\Phi| = \int dz\, \mathbf{j}, \tag{30}$$

where the integration is carried out near the interface. On the other hand, the expression for the three-dimensional bracket is well known:

$$\{j_i(\mathbf{r}_1),\ j_k(\mathbf{r}_2)\} = j_k(r_1)\nabla_i\delta(\mathbf{r}_1-\mathbf{r}_2) + \nabla_k\delta(\mathbf{r}_1-\mathbf{r}_2)j_i(\mathbf{r}_2). \tag{31}$$

Integrating this expression with respect to z_1 and z_2 near the interface, we find the following expressions for the Poisson brackets:

$$\begin{aligned}&\{|\nabla\Phi|j_{s\alpha}(\mathbf{r}_1),\ |\nabla\Phi|j_{s\beta}(\mathbf{r}_2)\}\\ &=|\nabla\Phi|j_{s\beta}(\mathbf{r}_1)\nabla_\alpha(\delta(x_1-x_2)\delta(y_1-y_2))\\ &+\nabla_\beta(\delta(x_1-x_2)\delta(y_1-y_2))|\nabla\Phi|j_{s\alpha}(\mathbf{r}_2),\end{aligned} \tag{32}$$

$$\begin{aligned}&\{|\nabla\Phi|j_{s\alpha}(\mathbf{r}_1),\ |\nabla\Phi|j_{sz}(\mathbf{r}_2)\}\\ &=|\nabla\Phi|j_{sz}(\mathbf{r}_1)\nabla_\alpha(\delta(x_1-x_2)\delta(y_1-y_2)).\end{aligned} \tag{33}$$

We recall that the indices identified by Greek letters have two values: x and y. Proceeding similarly and reducing the three-dimensional brackets, we obtain the expressions

$$\begin{aligned}&\{|\nabla\Phi|j_{s\alpha}(\mathbf{r}_1),\ |\nabla\Phi|\rho_s(\mathbf{r}_2)\}\\ &=|\nabla\Phi|\rho_s(\mathbf{r}_1)\nabla_\alpha(\delta(x_1-x_2)\delta(y_1-y_2)),\end{aligned} \tag{34}$$

$$\begin{aligned}&\{|\nabla\Phi|j_{s\alpha}(\mathbf{r}_1),\ |\nabla\Phi|s_s(\mathbf{r}_2)\}\\ &=|\nabla\Phi|s_s(\mathbf{r}_2)\nabla_\alpha(\delta(x_1-x_2)\delta(y_1-y_2)).\end{aligned} \tag{35}$$

In the case of a three-dimensional smectic, we obtain the following expression[10]:

$$\{j_i(\mathbf{r}_1),\ W(\mathbf{r}_2)\} = -\nabla_i W\delta(\mathbf{r}_1-\mathbf{r}_2). \tag{36}$$

In the case of a Langmuir film with a smectic ordering the function W is specified only at the interface and the expression for the bracket $\{\mathbf{j}_s,\ W\}$ is obtained from Eq. (36) by integration with respect to z_1 near the interface:

$$\{|\nabla\Phi|j_{si}(\mathbf{r}_1),\ W(\mathbf{r}_2)\} = -\nabla_i W\delta(x_1-x_2)\delta(y_1-y_2). \tag{37}$$

There is another similar bracket

$$\{|\nabla\Phi|j_{si}(\mathbf{r}_1),\ W_\alpha(\mathbf{r}_2)\} = -\nabla_i W_\alpha\delta(x_1-x_2)\delta(y_1-y_2), \tag{38}$$

where W_α are the phases of the density modulation in a crystalline film. The film itself can be regarded near the interface as one smectic layer, because Φ for this film is described by a relationship analogous to Eq. (36). Hence, we obtain

$$\{|\nabla\Phi|j_{si}(\mathbf{r}_1),\ \Phi(\mathbf{r}_2)\} = -\nabla_i\Phi\delta(x_1-x_2)\delta(y_1-y_2). \tag{39}$$

The expression for the three-dimensional bracket

$$\{j_i(\mathbf{r}_1),\ \varphi(\mathbf{r}_2)\} = -\nabla_i\varphi\delta(\mathbf{r}_1-\mathbf{r}_2) - \varepsilon_{ikn}\nabla_k\delta(\mathbf{r}_1-\mathbf{r}_2)l_n(\mathbf{r}_2) \tag{40}$$

was found in Ref. 11. Hence, the surface density is given by

$$\begin{aligned}\{|\nabla\Phi|j_{si}(\mathbf{r}_1),\ \varphi(\mathbf{r}_2)\} &= -\nabla_i\varphi\delta(x_1-x_2)\delta(y_1-y_2)\\ &-\varepsilon_{i\alpha n}\nabla_\alpha[\delta(x_1-x_2)\delta(y_1-y_2)]l_n(x_2,\ y_2).\end{aligned} \tag{41}$$

We must mention that in the case of a nematic film (with the D_2 symmetry) the right-hand side of Eq. (41) contains also additional anisotropic terms. Their presence gives rise to corresponding anisotropic terms in the equations for the dynamics of a film. However, these equations "die out" over large scaling distances because of large fluctuations of the director. In other words, isotropization of not only static, but also of dynamic characteristics of the system takes place. Therefore, we shall ignore the anisotropic terms on the right-hand side of Eq. (41).

We now have all the necessary brackets for the derivation of the nondissipative equations of film dynamics (without allowance for the effects of the adjoining gas and liquid). They are the Liouville equations with a Hamiltonian in the form of the surface energy E_s. Using Eq. (8), we can write it down in the form of a two-dimensional integral:

$$E_s = \int dx\, dy\, |\nabla\Phi|\varepsilon_s. \tag{42}$$

In the derivation of the dynamic equations for the surface variables, they should be regarded as functions of x and y.

The explicit form of the equations for the surface variables can be found using Eq. (24) and the thermodynamic identity for ε_s of the (25) type which follows from it. We thus obtain

$$\partial\Phi/\partial t = \{E_s,\ \Phi\} = -v_{si}\nabla_i\Phi, \tag{43}$$

$$\partial W/\partial t = \{E_s,\ W\} = -v_{si}\nabla_i W, \tag{44}$$

$$\partial W_\alpha/\partial t = \{E_s,\ W_\alpha\} = -v_{si}\nabla_i W_\alpha, \tag{45}$$

$$\partial\varphi/\partial t = \{E_s,\ \varphi\} = -v_{si}\nabla_i\varphi - \varepsilon_{ikn}l_i\nabla_k v_{sn}, \tag{46}$$

$$\partial(|\nabla\Phi|\rho_s)/\partial t = \{E_s,\ |\nabla\Phi|\rho_s\} = -\nabla_i(|\nabla\Phi|j_{si}), \tag{47}$$

$$\partial(|\nabla\Phi|s_s)/\partial t = \{E_s,\ |\nabla\Phi|s_s\} = -\nabla_i(|\nabla\Phi|s_s v_{si}), \tag{48}$$

$$\partial(|\nabla\Phi|n_s)/\partial t = \{E_s,\ |\nabla\Phi|n_s\} = -\nabla_i(|\nabla\Phi|n_s v_{si}). \tag{49}$$

In general, because independence of the variables z is implied in the derivation of these equations, it follows that the terms with $\partial/\partial z$ in Eqs. (44)–(49) vanish. It is worth noting that the proposed system of equations is, as demonstrated below, independent of the method used to continue the surface variables to the third dimension.

The equation for the surface density of the momentum $\mathbf{j}_s$ seems much more complex than the equations given above and, moreover, the actual form of this equation depends on the film symmetry. However, the right-hand side of this equation can always be represented in the form of the total divergence:

$$\frac{\partial}{\partial t}(|\nabla\Phi|j_{si}) = \{E_s,\ |\nabla\Phi|j_{si}\} = -\nabla_k(T_{sik}|\nabla\Phi|). \tag{50}$$

The derivative $\partial/\partial z$ is introduced into the above equation with the same aim as before, i.e., to make the form of the equation independent of the method of continuation of the surface quantities to the third dimension.

We shall now give the stress tensor for films of different symmetry, which occurs in Eq. (50):

$$T_{sik}^{(liq)} = (-\alpha\delta_{ik}{}^{\perp} + v_{sk}j_{si}), \tag{51}$$

$$T_{sik}^{(cr)} = T_{sik}^{(liq)} + \frac{\partial\alpha}{\partial\nabla_k{}^{\perp}W_\beta}\nabla_i{}^{\perp}W_\beta, \tag{52}$$

$$T_{sik}^{(sm)} = T_{sik}^{(liq)} + \frac{\partial\alpha}{\partial\nabla_k{}^{\perp}W}\nabla_i{}^{\perp}W - \nabla_i{}^{\perp}W\,\delta_{jk}{}^{\perp}\nabla_m$$

$$\times\left(\delta_{jm}^{\perp}|\nabla\Phi|\frac{\partial\alpha}{\partial\nabla^{\perp 2}W}\right)\frac{1}{|\nabla\Phi|}$$

$$+\frac{\partial\alpha}{\partial\nabla^{\perp 2}W}(\delta_{im}-2l_il_m)\nabla_k^{\perp}\nabla_m^{\perp}W-\frac{\partial\alpha}{\partial\nabla^{\perp 2}W}l_i\nabla_k^{\perp}\nabla_n l_n, \tag{53}$$

$$T_{sik}^{(or)}=T_{sik}^{(liq)}+\frac{\partial\alpha}{\partial\nabla_k^{\perp}\varphi}\nabla_i^{\perp}\varphi+\frac{1}{|\nabla\Phi|}\varepsilon_{ikn}l_n\nabla_j\left(\frac{\partial\alpha}{\partial\nabla_j^{\perp}\varphi}|\nabla\Phi|\right). \tag{54}$$

Here the liquid, crystalline, smectic, and nematic films are labelled *liq*, *cr*, *sm*, and *or*, respectively. We recall that in the case of a nematic film we ignore the explicit dependence of α on the director, in view of the fluctuation isotropization discussed above.

We shall now supplement the new nondissipative equations with dissipative terms. These dissipative terms are absent from Eq. (47) for ρ_s, because due to the Gallilean invariance the mass flux density should be identical with the momentum density. The dissipative terms are also missing from Eq. (43) for Φ, because it simply states that a film travels at a velocity v. It should be noted that Eq. (47) can be derived as the condition of invariance of Eq. (47) under the transformations $\rho_s \to \rho_s(r_i+f_i(\Phi))$ and $j_s \to j_s(r_i+f_i(\Phi))$.

In the equation for the other variables we have to include the dissipative terms. For example, the right-hand side of Eq. (50) should be supplemented with

$$\nabla_k[\eta_s(\delta_{ij}^{\perp}\delta_{kn}^{\perp}(\nabla_j v_{sn}+\nabla_n v_{sj})-\delta_{ik}^{\perp}\delta_{jn}^{\perp}\nabla_j v_{sn}) +\zeta_s\delta_{ik}^{\perp}\delta_{jn}^{\perp}\nabla_j v_{sn}], \tag{55}$$

where η_s and ζ_s are the surface viscosities. The equation for the angle becomes

$$\frac{\partial\varphi}{\partial t}=-v_s\nabla\varphi-\varepsilon_{ikn}l_i\nabla_k v_{sn}+\frac{\Gamma}{|\nabla\Phi|}\nabla_i\left(\frac{\partial\alpha}{\partial\nabla_i^{\perp}\varphi}|\nabla\Phi|\right), \tag{56}$$

where Γ is a positive kinetic coefficient. In Eq. (48) for the values of s_s we have to allow for the dissipation associated with the thermal conductivity, whereas in Eqs. (44) and (45) describing W and W_α we have to include the terms describing percolation, whereas in Eq. (49) for n_s we need to allow for the term describing the diffusion of surfactant molecules. Moreover, in these equations there are many cross kinetic terms. However, these terms will not be needed later and, therefore, we shall not consider their explicit form.

Equations (47)–(50) have the form of the laws of conservation of the surface mass, entropy, number of surfactant molecules, and momentum. It is understood that the individual laws of conservation of the surface quantities do not exist. Therefore, these equations must be corrected by supplementing the right-hand sides of the fluxes of the corresponding quantities from the bulk to the surface. We thus obtain

$$\partial(|\nabla\Phi|\rho_s)/\partial t+\nabla(|\nabla\Phi|\mathbf{j}_s)=-\rho(\mathbf{v}_s-\mathbf{v})\nabla\Phi+\rho'(\mathbf{v}_s-\mathbf{v}')\nabla\Phi, \tag{57}$$

$$\partial(|\nabla\Phi|s_s)/\partial t+\nabla(|\nabla\Phi|s_s\mathbf{v}_s)=-s(\mathbf{v}_s-\mathbf{v})\nabla\Phi +s'(\mathbf{v}_s-\mathbf{v}')\nabla\Phi+(\mathbf{q}-\mathbf{q}')\nabla\Phi, \tag{58}$$

$$\partial(|\nabla\Phi|j_{si})/\partial t+\nabla_k(|\nabla\Phi|T_{sik})=(P-P')\nabla_i\Phi-(v_{sk}-v_k)\nabla_k\Phi j_i +(v_{sk}-v_k')\nabla_k\Phi j_i'+(\Pi_{ik}-\Pi_{ik}')\nabla_k\Phi. \tag{59}$$

The left-hand sides of Eqs. (57)–(59) are simplified by dropping the surface kinetic terms. They are of higher order in the gradient than the terms retained in Eqs. (57)–(59) and, therefore, they are unimportant in the long-wavelength limit.

In general, the equation for n_s should also contain the flux of surfactant molecules to the surface. However, we shall assume that all the surfactant molecules are concentrated at the surface. In this approximation there is no flux of surfactant molecules from the bulk to the surface and we return back to Eq. (49).

Equations (57)–(59) represent essentially the boundary conditions for the three-dimensional problem of hydrodynamic motion of a liquid and a gas. In addition, there are many other boundary conditions that relate the bulk and surface quantities.[12] These conditions [together with Eqs. (43)–(45), (49), and (57)–(59)] should ensure the energy conservation law (21) and the positive definite nature of the entropy production process the corresponding term should be added in Eq. (48) for the surface entropy]. These requirements dictate the kinetic relationships between the fluxes of the mass, entropy, and momentum from the bulk to the surface and the corresponding generalized forces, which are the quantities

$$\begin{gathered}T_s-T,\quad T_s-T',\quad \delta_{ik}^{\perp}(\mathbf{v}_s-\mathbf{v}),\quad \delta_{ik}^{\perp}(\mathbf{v}_s-\mathbf{v}'),\\ \mu_s+(\mathbf{v}_s\mathbf{l})(\mathbf{v}\mathbf{l})-\mu-(\mathbf{v}\mathbf{l})^2-\Pi_{ik}l_il_k/\rho,\\ \mu_s+(\mathbf{v}_s\mathbf{l})(\mathbf{v}'\mathbf{l})-\mu'-(\mathbf{v}'\mathbf{l})^2-\Pi_{ik}'l_il_k/\rho'.\end{gathered} \tag{60}$$

We shall not give the explicit form of these relationships. We shall simply note that the contributions to the dissipative function associated with the longitudinal (i.e., along the z axis) fluxes of the momentum and mass are indistinguishable because of the Gallilean invariance. Therefore, the differences $v_{sz}-v_s$ and $v_{sz}-v_z'$ do not occur in Eq. (60) as the generalized forces.

The most informative, from the point of view of establishment of the symmetry of a film, is the boundary condition (59). This is because it includes the surface stress tensor T_{sik}, which according to Eqs. (51)–(54) contains terms specific for each type of symmetry. The condition (59) also demonstrates that fluctuations of the surface parameters are necessarily related to fluctuations of the velocity in the bulk.

SPECTRUM OF SURFACE MODES

Linearized dynamic equations are needed in the study of the oscillation spectrum. These linearized equations for three-dimensional hydrodynamics are well known and we shall not give them explicitly. Their solutions describe an acoustic mode associated with oscillations of the irrotational component of the velocity, a relaxation mode associated with the rotational component of the velocity, and a thermal diffusion mode associated with relaxation of the specific entropy.

The boundary conditions for linearized three-dimensional equations are obtained by linearizations of Eqs. (43) and (57)–(59). We shall now drop from these boundary conditions the terms associated with the gas. Inclusion of these terms does not alter qualitatively the spectrum, but simply gives rise to small (because of the low gas density) corrections to the dispersion laws. We also recall that under the conditions of Eqs. (57)–(59) the surface kinetic terms are omitted. These terms are unimportant in the long-wavelength limit, but they may play some role in real experiments if the corresponding kinetic terms are for some reason anomalously large.[13]

In linearization of the boundary conditions we shall still assume that under equilibrium conditions the interface lies in the $z = 0$ plane. In this case the deviations of the shape of the surface from equilibrium are described by a displacement vector $u(x, y)$ given by Eq. (8). Assuming also that all the surface quantities are functions of x and y, we obtain the following linearized conditions:

$$\partial u_z/\partial t = v_z, \tag{61}$$
$$\partial \rho_s/\partial t + \rho_s \nabla_\alpha v_{s\alpha} = -\rho(v_{sz} - v_z), \tag{62}$$
$$\partial s_s/\partial t + s_s \nabla_\alpha v_{s\alpha} = -s(v_{sz} - v_z) + q_z, \tag{63}$$
$$\rho_s \partial v_{sz}/\partial t - \alpha \nabla_\alpha^2 u = P - P' + \Pi_{zz}, \tag{64}$$
$$\rho_s \partial v_{s\alpha}/\partial t + \nabla_\beta T_{s\alpha\beta} = \Pi_{\alpha z}. \tag{65}$$

Moreover, we have to linearize the conditions relating the fluxes of the mass momentum, and entropy on the surface, on the one hand, to the quantities in Eq. (60) on the other. In the long-wavelength limit we can ignore the fluxes under these conditions. Ignoring also the viscous stress tensor $\hat{\Pi}$, we find very simple mutual relationships:.

$$T_s = T, \quad v_{s\alpha} = v_\alpha, \quad \mu_s = \mu. \tag{66}$$

The expression for the surface stress tensor $T_{s\alpha\beta}$ occurring in Eq. (65) is given, depending on the film symmetry, by one of the formulas (51)-(54). Explicit expressions for the derivatives of α occurring in Eqs. (52)-(54) are obtained using Eqs. (10), (11), and (19). The orientational energy of Eq. (19) includes only the first term, because the second term in Eq. (19) "dies out" over long distances because of fluctuations of the director. As a result of substitution and some cancellations, we obtain the following relationships for films of different symmetry:

$$T_{s\alpha\beta}^{(liq)} = -\alpha^{(1)} \delta_{\alpha\beta}, \tag{67}$$

$$T_{s\alpha\beta}^{(cr)} = -\alpha^{(1)} \delta_{\alpha\beta} - B_l (\nabla_\gamma u_\gamma) \delta_{\alpha\beta} - B_t \varepsilon_{\gamma\delta} \nabla_\gamma u_\delta \varepsilon_{\alpha\beta}, \tag{68}$$

$$T_{s\alpha\beta}^{(sm)} = -\alpha^{(1)} \delta_{\alpha\beta} + {}^1/{}_2 B q_0^{-2} \nabla_\alpha W \nabla_\beta W [q_0^{-2} (\nabla_\gamma W)^2 - 1] - K q_0^{-2} \nabla_\alpha W \nabla_\beta \nabla_\gamma^2 W, \tag{69}$$

$$T_{s\alpha\beta}^{(or)} = -\alpha^{(1)} \delta_{\alpha\beta} + A \varepsilon_{\alpha\beta} \nabla_\gamma^2 \varphi. \tag{70}$$

Equations (67)-(70) contain the combination $\alpha^{(1)}$, which is obtained as a result of linearization of α with respect to deviations of the quantities μ_s, T_s, and ν_s from equilibrium. In the case of a crystalline film we have to include in $\alpha^{(1)}$ the terms which are proportional to these deviations and which appear as a result of linearization of the elastic part of the tensor T_s due to the dependence of the wave vector q_0 (governing the density modulation period) on μ_s, T_s, and ν_s.

In the derivation of Eqs. (67)-(70) we linearized the surface stress tensor for all the variables, with the exception of the smectic variable W. In Eq. (69), which is valid for a smectic film, there are terms nonlinear in respect of ΔW. This is because both in dynamics and statics the fluctuations of W modify significantly the long-wavelength behavior of the system. In a study of the effects associated with these fluctuations we have to retain in the dynamic equations the principal terms nonlinear in W. Among all the terms nonlinear in W only those retained in Eq. (69) are important.

These boundary conditions should be supplemented by the linearized equations (44), (45), (49), and (56). Using the notation of Eqs. (9) and (12), these become:

$$\partial u_\alpha/\partial t = v_{s\alpha}, \tag{71}$$

$$\partial n_s/\partial t + n_s \nabla_\alpha v_{s\alpha} = 0, \tag{72}$$

$$\partial \varphi/\partial t = -\varepsilon_{\alpha\beta} \nabla_\alpha v_{s\beta} + \Gamma A \nabla_\alpha^2 \varphi. \tag{73}$$

Following the above procedure, we wrote down the equations for φ including only the first (isotropic) term in the orientational energy of Eq. (19). It should be noted that in the linear approximation the angle φ can be regarded as holonomic, since the right-hand side of Eq. (18) is quadratic in the displacement vector u_z.

We shall now investigate the spectrum of surface modes assuming that all the quantities are expanded in the Fourier series in terms of t, x, and y and considering a harmonic of frequency ω with a wave vector k_α along the surface. We shall consider separately the dependences of the bulk quantities on z.

In the course of excitation of surface modes near an interface we can expect oscillations of the rotational and irrotational components of the velocity. For all the modes under consideration the frequency can be regarded as low compared with the acoustic frequency (for the same wave vector), so that the potential ψ of the irrotational component of the velocity is given by

$$\psi(z) = \psi_s \exp(kz). \tag{74}$$

We recall that the variable part of the pressure is related simply to the potential ψ:

$$P = i\omega\rho\psi. \tag{75}$$

For the majority of the modes we can assume that $\rho\omega \gg \eta k^2$. In this case the dependence of the rotational component of the velocity on z is of the form

$$v_{\perp\alpha}(z) = v_{s\perp\alpha} \exp\left[\frac{1-i}{\sqrt{2}}\left(\frac{\rho\omega}{\eta}\right)^{1/2} z\right],$$
$$v_{\perp z}(z) = \frac{1-i}{\sqrt{2}}\left(\frac{\eta}{\rho\omega}\right)^{1/2} k_\alpha v_{\perp\alpha}(z). \tag{76}$$

It should be noted that it follows from Eq. (62) that $v_s = v_{sz}$ applies to all the modes under consideration. Using also Eq. (60), we can conclude that the velocity of transport of a film v_{si} can be regarded as identical with the limiting value of the bulk velocity v_i in the limit $z \to 0$.

We shall first consider an ordinary capillary wave which is characterized by $\omega \propto \varkappa$. In this case it follows from Eq. (72) that $k_\alpha v_{s\alpha} = 0$, which also implies that $v_{s\alpha} = 0$ is satisfied by this wave. Consequently, $v_{s\perp\alpha} = -ik_\alpha \psi_s$. Substituting this value in Eq. (76) using Eq. (74), we find from Eq. (61) that

$$-i\omega u = k\psi_s - \frac{i+1}{\sqrt{2}}\left(\frac{\eta}{\rho\omega}\right)^{1/2} k^2 \psi_s.$$

Under the conditions of Eq. (65) it is sufficient to retain the leading terms, which on the strength of Eq. (75) make a contribution

$$\alpha k^2 u = i\rho\omega\psi_s.$$

Comparing the above equalities, we find the dispersion law

$$\omega = \left(\frac{\alpha k^3}{\rho}\right)^{1/2}\left[1 - \frac{i}{2}\left(\frac{\eta^2}{4\rho\alpha}\right)^{1/4} k^{1/4}\right]. \tag{77}$$

This is the usual dispersion law for capillary waves in the presence of a surface film.

In addition to a conventional capillary wave, there is a further low-frequency surface mode (even in the case of a liquid film), but the existence of this mode has been ignored completely. This mode is associated with oscillations of the surface density of surfactant molecules. It follows from Eq. (72) that

$$\omega n_s = n_s k_\alpha v_{s\alpha}.$$

We may assume that only the rotational velocity is excited in this mode and, in accordance with Eq. (76), its value is found assuming that $v_{s\perp\alpha} = v_{s\alpha}$. The boundary condition (65) together with Eq. (67) gives for this case the following first-approximation expression:

$$\frac{\partial \alpha}{\partial n_s} k_\alpha n_s = -\frac{1+i}{\sqrt{2}}(\eta\rho\omega)^{1/2} v_{s\alpha}.$$

Comparing the above equalities, we find the dispersion law:

$$\omega = \left(\frac{\sqrt{3}}{2} - \frac{i}{2}\right)\frac{1}{(\eta\rho)^{1/3}}\left(\frac{\partial\alpha}{\partial \ln n_s}\right)^{2/3} k^{4/3}. \tag{78}$$

The boundary conditions that follow from Eq. (60) demonstrate that the derivative of α with respect to n_s in Eq. (78) should be taken at constant values of μ_s and T_s.

The range of validity of the dispersion law (78) is limited on the low-frequency side. This is because it is derived on the assumption that the law of conservation of the number of surfactant molecules on the surface is satisfied and this gives rise to an additional Goldstone mode. At the lowest frequencies we have to allow for the exchange of surfactant molecules between a film and the bulk, which suppresses this mode.

We can similarly consider the surface modes which are associated with a crystalline film. Once again the rotational velocity is excited mainly in these modes. The relationship between the velocity component and the variables n_s and u_α describing the mode is given by Eqs. (71) and (72). There is one further relationship that can be obtained from Eq. (66) and in this case we have to ignore the first term and substitute Eq. (68). We thus obtain a system of equations describing oscillations which are longitudinal and transverse to the wave vector k and obey the following dispersion laws:

$$\omega_l = \left(\frac{\sqrt{3}}{2} - \frac{i}{2}\right)\left(\frac{\tilde{B}_l^2}{\eta\rho}\right)^{1/3} k^{4/3}, \tag{79}$$

$$\omega_t = \left(\frac{\sqrt{3}}{2} - \frac{i}{2}\right)\left(\frac{B_t^2}{\eta\rho}\right)^{1/3} k^{4/3}. \tag{80}$$

Here, $\tilde{B}_l = B_l - n_s \partial\alpha^{(1)}/\partial n_s$.

The dispersion laws (79) and (80) apply directly to crystalline films with the hexagonal symmetry. In the case of films of lower symmetry the situation is basically the same: there are two modes with the dispersion laws (79) and (80). These modes cannot be simply interpreted as longitudinal and transverse and, moreover, the dispersion laws become anisotropic. It should be stressed that these modes are associated with the spontaneous breaking of the translational symmetry of the film and, therefore, the range of their existence is not limited on the low-frequency side, which distinguishes them from the mode considered above in the case of a liquid Langmuir film. It should be pointed out that in the range of frequencies where the exchange of surfactant molecules between the bulk and the surface becomes important, we can simply replace $\tilde{B}_l$ in Eq. (79) with B.

An analysis of a mode associated with spontaneous breaking of the rotational invariance of a film is very simple. Estimates indicate that in the calculation of the spectrum of a mode described by oscillations of the angle φ we can ignore the terms with the velocity in Eq. (73). This gives the following dispersion law:

$$\omega = -i\Gamma A k^2. \tag{81}$$

We recall that this dispersion law is obtained without allowance for the anisotropy. In the case of a nematic film we find that, in addition to the term described by Eq. (81), the dispersion law contains an anisotropic term proportional to $k^{2+\xi}$, where $\xi = T/4\pi A$.

We shall now consider the spectrum of surface modes of a smectic film. In general, this spectrum can be found by the same method as for a crystalline film. This can be done using a surface stress tensor (69), which is linearized in terms of the displacement vector u_x introduced in Eq. (12). As a result, we obtain a dispersion equation describing the two modes. One of these modes is determined by the dispersion law (78) and it is related, as in the case of a liquid film, to the oscillations of n_s. The range of existence of this mode is correspondingly limited on the low-frequency side.

A second mode typical of a smectic film has the dispersion law

$$\omega = \left(\frac{\sqrt{3}}{2} - \frac{i}{2}\right)\left(\frac{B^2}{\rho\eta}\right)^{1/3}\left(\frac{k_x k_y}{k}\right)^{4/3}. \tag{82}$$

This mode is related to spontaneous breaking of the translational invariance and, therefore, the range of its validity is not limited on the low-frequency side. In the range of frequencies where the mode with the dispersion law (78) is missing, we can replace k_y/k with unity on the right-hand side of Eq. (82).

The dispersion law (82) is strongly anisotropic and leads to $\omega \to 0$ in the limit $k_x \to 0$ or $k_y \to 0$. At low values of k_y we have to modify the right-hand side of Eq. (44) by inclusion of a kinetic term describing percolation. This term limits the range of validity of the dispersion Eq. (82) at low values of k_y. Much more interesting is the range of small values of k_x, because it is in this wave vector range that the main fluctuation effects take place. Therefore, in studies of this range we cannot ignore the nonlinear terms in Eq. (69). Moreover, at low values of k_x we have to include the last term in Eq. (69), although it was omitted in the derivation of the dispersion law (82).

At low values of k_x a characteristic smectic mode is very soft, so that it obeys an inequality $\rho\omega \ll \eta k^2$. Therefore, in a study of this mode we can assume that the velocity in the surface layer depends in the following way on z:.

$$v_i = v_{si}\exp(kz).$$

Combining Eq. (44) with the x component of Eq. (64) and dropping the unimportant terms, we obtain the following equation:

$$\eta k\frac{\partial W}{\partial t} - \nabla_\alpha\left\{\frac{B}{2}\nabla_\alpha W[q_0^{-2}(\nabla W)^2-1]\right\} + K\nabla_\alpha^2\nabla_\beta^2 W = 0.$$

In the linear approximation this equation leads to the following dispersion law:

$$\omega = -\frac{i}{\eta k}(Bk_x^2 + Kk^4). \tag{84}$$

Equation (83) contains the main nonlinearity necessary for the investigation of dynamic fluctuation effects. In such an investigation it is convenient to use a diagram technique described in Ref. 14. In the case under discussion this diagram technique yields the effective action with a Lagrangian deduced on the basis of Eq. (83):

$$\mathscr{L} = \frac{B}{2q_0}\nabla_\beta p\,\nabla_\beta W[q_0^{-2}(\nabla W)^2-1] + \frac{K}{q_0}\nabla_\alpha^2 p\,\nabla_\beta^2 W + \frac{\eta}{q_0}pk^{2-\varepsilon}\frac{\partial W}{\partial t} + 2iT\eta pk^{2-\varepsilon}p, \tag{85}$$

where $\varepsilon = 1$ and p is an auxiliary field.

The action with the Lagrangian (85) is renormalizable at $\varepsilon = 0$ in the three-dimensional space.[15] We shall therefore seek the scaling behavior of its parameters in the two-dimensional case by the method of ε expansion from the three-dimensional space. The correctness of this procedure should be tested by an additional investigation, because in the $\varepsilon \neq 0$ case the Lagrangian (85) is not local. We shall assume, however, that the proposed method makes it possible to draw quantitative conclusions on the long-wavelength dynamics of the system.

The renormalization group equations for the moduli B and K derived using Eq. (85) in the one-loop approximation are naturally identical with the static equations (14). The viscosity η in Eq. (85) is described by the following equation obtained as a result of the ε continuation of the equations of Ref. 15:

$$\eta_1 = \eta + k_y^\varepsilon \int \frac{dL}{q_y^\varepsilon}\frac{g}{2}\eta_1. \tag{86}$$

Here, η is the unrenormalized value, η_1 is the renormalized value, and q is the characteristic wave vector. Substituting $g = 2\varepsilon/5$ in Eq. (86), we obtain

$$\eta_1 = {}^5/_4\eta. \tag{87}$$

Therefore, the effective viscosity is constant and it differs only by a factor from the unrenormalized viscosity.

Fluctuations with the dispersion law describe by Eq. (84) are responsible for the renormalization group of the modulus B also in the range of validity of the dispersion law (82). We can show that in the renormalization group equation (14) the main cutoff factor is in this range the frequency ω. Therefore, in the first (with respect to ε) approximation the modulus B in Eq. (82) obeys the following scaling law:

$$B \propto \omega^{2\varepsilon/5}. \tag{88}$$

We can also show that in this range there are no fluctuation corrections to η, so that the unrenormalized value occurs in Eq. (82).

DIPOLE INTERACTION

Surfactant molecules themselves have a dipole moment so that the dipole moment of a Langmuir film is directed along the film normal. This gives rise to an additional dipole contribution to the energy of an inhomogeneous deformation of the film. However, the corresponding contribution is small compared with the usual surface tension, so that the dipole interaction is not reflected in the long-wavelength properties of an isotropic film.

The situation is different in a nematic film. In this case the dipole moment may have a component tangential to the film and directed along the vector **n**, which depends on the structure of the ground state of the film. If we ignore fluctuations of the displacement of the film, the corresponding dipole energy is

$$\int d^2r_1\,d^2r_2\,\frac{\mu_d}{2}\frac{\nabla\mathbf{n}(\mathbf{r}_1)\nabla\mathbf{n}(\mathbf{r}_2)}{2\pi|\mathbf{r}_1-\mathbf{r}_2|}. \tag{89}$$

The existence of this energy gives rise to additional dipole terms in the pair correlation function and $\langle\varphi\varphi\rangle$ in the dispersion law of the orientational mode [Eq. (81)]. These dipole terms "harden" the correlation function $\langle\varphi\varphi\rangle$ and suppress the fluctuations of **n**. Therefore, even in the long-wavelength limit we cannot ignore the second term to Eq. (19). The dispersion law (81) now becomes

$$\omega = -i\Gamma\left[Ak^2 + A_1(k_y^2 - k_x^2) + \frac{\mu_d}{4}\frac{k_y^2}{k}\right]. \tag{90}$$

We recall that the x axis is directed along the equilibrium position of **n** and the parameter μ_d describes the dipole interaction.

The tangential dipole moment of a smectic film can be directed either along the vector ∇W or along $[l\times\nabla W]$. In the latter case the dipole contribution is unimportant. However, in the former case the dipole interaction "hardens" the pair correlation function $\langle u_x u_x\rangle$, which suppresses the fluctuation effects. This means, in particular, that in the long-wavelength limit the modulus B in the dispersion law (82) remains constant. At low values of k_x we obtain instead of Eq. (84) the dispersion law

$$\omega = -\frac{i}{\eta k}(Bk_x^2 + \mu_d k^3). \tag{91}$$

In the calculation of Eq. (91) we shall use the explicit expression for the dipole energy (89) and substitute in it $\mathbf{n} = \nabla W/|\nabla W|$.

We can readily show that the presence of a tangential dipole moment in crystalline Langmuir films does not affect their long-wavelength spectrum.

CONCLUSIONS

We investigated theoretically the spectrum of surface modes of a liquid in the presence of a Langmuir film at an interface with a gas. We found that the spectrum of capillary waves is not very sensitive to the film symmetry. On the other hand, there are other surface modes which are very sensitive to the film symmetry.

Even in the case of a liquid film the spectrum includes a surface mode with a very special dispersion law [Eq. (78)]

and this mode exists in the range of frequencies where we can assume that the number of surfactant molecules on the surface is conserved. In the case of a crystalline film the spectrum includes two surface modes with similar dispersion laws Eqs. (79) and (80)]. However, we must stress that in contrast to the above-mentioned mode for a liquid Langmuir film, the mode with the dispersion laws (79) and (80) are true Goldstone modes associated with the elastic properties of a film.

In the case of a smectic film the spectrum has a characteristic smectic mode which is described by a strongly anisotropic dispersion law of Eq. (82). The modulus B in this law falls in the low-frequency limit in accordance with a power dependence and this is due to fluctuations of smectic layers. The power exponent in this dependence can be estimated from Eq. (88). The existence of a dipole moment along the normal to a smectic film suppresses the fluctuation effects. In particular, the modulus B in Eq. (82) remains constant.

Finally, in the case of a film with a broken rotational invariance the spectrum has one orientational mode and its dispersion law is of the diffusion type. Fluctuations of the director of a nematic film results in isotropization of the dispersion law of an orientational mode. The presence of a dipole moment in such a film suppresses fluctuations of the director and gives rise to a more complex anisotropic dispersion law (90).

We ignored gravity in our analysis. However, the system can be readily generalized by including the gravitational energy. It is known that the force of gravity alters, compared with Eq. (77), the spectrum of capillary waves at very low frequencies.[3,4] However, the spectrum of specific surface modes discussed by us above is not affected by the force due to gravity.

We would hope that all these modes could be observed experimentally in view of their low-frequency nature.

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