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Dynamics of viscous amphiphilic films supported by elastic solid substrates

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Abstract. The dynamics of amphiphilic films deposited on a solid surface is analysed for the case in which shear oscillations of the solid surface are excited. The two cases of surface and bulk shear waves are studied with the film exposed to a gas or to a liquid. By solving the corresponding dispersion equation and the wave equation while maintaining the energy balance, we are able to connect the surface density and the shear viscosity of a fluid amphiphilic overlayer with the experimentally accessible damping coefficient, phase velocity, dissipation factor, and resonant frequency shifts of shear waves.

1. Introduction

Measurements of the properties of thin adsorbed films have long constituted an important subfield of interface studies [1–10]. Scientific and technological applications of thin films, such as Langmuir–Blodgett (LB) films [11–20], self-assembled monolayers (SAM) [21], and protein monolayers and multilayers [22, 23], have stimulated detailed studies of the physical properties of such structures. With these model systems it is possible to construct multilayer amphiphilic films with controlled monolayer thickness $h_j \simeq 25 \text{ \AA}$, and to create situations leading to different couplings between the adsorbed film and the chemically modified substrate [12–16]. Specifically, measurements of the surface density and viscosity of these films are important, both scientifically and, for example, as regards their possible application in acoustical biosensors in which they can serve as sensitive elements [13, 16, 18, 19].

The dynamic (shear) viscosity of amphiphilic films is a very important rheological characteristic of a protein film or a fluid membrane, which is strongly dependent on the temperature and phase state of the film, and on environmental conditions [13, 24, 25]. Usually LB or SAM film acoustic sensors operate in vacuum or in a gaseous environment. In contrast, a lipid–water system or a protein layer adsorbed onto a solid surface in a fluid experiences ‘wet’ conditions or a bulk aqueous medium [23, 26] at room temperature, which can change the viscosity of the film. In addition, the biomolecular layer adsorption process is extremely sensitive to the nature of the solid substrate, in the sense that it can modify the overlayer structure [13, 16, 20, 21, 22]. In view of this, a rigorous description of the dynamics of the existing interfaces of combined solid-substrate–adsorbed-layer–bulk liquid systems, as well as of solid-surface–amphiphilic-film–gas systems seems to be much needed.

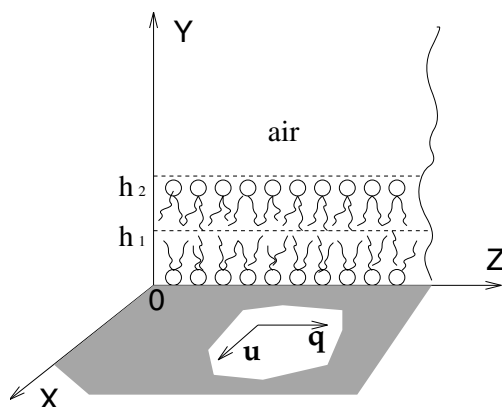


Figure 1. An illustration of surface shear waves (SSW) with horizontal polarization propagating in a system of an elastic half-space with an adsorbed thin amphiphilic fluid bilayer on top. The system is in a gaseous environment.

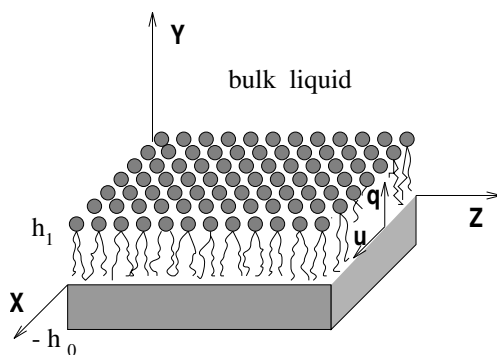


Figure 2. Shear bulk waves propagating in an AT-cut quartz plate covered with a thin amphiphilic layer. The system is immersed in a bulk liquid.

In the present paper we investigate the dynamics of thin amphiphilic layer(s) attached to a solid substrate oscillating in a shear mode and in contact with (i) a gas or (ii) a bulk Newtonian liquid. Figures 1–3 show schematically the geometry of such sandwich systems.

Amphiphilic bilayer films can imitate the behaviour of a bilayer lipid membrane. The constituent bilayer molecules are composed of hydrophilic groups attached to hydrophobic chains of different length. The phase diagrams of such amphiphilic molecules demonstrate a rich variety of properties and behaviour depending on temperature and water content [13, 20, 24, 27, 28]. Above the liquid-crystalline–gel transition the hydrocarbon chains are approximately liquid, and a bilayer membrane behaves like a two-dimensional fluid in the lateral plane due to the vanishing shear modulus of elasticity [27, 28]. Such a peculiar fluid is isotropic in its plane but it is anisotropic in the normal direction, due to the sublayered head-and-tail structure [24]. The viscous layer's response to shear deformation can be characterized by different shear viscosity coefficients, namely, the surface viscosity, η_s [13], and a bulk shear viscosity, η_M (a component of the tensor η_{jklm} ; index 'M' corresponds to the classification according to reference [28]).

When the system is immersed in water, anisotropy can arise from water being trapped

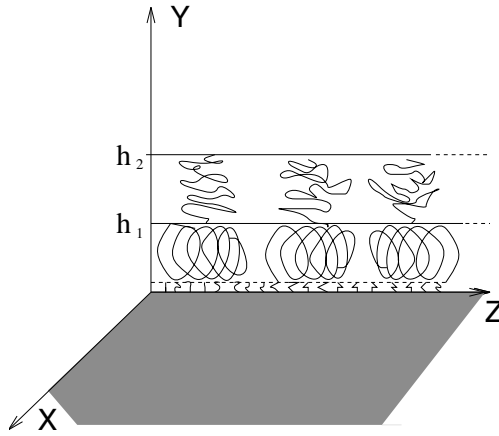


Figure 3. A schematic depiction of two distinct regions of a protein layer adsorbed from the bulk solution onto a solid substrate. The dotted line corresponds to the surface-adjacent amphiphilic layer.

in the layer. This can result in a value of the overlayer viscosity, η_M , which is distinctly different compared to the case of a gaseous (air) environment. This is especially important for protein adsorbed layers with nonuniform interfacial domain structure and nonuniform water distribution in the normal direction. Such nonuniformity effects have been analysed in a recently published hydrodynamic model of ‘porous’ polymer surface films in liquids (for a review, see reference [26] and references therein).

In the present paper, we have considered both the surface viscosity η_s and the bulk shear viscosity η_M of adsorbed amphiphilic films. These can be measured in different acoustic experiments, when acoustic shear waves propagate along the plane of the layer (horizontally polarized surface shear waves) and in the direction normal to it (bulk acoustic shear waves). In order to be able to describe both air and liquid environmental experiments, corresponding shear viscosity coefficients, η_M ‘in air’ and η_M ‘in liquid’, have been noted.

The paper is organized as follows: in the framework of continuum mechanics we derive in section 2 the dispersion equation for elastic shear waves propagating in the system. We also treat the interaction between horizontally polarized elastic surface shear waves (SH SSW) and a fluid layer adsorbed on the surface of a semi-infinite solid substrate. In section 3 we analyse the response of bulk acoustic shear waves (BAW) propagating in a finite quartz plate with a viscous overlayer. Our results allow us to connect the surface density and shear viscosity of amphiphilic overlayers with the experimentally accessible damping coefficient, phase velocity, dissipation factor, and resonant frequency shifts of shear waves. These can be measured by modern piezo-acoustical devices of different types [23, 26, 29].

2. Dynamics of a viscous bilayer film on a solid substrate oscillating in a gaseous medium or in vacuum

Within continuum mechanics [30, 31], the dynamics of a liquid film can be described by the equation

$$\rho \frac{dv_j}{dt} = \rho (\partial v_j / \partial t + (\mathbf{v} \cdot \nabla) v_j) = \partial_k \sigma_{jk}.$$

This corresponds to the Navier–Stokes equation for the motion of a viscous liquid. Recently, it was shown that hydrodynamical properties of fluid amphiphilic (lipid) films can be analysed within the continuum mechanics scheme with viscous tensions defined as follows [28]:

$$\begin{aligned}\sigma_{jk} &= \mathcal{A}_{lm} \eta_{jklm} \\ \mathcal{A}_{lm} &= \frac{1}{2} (\partial_l v_m + \partial_m v_l) \quad \partial_l \equiv \partial / \partial x_l.\end{aligned}$$

Here η_{jklm} is a viscosity matrix; such matrices were introduced explicitly in reference [32].

For a fluid lipid layer in the incompressible-liquid approximation and in the absence of a pressure gradient, these expressions can be simplified [28]. In particular, for the case in which a strain is applied along the x -direction, one finds

$$\sigma_{xy} = \eta_M (\partial_y v_x).$$

Here the viscosity coefficient η_M is a component of the viscosity matrix η_{jklm} ; the y -axis is perpendicular to the layer plane.

In our model we use the notation $\eta_M(\text{liquid})$ and $\eta_M(\text{gas})$ for describing fluid films bounded (in different experiments) by a liquid or a gas.

Below, we analyse the influence of the viscosity and surface density of a thin bilayer on the phase velocity and the damping of elastic shear waves.

2.1. Surface shear wave propagation: the semi-infinite quartz crystal substrate

We treat here horizontally polarized surface elastic waves on a solid substrate interacting with a thin fluid double layer, which on the other side has an interface to vacuum or to a gaseous phase (figure 1). Surface waves on plane interfaces have an amplitude which decays exponentially with the normal distance from the solid surface on which they propagate [2]. Phase velocities of surface shear waves (SSW) V are lower than those of bulk shear waves V_0 in the semi-infinite elastic half-space (i.e. the substrate).

Let us now consider how the shear vibration of the substrate generates a viscous wave in the adjacent fluid layer [2, 5, 17]. In the framework of fluid mechanics, the motion of an adsorbed viscous film is described by the linearized Navier–Stokes equation:

$$\begin{aligned}\partial v_x(y, z, t) / \partial t &= \nu_1 \Delta v_x \\ \nu_1 &\equiv \eta_1 / \rho_1 \\ \eta_1 &= \eta_M(\text{gas}).\end{aligned}\tag{1}$$

Equation (1) is valid in the regime of small Reynolds number:

$$Re = \frac{\omega u_0 h_1}{\nu_1} \ll 1$$

for small oscillation frequency ω and small amplitude u_0 , and for a thin overlayer thickness h_1 . Here v_x denotes the x -component of the velocity of the fluid film and the y -axis is perpendicular to the z -direction of wave propagation.

The boundary conditions at the fluid–solid interface ($y = 0$) correspond to the

assumption of *no-slip* conditions [6, 26, 28, 30]:

$$\begin{aligned}
 y = 0 \quad v_x &= \frac{\partial u_x(y, z, t)}{\partial t} \\
 \sigma_{yx} &= \eta_1 \frac{\partial v_x}{\partial y} \\
 \sigma_{yx} &= C_{44} \frac{\partial u_x}{\partial y}.
 \end{aligned} \tag{2}$$

Here u_x is a component of the substrate boundary displacement vector

$$u_x = u_0 \exp(\kappa_t y + iqz) \exp(i\omega t)$$

and $\kappa_t = (q^2 - \rho_0 \omega^2 / C_{44})^{1/2}$ is the inverse penetration depth of surface shear waves into the solid substrate; ω and q are the wave frequency and wavenumber, while ρ_0 and C_{44} are the substrate density and shear modulus, respectively. The substrate boundary motion is described by the equation

$$\rho_0 \ddot{u}_x = C_{44} \left(\frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2} \right)$$

which corresponds to elastic vibrations of the solid surface.

Boundary conditions at the moving interface between fluid 1 and fluid 2 ($y = h_1$, figure 1) follow from the condition that the friction forces must be the same [30]:

$$\begin{aligned}
 y = h_1 \quad n_k \sigma_{ik}^{(1)} &= n_k \sigma_{ik}^{(2)} \\
 \sigma_{ik}^{(1)} &= -p_1 \delta_{ik} + \eta_1 \left(\frac{\partial v_i^{(1)}}{\partial x_k} + \frac{\partial v_k^{(1)}}{\partial x_i} \right) \\
 \sigma_{ik}^{(2)} &= -p_2 \delta_{ik} + \eta_2 \left(\frac{\partial v_i^{(2)}}{\partial x_k} + \frac{\partial v_k^{(2)}}{\partial x_i} \right) \\
 v_x^{(1)} = v_x^{(2)} \quad v_z^{(1)} = v_z^{(2)} &= 0.
 \end{aligned} \tag{3}$$

At the free surface, finally, the boundary condition is

$$y = h_2 \quad \eta_2 \frac{\partial v_x^{(2)}}{\partial y} = 0. \tag{4}$$

Equations (1)–(4), together with the equation for the elastic substrate motion, lead to the following dispersion equation for horizontally polarized surface shear waves in our system:

$$\kappa_t = \frac{i\omega\eta_1\xi_1 (\xi_1/\xi_2 + \epsilon \tanh(\Delta h\xi_2)) \exp(2h\xi_1) - (\xi_1/\xi_2 - \epsilon \tanh(\Delta h\xi_2))}{C_{44} (\xi_1/\xi_2 + \epsilon \tanh(\Delta h\xi_2)) \exp(2h\xi_1) + (\xi_1/\xi_2 - \epsilon \tanh(\Delta h\xi_2))} \tag{5}$$

where $\xi_j = (q^2 + i\omega/\nu_j)^{1/2}$, $j = 1, 2$, $\epsilon \equiv \eta_2/\eta_1$, and $\Delta h = h_2 - h_1$.

Here we introduce the viscous penetration depth $\delta \equiv (2\nu/\omega)^{1/2}$ corresponding to the distance over which the transverse wave amplitude falls off by a factor of e . For two sufficiently thin viscous overlayers one can assume that $h_j/\delta_j \ll 1$, and we will always consider the long-wavelength limit, where $q^2 \ll \delta^{-2}$. Within these limits, we can from equation (5) find the SSW damping coefficient as a function of the viscosities and the surface densities of the overlayers.

The result for the damping coefficient Γ of the SSW—simply the imaginary part of the wave vector q —is

$$\Gamma = \Gamma_{mon} \left\{ 1 + \frac{\eta_{2s}}{\eta_{1s}} \left(1 + \frac{\eta_{1s}\rho_{2s}}{\eta_{2s}\rho_{1s}} \left(1 + \frac{\eta_{2s}}{\eta_{1s}} \right) \right) \right\}. \tag{6}$$

Here $\eta_{js} \equiv \eta_M h_j$ is the surface viscosity component of each layer, $\rho_{js} \equiv \rho_j h_j$ is a corresponding surface density, and Γ_{mon} denotes the damping coefficient for the case of a monolayer [17]:

$$\Gamma_{mon} = \frac{q_0 \omega^3 \rho_{1s} \eta_{1s}}{C_{44}^2}.$$

One can estimate the value of Γ to be $\sim 10^{-5}$ for a phospholipid bilayer. Experimental data for egg lecithin at $T = 25$ °C are taken from reference [24], which provides the following values: bilayer thickness: $h_b = 46$ Å; bilayer density: $\rho \approx 1$ g cm $^{-3}$; and bilayer ‘microviscosity’ (measured by a probe technique) $\eta \approx 1.2$ dyn s cm $^{-2}$. The resonator frequency is $\omega_0 \approx 10^9$ Hz, and $C_{44} \approx 2.6$ dyn cm $^{-2}$ is the corresponding quartz shear modulus.

Using the dispersion equation (5), one can also obtain the change in the SSW phase velocity, $\Delta V/V_0$, caused by the presence of the adsorbed bilayer. One finds that

$$\frac{\Delta V}{V_0} \approx \frac{1}{2} \left(\frac{\omega \rho_{s1}}{V_0 \rho_0} \right)^2 \left(1 + \frac{\rho_{s2}}{\rho_{s1}} \right)^2 \quad (7)$$

$$V_0 \equiv \sqrt{C_{44}/\rho_0} = \text{constant}.$$

As a consequence of the no-slip and thin-layer assumptions, the SSW velocity shift is sensitive only to the overlayer surface densities ρ_{sj} and not to their viscosities. This corresponds to the Love type of wave propagation. Equation (7) allows one to determine the surface density of the upper or lower half of the bilayer if the density of the other layer is known or can be determined by an independent experiment. For the lipid bilayer (with the same parameters as above) the SSW phase velocity shift is small, $\Delta V/V_0 \sim 10^{-8}$. However, this shift may be detectable (of order $\sim 10^{-6}$) at high frequencies, $\omega \approx 2\pi \times 10^9$ Hz, since the SSW velocity change is a quadratic function of frequency. Such high frequencies can be generated by modern acoustic SSW devices [29]. At low frequencies, $f \lesssim 10^8$ Hz, it is more reasonable to use another type of shear wave for surface density analysis excited by quartz crystals oscillating in the thickness shear mode (see section 3.2 below).

3. A solid substrate with a viscous overlayer oscillating in a bulk viscous medium

3.1. The resonant frequency and dissipation factor for bulk shear waves: the finite quartz-crystal resonator

In addition to ‘genuine’ surface waves, another type of shear wave can propagate in the plane of the overlayer–substrate interface. These are bulk acoustic waves (BAW). In contrast to the SSW case considered above, the acoustical response of unloaded BAW resonators depends on the quartz slab thickness h_0 as well as on its density ρ_0 and shear modulus C_{66} :

$$f_0 = (C_{66}/\rho_0)^{1/2} h_0.$$

It has been shown [3, 6, 23, 26, 33] that the resonant frequency of such quartz plates decreases when its surface is coated with an overlayer constituting a mass load. For a thin surface film, uniformly covering the entire vibrating area of the slab, Sauerbrey deduced a linear relation between the frequency change and the added mass per unit area in a vacuum (gaseous) environment [3]. Kanazawa and Gordon [6] later described the resonant response of quartz oscillators in bulk viscous liquids. Recent experimental and theoretical investigations of the BAW in composite media (see references [23, 26, 33] for a review)

have demonstrated possible applications to the study of nonuniform polymer and protein thin films, and have included both resonant frequencies and viscous dissipation in the interface region. Experimentally, it is convenient to obtain this viscous dissipation as the width of the resonant frequency [26] or as the dissipation factor D [23]:

$$D = E_{\text{dissipated}}/2\pi E_{\text{stored}} = 1/\pi f \tau$$

where τ is the time constant for the decay of the vibration amplitude.

In this section we calculate the shifts Δf of the resonance frequency and ΔD of the dissipation factor, respectively, for the case of a viscous amphiphilic (lipid) film attached without slip to the surface of the quartz slab oscillating in the thickness shear mode in the presence of a bulk viscous liquid.

The wave equation for shear waves propagating in the vertical direction (figure 2) is

$$\frac{\partial^2 u_x(y, t)}{\partial y^2} = \frac{i\rho_1\omega}{\eta_1} u_x(y, t) \quad \eta_1 \equiv \eta_M(\text{liquid}). \quad (8)$$

Its general solution has the form

$$\begin{aligned} u_x &= e^{i\omega t} (U_1 e^{-\xi_1 y} + U_2 e^{\xi_1 y}) \\ \xi_1 &= (1 + i)/\delta_1. \end{aligned} \quad (9)$$

Using the same boundary conditions (2)–(4) as above, we find for the x -component of the liquid velocity

$$\begin{aligned} v_x &= v_0 \frac{e^{\xi_1 y} + A e^{-\xi_1(y-2h_1)}}{1 + A e^{2h_1\xi_1}} \\ A &= \frac{\delta_2 + \epsilon\delta_1 \tanh[(1+i)\Delta h/\delta_2]}{\delta_2 - \epsilon\delta_1 \tanh[(1+i)\Delta h/\delta_2]}. \end{aligned} \quad (10)$$

The shift of resonant frequency Δf and dissipation factor ΔD , due to the overlayer on the substrate, can be calculated from the balance between dissipated and stored energy in the system [33, 26, 23]. Using this energy balance, we find from equation (10)

$$\Delta f \approx -\text{Im}\left(\eta_1 \xi_1 \frac{A e^{2h_1\xi_1} - 1}{A e^{2h_1\xi_1} + 1}\right) / 2\pi\rho_0 h_0 \quad (11)$$

$$\Delta D \approx -\text{Re}\left(\eta_1 \xi_1 \frac{A e^{2h_1\xi_1} - 1}{A e^{2h_1\xi_1} + 1}\right) / \pi f \rho_0 h_0. \quad (12)$$

In the limiting case $h_1/\delta_1 \ll 1$, $\Delta h/\delta_2 \gg 1$, we obtain for the resonant frequency shift

$$\Delta f_{\text{res}} = -f_0 \left(\frac{f\eta_2\rho_2}{\pi\rho_0 C_{66}}\right)^{1/2} \left\{ 1 + h_1\rho_1 \left(\frac{4\pi f}{\eta_2\rho_2}\right)^{1/2} - (4\pi f\eta_2\rho_2)^{1/2} \frac{h_1}{\eta_1} \right\}. \quad (13)$$

This expression contains contributions from both the lower and the upper layer. For sufficiently viscous solutions, $\eta_2 \approx \eta_1\rho_1/\rho_2$, the second and third terms may be of the same order.

In contrast, the result for ΔD is practically insensitive to the ultrathin overlayer parameters. In the linear approximation, corresponding to a small value of h_1/δ_1 , it depends only on the upper (bulk) liquid viscosity and its density:

$$\Delta D = 2f_0 \left(\frac{\eta_2\rho_2}{\pi f \rho_0 C_{66}}\right)^{1/2} \left\{ 1 - \frac{2\pi h_1^2 \rho_1 f}{\eta_1} \left(\frac{\eta_2\rho_2}{\eta_1\rho_1} - 1\right) \right\}. \quad (14)$$

In the limit of $\eta_2 \rightarrow 0$ we obtain the Sauerbrey formula:

$$\Delta f = -\frac{2f_0^2 \rho h}{\sqrt{\rho_0 C_{66}}}. \quad (15)$$

In the opposite case and for $h_1 = 0$, the results of Kanazawa and Gordon follow:

$$\Delta f_{res} = -f_0 \left(\frac{f \eta_2 \rho_2}{\pi \rho_0 C_{66}} \right)^{1/2}. \quad (16)$$

Formulae (14) and (15) form a set of equations. From these expressions it is possible to determine the η_M -component of the overlayer shear viscosity and the thickness (mass) of the adsorbed layer, and compare them with the results of surface viscosity measurements. Also, it is possible to determine the viscosity and density of the adjacent bulk liquid if the parameters of the overlayer are known.

It is essential to note that our model is valid for an arbitrary ratio ϵ between the viscosities η_2 and η_1 , i.e. even for $\epsilon \geq 1$. The latter possibility may be relevant for a thin amphiphilic substrate-adjacent film under a thick protein layer (for example, a sandwich structure, such as the one schematically shown in figure 3, can be realized by an adsorbed protein layer attached to the substrate via an amphiphilic self-assembling monolayer [22]).

4. Discussion

In addition to its importance in technological applications, the study of the hydrodynamic modes of fluid amphiphilic films and adsorbed proteins is generally important for understanding the dynamics of the swelling of lipid–water systems [28, 34, 35] and the rheology of biological membranes. It is known, for instance, that living cell membranes, e.g. in red blood cells, experience shear stress in hydrodynamic flow through capillaries [36, 37]. As the lipid bilayer matrix of the membrane is a two-dimensional incompressible liquid adjacent to an elastic protein (spectrin–actin) network, the hydrodynamics of this layered structure is governed by the coupling of the fluid membrane to shear flows in an external bulk liquid [36, 37].

The surface viscosity of a fluid amphiphilic film is often considered to be a two-dimensional analogue of the bulk viscosity, and is defined as the coefficient of proportionality between the tangential force per unit length and the gradient of the flow velocity of the liquid. These averaged surface characteristics can be measured, e.g. by an interface shear rheometer at air–liquid interfaces [13, 25] or by using the oscillating barrier method in a LB trough [25]. In contrast to η_s , the ‘microscopic’ shear viscosity may be defined as a contribution of fluid disordered chains. The ‘microviscosity’ of the membrane core can be determined experimentally, e.g. by a probe technique, and describes the local viscosity near the probe [24]. This ‘microviscosity’ is often identified with the true membrane viscosity. However, this experimental technique could give rather different results, with a strong dependence on the probe material and on the interaction between the probe and its local surroundings [24]. Both of these viscosities may be changed after the deposition of an amphiphilic layer on the solid surface.

The results of our theory can be applied for direct acoustic measurements of surface densities and/or shear viscosities η_s and η_M for a thin amphiphilic film after transferring it onto the solid substrate and in both the liquid and gaseous experimental conditions. A possible strong coupling between the end groups of the lipid layer, LB film, or SAM, and the surface of the substrate [12–16] would improve the validity of our model; thus for the interfacial solid–fluid region, the no-slip assumption seems to be valid.

In our work we found the dispersion equation for surface shear acoustic waves with horizontal polarization, and solved it, as well as the wave equation, for shear bulk acoustic waves. The solution of these equations, together with energy balance, allows us to calculate the analytical expressions for the damping coefficients, phase velocities, dissipation factor, and resonant frequency shifts of both types of shear wave as functions of the lipid film surface density and two different components of its in-plane viscosity. These acoustic waves can be excited by means of two different types of piezoelectric oscillator [23, 29].

We suggest measuring the acoustical response of the above-mentioned sandwich system in the region of lipid phase transition, where the viscosity of the overlayer is subject to dramatic changes. For instance, during the liquid-crystal–gel transformation of a lipid membrane, the viscosity of the bilayer changes by more than a factor of ten, while the membrane density remains practically constant [17, 24]. It is an interesting experimental fact [34] that the two halves of a bilayer lipid membrane are so weakly coupled that they can undergo the thermotropic phase transition independently. In accordance with our results, this must provide the changes in the SSW damping coefficient, while the corresponding SSW phase velocity shift due to the presence of the bilayer will be constant.

On a more speculative note, our results may also be valid within the segregated (sublayer) structure model of adsorbed protein layers (figure 3). In accordance with this model (see, e.g., [21, 22]), the structure of the protein overlayer resembles a surfactant film composed of segregated head-and-tail regions. Recent neutron scattering experiments [22] have provided evidence for such an anisotropic sublayer structure of protein monolayers adsorbed onto solid surfaces through the self-assembling amphiphilic sublayer. In this case, the relation between the upper and lower layer viscosities may vary strongly with the phase state of the protein and the amphiphilic monolayer, respectively.

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