Fluctuations in a crystalline monolayer on a liquid

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The structure factor of a crystalline monolayer on the surface of a liquid is calculated. It is shown that in the first approximation the finite rigidity of the monolayer maintains the power-law profile of quasi-Bragg peaks typical for two-dimensional systems but leads to a reduction of the x-ray scattering intensity. It is found that this effective Debye–Waller factor has very strong dependence on the length h of the chains composing the monolayer. Specifically, it is proportional to $\exp(-h^3/\xi a^2)$, where ξ is a chain persistence length and a is a characteristic atomic scale. We have also studied the spectrum of modes where the motion of the liquid is localized near the film. It turns out that for thick films there are three propagating sound-like modes: the transverse sound with a velocity which becomes zero if the wave vector $\mathbf{q}$ is directed along the normal to the film (z-axis); the conventional longitudinal sound with an almost isotropic velocity (determined mainly by the compressibility of the film); and the mode analogous to second sound in smectics. For thin films the latter mode transforms into the fast pure relaxational one. For tilted or hexatic layers there is also an orientational diffusion mode. This mode strongly influences the viscosity of the system. The fluctuation contribution to the viscosity coefficients is proportional to $(T/\Gamma)\ln(qa)$, where Γ is the orientational diffusion coefficient. Transverse and longitudinal sound are transformed into overdamped modes with a dispersion law $\omega\propto(\sqrt{3}-i)q^{4/3}$.
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1. INTRODUCTION

Recently a wide variety of properties related to surface crystallization of different substances at the surface of a liquid have been studied.[1–3] In particular we mention the very systematic x-ray diffraction and thermodynamic measurements of crystalline monolayers of fatty alcohols on a water surface.[4,5] It has been shown in these experiments[4,5] that almost all internal degrees of freedom are frozen in the monolayer (especially for short-chain monolayers), but nevertheless even for two-dimensional ($2d$) crystalline monolayers there are some internal degrees of freedom (related to conformational and elastic fluctuations of chains).

In this paper we formulate a simple model describing the role of these internal degrees of freedom for the fluctuations of the displacements in a $2d$ lattice composed of finite-length chains. Our aim here is not to claim that our oversimplified phenomenological description necessarily holds for real systems investigated in Ref. 4, but rather to explore the consequences of this simplest model.

The structure of this paper is as follows. In Sec. 2 we compare briefly two alternative theories of $2d$ crystallization: namely Berezinskiĭ–Kosterlitz–Thouless (BKT)[6,7] and Landau weak-crystallization theory (see, e.g., Ref. 8). As we will see, the two theories lead to fairly different physical consequences. For example, BKT theory predicts one (or two) continuous transitions, whereas in the framework of the Landau theory one should always have a first-order phase transition. The experimental situation is not clear so far, but anyway it is not necessary that melting transitions in $2d$ systems should be always continuous BKT type transitions. Moreover there are many examples of first order melting transitions in liquid crystalline films (see, e.g., Ref. 9).

Section 3 contains our calculation of the elastic energy for a finite-thickness crystalline film constructed from chains having a finite rigidity.

In Sec. 4 we find the static structure factor of the system. It turns out that a finite chain rigidity considerably reduces static fluctuations. This is especially relevant to higher order peaks in the x-ray scattering. Nevertheless, it does not change the shape of the peaks.

In Sec. 5 we consider dynamical phenomena. We find eigenmodes for a free monolayer and then take into account interactions of these modes with excitations in a liquid. It turns out that these interactions considerably modify the eigenmode spectrum, leading to overdamped modes $\propto(\sqrt{3}-i)q^{4/3}$, whereas the finite rigidity of chains is not very relevant to dynamical phenomena and it leads to only small corrections to the dispersion laws.

In Sec. 6 we discuss the case of tilted or hexatic layers, where there is an additional Goldstone mode associated with an orientational diffusion. This mode is not changed by the interaction with a liquid but it leads to an enhancement of the internal viscosity of a film.

2. TWO-DIMENSIONAL CRYSTALLIZATION

Berezinskiĭ[6] and Kosterlitz and Thouless[7] have proposed a theory for $2d$ melting. According to this theory, the transition from solid to liquid in $2d$ systems (which can be very thin films on a smooth substrate or on the surface of a liquid) takes place in two steps with increasing temperatures. Dissociation of dislocation pairs first drives a transition from a low-temperature solid phase with algebraic decay of translational order and long-range orientational order into a so-called hexatic (or liquid crystalline) phase characterized by short-range translational order (i.e., by exponential decay of this order) and power-law decay of orientational order. Dissociation of disclination pairs at a higher temperature then produces an isotropic liquid.

The BKT mechanism assumes that at $0<T<T_m$ (where T_m is the melting temperature) in $2d$ crystals there are not only conventional thermal excitations (long wavelength phonons) but there is also a finite concentration of dislocation pairs (each pair consists of two dislocations with opposite Burgers vectors). The energy of one pair of dislocations with a characteristic size R can easily be estimated as

$$E_d=\frac{Ba^2}{2\pi}\ln\left(\frac{R}{a_0}\right)+E_0.$$

Here B is the elastic modulus (for more precise definitions see below in Sec. 3), a_0 is the radius of the core (which can be different from the lattice parameter a) and E_0 is the energy of the core.

One can also find (see e.g., Ref. 10) that the existence of pairs does not change the power-law decay of the correlation function, but they renormalize (decrease) the magnitude of the elastic modulus. The average size of pairs is given by

$$\langle R^2\rangle=\int d\Omega\,\exp\left(-\frac{E_d(R)}{T}\right)R^2, \tag{1}$$

where the integration is performed over different orientations of dislocations.

Thus, the average size of pairs is determined by $E_d(R)$, which includes the elastic energy produced by a pair, while the concentration of pairs is governed mainly by the core energy E_0. Physically the BKT mechanism of melting is analogous to ionization of a $2d$ plasma. For $T<T_m$ there are only neutral molecules (pairs), and at $T=T_m$ the decomposition of these pairs into individual charges occurs. It is relevant to this mechanism that owing to the polarizability of molecules the dielectric constant of the plasma depends on the scale. Fields created by pairs with characteristic size R play the role of the external fields for all smaller pairs. Therefore, the existence of large enough pairs is a crucial condition for the BKT transition.

If owing to some specific properties of the material over its whole region of existence $E_d(R)\gg T$ for this system, the BKT mechanism will be inefficient. In other words, in this case the amplitude of the density modulation (which is in fact responsible for the existence of $2d$ crystals) becomes zero before the dissociation of dislocation pairs. If this transition is a weakly first-order phase transition (which allows us to use Landau expansion), then it corresponds to the Landau theory of weak crystallization.

Landau weak-crystallization theory assumes that the thermodynamical potential (e.g., free energy) can be expanded in a series in the order parameter ϕ. In the case under consideration, it is the ratio of the short-wavelength density modulation to the average density. We believe that $\phi\ll 1$ and the main terms of the Landau expansion can be represented in the form

$$F=\int d^2r\left(\frac{1}{2}\tau\phi^2-\frac{1}{6}\mu\phi^3+\frac{1}{24}\lambda\phi^4+\frac{\alpha}{8q_0^2}[(\nabla^2+q_0^2)\phi]^2\right). \tag{2}$$

Here τ, μ, λ, and α are phenomenological coefficients. The structure of the gradient term in this expansion is accounted for by the fact that we are dealing with crystallization from a liquid (i.e., rotationally invariant state) and therefore the softening of the order parameter (which is a precursor of the transition) does not depend on the orientation: it takes place on a complete circle in the reciprocal space: $|\mathbf{q}|=q_0$.

Owing to this circumstance, fluctuations of the order parameter are rather strong near the circle and lead to renormalization of the correlation function[8,11]:

$$\langle\phi(q)\phi(-q)\rangle=\frac{T}{\Delta+\alpha(q-q_0)^2},$$

where for Δ there is the following self-consistent equation:

$$\Delta=\tau+\frac{\lambda T q_0}{4\pi\sqrt{\alpha\Delta}}, \tag{3}$$

which can easily be solved numerically.

The parameter Δ (a «gap» in the correlation function) in this theory plays the role of the controlling parameter for weak-crystallization transitions. For self-consistency of the theory one must suppose

$$\Delta\ll\alpha q_0^2. \tag{4}$$

From Eq. (2) it is easy to estimate the elastic energy of a dislocation pair in $2d$ crystals created by the weak-crystallization mechanism[12]:

$$E_d\simeq\frac{\alpha\Delta q_0^2}{\lambda}\ln\frac{R}{a_0}.$$

However, it follows from Eq. (3) that near the weak-crystallization transition point

$$\Delta\simeq\left(\frac{T^2q_0^2\lambda^2}{\alpha}\right)^{1/3}$$

and therefore

$$\frac{E_d}{T}\simeq\sqrt{\frac{\alpha}{\Delta}}\,q_0\ln\frac{R}{a_0},$$

which according to Eq. (4) is much greater than unity. Therefore, the dislocation pairs remain binding and the BKT mechanism does not work. We emphasize that the crucial

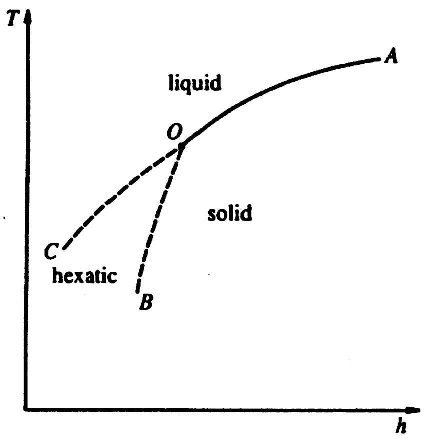

FIG. 1.

point for this conclusion is just the condition given by Eq. (4) providing the applicability of the Landau weak-crystallization theory.

Very schematically one can represent the following $T-h$ (temperature-length of chains) phase diagram of the system (Fig. 1). At OA there is a first order weak-crystallization transition, at OB and OC we have continuous transitions. The point O is the so-called bicritical point. Recall that the BKT mechanism does not work at OA because the energy of an isolated dislocation is higher than the temperature, and the mechanism of weak crystallization is inefficient at OC and OB since due to the hexatic orientational ordering the softening of the order parameter takes place not near a circle but only near six points in reciprocal space. At the bicritical point, the transition temperatures coincide and therefore we have the universal relations

$$T_0=\frac{\pi}{72}K_h=\frac{B_t(B_l+B_t)a^2}{4\pi(B_l+2B_t)},$$

where K_h is the Frank constant for the hexatic phase.[10] The same temperature given by weak-crystallization theory is (see Eq. (2)):

$$\tau_0=\frac{4}{45}\frac{\mu^2}{\lambda}.$$

Therefore at the bicritical point there are two relations between the elastic moduli, the Frank modulus, and coefficients entering the Landau expansion.

Thus, there are two alternative mechanisms of melting in $2d$ systems (BKT and Landau). The BKT mechanism leads to a continuous transition with a correlation length that diverges as T approaches T_m from above,[10] i.e.,

$$\xi_+(T)\simeq\exp\frac{\text{const}}{(T-T_m)^{\bar{\nu}}},$$

where $\bar{\nu}=0.3693$. Due to this fact, the specific heat displays an essential singularity

$$C_p(T)\simeq\xi_+^{-2}(T).$$

The elastic constants B_l and B_t approach the finite limiting values as $T\rightarrow T_m^-$. Just below T_m, for example, one can obtain for the shear elastic modulus[10]

$$B_t=B_t(T_m^-)|1+\text{const}\cdot|T_m-T|^{\bar{\nu}}|.$$

The very specific feature of the BKT mechanism is the fact that there is a universal relationship involving two elastic moduli (B_l and B_t) of the hexagonal lattice at the melting temperature:

$$\frac{1}{B_t(T_m)}+\frac{1}{B_t(T_m)+B_l(T_m)}=\frac{a^2}{4\pi T_m}.$$

Owing to this relationship the exponent η of the power-law singularity in the structure factor (typical of $2d$ crystals independently from the melting mechanism) has a maximum value at T_m. The magnitude of $\eta_{\max}$ depends on the structure and for hexagonal symmetry it is 0.33.[10]

In the Landau theory, we have fairly different predictions. The specific heat has a finite jump and power-law singularity of the following form:

$$C_p(T)=a+\frac{b}{\Delta^{3/2}},$$

where a and b can be considered constants near T_m.[8]

The shear modulus in the main approximation is proportional to Δ. The anomalous exponent η in the Landau theory is $\sqrt{\Delta/\alpha q_0^2}$, and therefore owing to Eq. (4), it should be small near the weak-crystallization transition point. However there is no definite maximum value $\eta_{\max}$.

Thus in principle from suitable experimental data one can distinguish between both possible scenarios of $2d$ melting phase transitions, although in a real situation (see, e.g., Ref. 13) it is not an easy and straightforward procedure. In particular, the effect of finite-chain rigidity discussed below makes this procedure even more difficult, since it leads to a considerable reduction in the intensity for higher peaks (see Sec. 4).

3. DIAGONALIZATION OF THE ELASTIC ENERGY

Let us consider a crystalline monolayer formed by chains. We believe these chains are rather stiff and therefore configurations with so-called hairpin defects are forbidden. The crystalline order in a system occurs only in a plane orthogonal (on average) to the chains. For simplicity, we consider only hexagonal crystalline structure (i.e., there is no cooperative tilt of the chains).

Thus, the elastic energy for such a monolayer can be written in the following form:

$$E=\frac{1}{2}\int_{-h/2}^{h/2}dz\int d^2r\left[B_l(\nabla_\alpha u_\alpha)^2+B_t\varepsilon_{\alpha\beta}(\nabla_\alpha u_\beta)^2+K\left(\frac{\partial^2u_\alpha}{\partial z^2}\right)^2\right], \tag{5}$$

where the Greek subscripts designate coordinates in the plane orthogonal to the chains, u_α is a displacement vector in this plane describing the elastic energy of a $2d$ hexagonal lattice, B_l and B_t are the elastic moduli of this lattice (longitudinal and transverse with respect to a wave vector), $\varepsilon_{\alpha\beta}$ is a $2d$ antisymmetric second-order tensor, K is the bending elastic modulus describing the chain elasticity, and z is a coordinate orthogonal to the monolayer surface. For the case of chains with purely steric repulsion, we can estimate the stiffness constants appearing in Eq. (5) (see, e.g., Ref. 14): $K \simeq T\xi/\rho_0$ and $B_l \simeq B_t \simeq (T\rho_0^{4/3})/\xi^{1/3}$, where ρ_0 is the surface density of chains.

Note that there are no terms proportional to $(\partial_z u_\alpha)^2$ in Eq. (5), which makes it possible for chains to slide past each other in a liquid-like manner. Note also that the last term in Eq. (5) is relevant only for wave vectors $p_z \gg p_\perp$. Therefore we must not take into account the terms proportional to $(\partial_z \nabla_\alpha u_\alpha)^2$ or to $(\partial_z \varepsilon_{\alpha\beta} \nabla_\alpha u_\beta)^2$.

We believe our system has large crystalline domains (with an area S), as was the case for the systems investigated in Ref. 4. Therefore, we can use Fourier transformation over coordinates along the monolayer (x and y). Thus instead of the energy E given by Eq. (5) it is convenient to use the following form:

$$E(q) = \frac{S}{2} \int_{-h/2}^{h/2} dz \left(A_{\alpha\beta} u_{q\alpha} u_{-q\beta} + K \left| \frac{\partial^2 u_{q\alpha}}{\partial z^2} \right|^2 \right), \tag{6}$$

where

$$A_{\alpha\beta} = B_l q^2 \delta_{\alpha\beta} + B_t q^2 \left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2} \right).$$

Our final aim in this paper is to find the static correlation function of displacements $\langle u_{q\alpha} u_{-q\beta} \rangle$ for the crystalline monolayer. This correlator can be represented as a sum of longitudinal and transverse parts:

$$\langle u_{q\alpha} u_{-q\beta} \rangle = \frac{T}{\Lambda_l(q)} \frac{q_\alpha q_\beta}{q^2} + \frac{T}{\Lambda_t(q)} \left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2} \right). \tag{7}$$

To find it, we have to know the two functions $\Lambda_l(q)$ and $\Lambda_t(q)$.

To calculate the functions $\Lambda_l(q)$ and $\Lambda_t(q)$, we must diagonalize the energy given by Eq. (6) or, in other words, solve the Euler–Lagrange equations following from Eq. (6). It is convenient to introduce longitudinal and transversal components of the displacement:

$$u_\alpha = u_l \frac{q_\alpha}{q} + u_t \varepsilon_{\alpha\beta} \frac{q_\beta}{q}.$$

There is no coupling between longitudinal and transversal components in our harmonic approximation, and both Euler–Lagrange equations have a similar form

$$K \frac{\partial^4 u_{l,t}}{\partial z^4} + A_{l,t} u_{l,t} = 0, \tag{8}$$

where $A_{l,t}$ are the longitudinal and transverse components of the matrix $A_{\alpha\beta}$, respectively.

To solve these equations, we have to know the boundary conditions. There are so-called natural boundary conditions which correspond to the surface contributions coming from the bulk energy given by Eq. (5). For our case, these contributions lead to the following conditions:

$$\left(\frac{\partial^2 u_{l,t}}{\partial z^2} \right)_{z=\pm h/2} = \left(\frac{\partial^3 u_{l,t}}{\partial z^3} \right)_{z=\pm h/2} = 0. \tag{9}$$

If there are specific surface energies E_s at the right-hand side of the second condition, one has to add terms $(\delta E_s / \delta u_{l,t})_{z=\pm h/2}$ to describe the surface elasticity. In the simplest approximation this surface elasticity can be represented in the following way:

$$E_s = \int d^2 r\, \delta(z \pm h/2) \epsilon_s^{(\pm)} (\nabla u_{l,t})^2,$$

where $\epsilon_s^{(\pm)} = -n_s \partial \gamma^{(\pm)} / \partial n_s$ is the surface elasticity modulus, $\gamma^{(\pm)}$ is the surface tension, n_s is the concentration of molecules constituting the monolayer, and superscripts ($\pm$) refer to either boundary ($z = \pm h/2$).

Taking account of these surface contributions modifies the results quantitatively, but not qualitatively (as we will see), and the correlation functions $\langle u_\alpha u_\beta \rangle$, which we are only interested in, are very similar. Therefore in what follows we neglect these surface contributions. Note also that even quantitatively these surface contributions are extremely small. All corrections are proportional to the parameter

$$\epsilon_s q^2 h^3 / K \ll 1,$$

which for real systems investigated in Ref. 4 is of the order of 10^{-6}.

Diagonalization of the functional (6) reduces to solving the following equation for eigenfunctions $\psi_{l,t}$ and eigenvalues $\Lambda_{l,t}$:

$$K \frac{\partial^4 \psi_{l,t}}{\partial z^4} + A_{l,t}(q) \psi_{l,t} = \Lambda_{l,t} \psi_{l,t}, \tag{10}$$

with the boundary conditions given by Eq. (9). There are symmetric and antisymmetric solutions

$$\psi_{l,t}^{(s)} = A \cosh(p_{l,t} z) + B \cos(p_{l,t} z),$$

and

$$\psi_{l,t}^{(a)} = C \sinh(p_{l,t} z) + D \sin(p_{l,t} z),$$

where

$$p_{l,t}^4 = \frac{\Lambda_{l,t} - A_{l,t}(q)}{K}.$$

It is easy to see that there are solutions of Eq. (10) that satisfy the boundary conditions (9) only at $p_{l,t}^4 > 0$, and in this case the quantities $p_{l,t}$ are solutions of the following equations:

(i) for the symmetric case

$$\tanh\left(\frac{p_m h}{2} \right) = -\tan\left(\frac{p_m h}{2} \right),$$

(ii) for the antisymmetric case

$$\tanh\left(\frac{p_m h}{2} \right) = \tan\left(\frac{p_m h}{2} \right).$$

Both equations have the set of solutions

$$p_0 = 0; \quad p_1^{(s)} h/2 = \pm 2.36502; \quad p_2^{(s)} h/2 = \pm 5.4978;$$

$$p_3^{(s)}h/2=\pm 8.6394\ldots$$

and

$$p_1^{(a)}h/2=\pm 3.9266;\quad p_2^{(a)}h/2=\pm 7.06858;$$

$$p_3^{(a)}h/2=\pm 10.2102\ldots$$

Finally, we can find the normalized eigenfunctions

$$\psi_s=\frac{1}{\sqrt{h}}\sum_m \sqrt{1+\tanh^2\left(\frac{p_m h}{2}\right)}\times\left[-\frac{\sin(p_m h/2)}{\sinh(p_m h/2)}\cosh(p_m z)+\cos(p_m z)\right]$$

and

$$\psi_a=\frac{1}{\sqrt{h}}\sum_m \sqrt{1+\tanh^2\left(\frac{p_m h}{2}\right)}\times\left[\frac{\sin(p_m h/2)}{\sinh(p_m h/2)}\sinh(p_m z)+\sin(p_m z)\right].$$

The eigenvalues are

$$\Lambda_{(l,t),m}^{(s,a)}=[Kp_{(l,t),m}^{(s,a)4}+A_{(l,t)}(q)]h. \tag{11}$$

4. STATIC FLUCTUATIONS

We have solved the problem of static fluctuations in the crystalline monolayer on the surface of a liquid. Let us discuss now the qualitative physical consequences of this solution.

First, let us estimate the contributions from different values of p_m entering the static correlation function of displacements (see Eq. (7)), or more accurately the eigenvalues (11). The contribution from $p_0=0$ gives us the pure $2d$ result

$$\langle u_0^2\rangle\simeq\frac{T}{Bh}\ln\frac{R}{a}, \tag{12}$$

where R is a characteristic size of a monodomain region for the crystalline monolayer and a is a characteristic atomic scale.

For the systems investigated in Ref. 4, the chains are rather short ($h\sim 10a$) and stiff ($K/B\gg h^4/a^2$). This means that the persistence length ξ (see, e.g., Ref. 15) is larger than $h^{1)}$.

Moreover, the contributions from the higher order terms in p_m decrease as p_m^{-4}, i.e., very rapidly. So in the first approximation one can restrict oneself only to the two terms with the smallest values of p_m. This gives us the following corrections to the $2d$ result, i.e., Eq. (12):

$$\langle u_1^2\rangle\simeq\theta\frac{T}{K}\frac{h^3}{a^2}, \tag{13}$$

where the numerical factor θ is of the order of 10^{-3}.

The physically interesting and measurable property is not the static given by Eq. (7), but the structure factor directly related to the x-ray scattering intensity:

$$S(\mathbf{Q})\simeq h\int d^2r\int_{-h/2}^{h/2}dzG(r,z)\exp(i\mathbf{QR}), \tag{14}$$

where the wave vector $\mathbf{Q}=\mathbf{b}+\mathbf{k},\mathbf{b}$ is a reciprocal lattice vector and $k\ll b$, and the function $G(r,z)$ can be represented as

$$G(r,z)=\exp\left(-\frac{1}{2}H(r,z)b^2\right),$$

where

$$H(r,z)=\frac{Tb^2}{Bh}\int\frac{dq}{q}[J_0(qr)-1)]+\theta\frac{Th^3b^2}{K}\int qdq[J_0(qr)\cos(p_1z)-1], \tag{15}$$

and J_0 is the zero-order Bessel function. Note that in Eq. (14) we keep explicitly only those factors that depend on h.

Let us consider the case when $Q_z=0$ (which corresponds to the really interesting situation). From Eqs. (15) and (14) we get

$$S(Q)\simeq\frac{h^2}{|\mathbf{b}-\mathbf{Q}|^{2-\eta}}\exp\left(-\frac{\theta Th^3b^2}{Ka^2}\right), \tag{16}$$

where $\eta=Tb^2/Bh$.

Thus in our approximation the role of the finite chain length is reduced to some effective Debye–Waller factor, which does not change the shape of the peaks that correspond to the well-known power-law behavior typical $2d$ systems. Note that this factor strongly reduces the intensity of higher-order peaks in the x-ray scattering.

We have used the expression (16) to adjust the data from Ref. 5 for the x-ray intensity for four compounds with h varying from $8a$ to $14a$. This gives us the rather reasonable estimate $\xi\simeq 2h$.

5. DYNAMICAL PHENOMENA

To find the spectrum of surface modes where the motion of the liquid is localized near the film, first we will need linearized dynamical equations for a film and for the liquid under it. The linearized equations of three-dimensional ($3d$) hydrodynamics are well known (see, e.g., Ref. 16). Their solutions describe an acoustic mode (associated with oscillations of the vortexless velocity component), a viscous mode (associated with a vortex velocity component), and a thermal diffusive mode (associated with relaxation of the specific entropy). The last mode is decoupled from the two former modes, and we will neglect it in what follows (one can assume adiabatic conditions, and the thermal diffusive mode vanishes in this case).

Bearing in mind that we only need linearized equations for the velocity and displacement components, we can write the following equations[17]:

$$\partial_t\delta\rho+\rho\partial_z v_z+\rho\partial_\alpha v_\alpha=0,$$

$$\rho\partial_t v_z+\partial_z\delta P+\partial_\gamma K\partial_z\partial^2u_\gamma=\eta_{zzmn}\partial_z\partial_m v_n+\eta_{z\gamma mn}\partial_\gamma\partial_m v_n,$$

$$\partial_t u_\alpha=v_\alpha,\quad \rho\partial_t v_\alpha+\partial_z K\partial_z\partial^2u_\alpha+\partial_\alpha\delta P+\partial_\beta\times[-B_l\delta_{\alpha\beta}\partial_\gamma u_\gamma-B_t(\partial_\alpha u_\beta+\partial_\beta u_\alpha-2\partial_\gamma u_\gamma\delta_{\alpha\beta})+K\partial_\beta\partial^2u_\alpha]$$

$$= \eta_{zzmn}\partial_z\partial_m v_n + \eta_{zymn}\partial_y\partial_m v_n . \qquad (17)$$

In thin monolayers with very rigid chains, we can neglect variations of hydrodynamic variables in the z-direction and in this limit we recover the results of Ref. 17 for the homogeneous $2d$ monolayer on the surface of a liquid. The system (17) is valid for $-h/2<z<h/2$. For $z<-h/2$ we have a bulk isotropic liquid. The solution of the bulk hydrodynamic equations for isotropic liquids is well known. We will only be interested in the solution where the motion of the liquid is localized near the surface.

It is convenient to introduce potential (vortexless) and vortex parts of the velocity:

$$\mathbf{v} = \nabla \psi + \mathbf{a},$$

where ψ is the potential of the velocity. In terms of these quantities, the surface solution of the bulk hydrodynamical equations can be represented as

$$\psi(z) = \psi_s \exp(kz), \quad \delta P = i\omega\tilde{\rho}\psi, \qquad (18)$$

and

$$a_\alpha(z) = a_{s\alpha} \exp\left(\frac{1-i}{\sqrt{2}} \sqrt{\frac{\tilde{\rho}\omega}{\tilde{\eta}}}\, z \right),$$

$$a_z(z) = \frac{1-i}{\sqrt{2}} \sqrt{\frac{\tilde{\eta}}{\tilde{\rho}\omega}}\, k_\alpha a_\alpha(z), \qquad (19)$$

where $\mathbf{k}$ is the wave vector and ω is the frequency of the motion under consideration, δP is the variation of the pressure due to this motion, and η is the viscosity of the liquid. The subscript s refers the corresponding variable to the monolayer-liquid interface (i.e., $z=-h/2$). To distinguish between parameters of the liquid and of the monolayer, we denote the former by letters with a tilde.

The boundary conditions for linearized $3d$ equations result from linearization of the dynamical equations for the film. In the monograph [17], a method is described for deriving these equations for the homogeneous distribution of hydrodynamical variables over the thickness of the film (corresponding to the case $K=\infty$ in our model). In this case, one can use hydrodynamic variables $\varphi_2(x,y)$ referring to the xy plane, which are simply related to the corresponding $3d$ densities $\varphi(x,y,z)$. Thus

$$\varphi_2 = \int dz \varphi.$$

In our case, we cannot use the variables φ_2. Instead we have to solve the linearized hydrodynamic equations, taking into account the z-dependence of the hydrodynamic variables. Using Fourier transforms for the x and y coordinates and the time (ω is the frequency) and the diagonalization procedure (as in Sec. 3), we can get from Eqs. (17) the dispersion laws for eigenmodes in the monolayer. Neglecting the thermodiffusion mode we can find the following three modes.

(i) Conventional first sound

$$\omega_l = \pm c_1 q - \frac{i}{\rho} \hat{\eta}_l q^2, \qquad (20)$$

where

$$c_1 = c + \frac{B_l}{2\rho c} \frac{q^4}{q^2 + p_s^2}$$

and the velocity c is determined by the bulk compressibility. We have denoted the corresponding combination of the viscosity coefficients here by $\hat{\eta}_l$ (the explicit expression for $\hat{\eta}_l$ will not be used later on).

(ii) Transverse sound

$$\omega_t = \pm \sqrt{\frac{B_t}{\rho}}\, q - \frac{i}{2\rho} \hat{\eta}_t q^2, \qquad (21)$$

where we have used the same notation as above.

The second-sound mode (see Ref. 17) is a propagating one only for

$$qh \gg \frac{\eta}{\sqrt{B\rho h}}.$$

For the thin films ($h \simeq 10^{-7}-10^{-6}$ cm) investigated in Ref. 4, the dimensionless parameter is

$$\delta \equiv \frac{\eta}{\sqrt{B\rho h}} \simeq 10^2,$$

and therefore this criterion cannot be satisfied.

If the criterion is violated, instead of second sound one obtains two diffusion modes. One is associated with velocity oscillations with frequency

$$\omega \simeq -i \frac{\eta}{\rho} q^2$$

for

$$\frac{1}{\sqrt{\delta}} \ll qh \ll \delta.$$

The second mode is associated with oscillations of the displacement vector u_α, and in the same range of qh it has a rather unusual dispersion law, i.e.,

$$\omega \simeq -i \frac{B_l}{\eta h^2 q^2}.$$

For $qh \ll 1/\sqrt{\delta}$ it transforms into a fast relaxation mode having a gap

$$\omega \simeq -i \frac{K}{\eta h^2}.$$

To find the spectrum of surface modes where the motion of the liquid is localized near the film, let us reconsider the third equation in (17) at the interface $z=-h/2$. Bearing in mind the situation with very rigid chains, we can neglect intrinsic dissipation in the monolayer (right-hand side of the equation). However to satisfy the kinetic relations between mass and momentum flows from the bulk to the film and the corresponding generalized forces, we must introduce into this equation the viscous stress tensor Π_{ik} in a liquid. Thus we obtain

$$\rho \partial_t v_\alpha + K \partial_z^2 \partial^2 u_\alpha + \partial_\beta T_{s\alpha\beta} = \Pi_{\alpha z}, \qquad (22)$$

where

$$\Pi_{ik}=-\tilde{\eta}\left(\nabla_i v_k-\frac{2}{3}\,\delta_{ik}\nabla\mathbf{v}\right)-\tilde{\zeta}\nabla\mathbf{v}\delta_{ik}. \tag{23}$$

Any variation of the quantities characterizing the film induces a motion of the liquid near the interface. Comparing the first term on the left-hand side of Eq. (22) and the right-hand side of this equation, we can see that for frequencies

$$\omega\gg\frac{\tilde{\rho}\tilde{\eta}}{\rho^2}$$

these motions in the liquid may be neglected, and we come back to the eigenmodes of the free layer which have been found above.

In the opposite limiting case, which we will be interested in later on, the frequency can be assumed to be small (this is true of all modes under consideration) and we can neglect the first term on the left-hand side of Eq. (22). Let us neglect as well for a moment the finite rigidity of chains (i.e., suppose $K=\infty$). In this case from Eq. (22) we can easily find that we have $\tilde{\rho}\omega\gg\tilde{\eta}q^2$, and under these conditions only the vortex component **a** (see Ref. 19) of the velocity is excited and we get the following dispersion laws for surface modes (see Ref. 17).

(i) Instead of first sound we have

$$\omega_l=\frac{1}{2}\,(\sqrt{3}-i)\left(\frac{B_l^2}{\tilde{\rho}\tilde{\eta}}\right)^{1/3}q^{4/3}.$$

(ii) Instead of transverse sound we have

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

The diffusion mode associated with the velocity oscillations does not change its spectrum due to interaction with the liquid, and it has the same dispersion law as for a free film.

Now let us include the finite rigidity of chains. We use perturbation theory over $1/K$ (as already done in calculating the static structure factor) taking into account only the leading correction to $2d$-results (which take place at $K=\infty$). This gives only a small modification of the longitudinal mode (i), which now reads

$$\omega_l=\frac{1}{2}\left(B_l+\gamma\,\frac{B_l^2h}{K}\right)^{2/3}(\tilde{\rho}\tilde{\eta})^{-1/3}q^{4/3},$$

where the numerical factor γ is of the order of unity.

Thus, the finite rigidity of chains only leads to small corrections to the dispersion law of the longitudinal mode, although (as we have seen in Sec. 4) it gives a considerable reduction of static fluctuations.

We have carried out a theoretical investigation of the spectrum of surface modes. One may say that these are modes in a liquid caused by the presence of a film on its interface with a gas. We have seen that such a system possesses rich dynamics, which is accounted for both by the complex structure of the film and by the interaction of the film with bulk degrees of freedom.

Several phenomena discussed in this section can in principle be observed by light-scattering experiments. A rough estimate for the above dispersion laws of surface modes shows that it is of the order of 10^5–10^6 s^{-1}. Because of relaxation of surface fluctuations, the scattered light has a broadened spectral distribution compared with the incident light. Although this broadening is small, the modern technique of light beating (intensity-fluctuation spectroscopy) may obtain information about eigenmodes of the system. At least, it does not seem to be absolutely impossible.

6. HEXATIC OR TILTED FILMS

To describe the state of a film with orientational order, in addition to variables introduced above one must also include the angle φ determining the orientational degree of freedom. In the case of a tilted film we have an anisotropy of the film which is described by the unit vector

$$\mathbf{n}_1=\frac{[\mathbf{nl}]}{|[\mathbf{nl}]|},$$

where **l** is the unit vector of a normal to the film and **n** is the unit vector giving the average orientation of chains.

A variation of the vector $\mathbf{n}_1$ neglecting the vertical displacement of the film (as above) is

$$\delta n_{1i}=-\frac{1}{2}\,[\mathbf{n}_1\mathbf{l}]_i\delta\varphi$$

determined just by the variation of one angular variable φ. Owing to the anisotropy of the film, the quadratic part of the energy will be anisotropic as well. However as has been shown by Nelson and Pelcovits,[18] the anisotropy of elastic coefficients decreases with increasing scale, and therefore we will neglect this anisotropy further. In this approximation (large scales) tilted films are completely equivalent to hexatic films.

Spontaneous breaking of the rotational invariance in these films gives one additional Goldstone mode describing a relaxation of the angle φ. It is easy to see that the interaction with a liquid does not change the dispersion law of this mode (as in the case of the diffusion mode associated with velocity oscillations). Thus we find the following dispersion law of the diffusive type:

$$\omega=-i\Gamma Mq^2, \tag{24}$$

where M is the orientational elastic modulus and Γ is the kinetic coefficient.

As we have seen in Sec. 5, the finite rigidity of chains has only a small influence on the dynamical phenomena. Therefore we will suppose $K=\infty$, which makes the situation effectively two-dimensional. The equation of motion for φ has the form (see Ref. 17)

$$\partial_t\varphi+\mathbf{v}\nabla\varphi=\Gamma\nabla^2\varphi. \tag{25}$$

Owing to the coupling of φ and **v** there is the following contribution to the stress tensor of the film:

$$M\left(\nabla_\alpha\varphi\nabla_\beta\varphi-\frac{1}{2}\,(\nabla\varphi)^2\delta_{\alpha\beta}\right).$$

One can prove that the above-mentioned interaction does not produce a fluctuational contribution to Γ (in fact, this is a consequence of the incompressibility, namely the condition $\nabla \mathbf{v}=0$). Thus Γ should be considered a scale-independent phenomenological constant.

However there is the backward contribution to the viscosity associated with fluctuations of φ. To calculate this contribution it is convenient to use the special diagram technique adapted for dynamical phenomena (see Refs. 17 and 19). The dynamical correlation functions of variables φ and $\mathbf{v}$ have in a harmonic approximation the standard form

$$\langle\varphi\varphi\rangle=\frac{2T\Gamma}{M(\omega^2+\Gamma^2q^4)},$$

and

$$\langle v_\alpha v_\beta\rangle=\frac{2T\eta(q^2\delta_{\alpha\beta}-q_\alpha q_\beta)}{\rho^2\omega^2+\eta^2q^4}.$$

Due to the interaction between φ and $\mathbf{v}$ (the convective term in Eq. (25)), these bare correlation functions change, and one can find the following fluctuational contribution to the viscosity of the film:

$$\eta_{fl}=\frac{M^2}{16T}\langle(\nabla\varphi)^2(\nabla\varphi)^2\rangle=\frac{M^2}{8T}\int\frac{d\omega d^2q}{(2\pi)^3}q^4\langle\varphi\varphi\rangle^2.$$

The simple calculation of the integral gives us

$$\eta_{fl}=\frac{T}{16\pi\Gamma}\ln(qa).$$

Note that such a behavior strongly suppresses the fluctuational contribution to Γ and therefore our approach is self-consistent.

Thus, in hexatic or tilted films there is a fluctuational contribution to the internal viscosity coefficient of a monolayer associated with the interaction between the orientational degree of freedom and hydrodynamic motions. This contribution is absent from films having no orientational degree of freedom. Note also that this contribution can be larger than the bare viscosity of the film if the diffusion coefficient Γ is small.

Very speculatively we can use this fluctuational contribution to the viscosity to explain observations known for many films of alcohol where is an abrupt enhancement of the viscosity at the phase transition between the so-called superliquid and liquid phases (see Ref. 20 and references therein) assuming that this transition is accompanied by some kind of orientational ordering.

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[1)] We use the conventional definition for the persistence length: $\xi=C_{\text{eff}}/T$, where the effective elastic modulus for a chain is related to our modulus by $K=T^2/2C_{\text{eff}}$.

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