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Scattering of Light on Surfactant-Laden Liquid-Liquid Crystal Interface

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The spectrum of surface quasi-elastic light scattering (SQELS) on a surfactant-laden interface between nematic liquid crystal and isotropic fluid is calculated for the case when the surfactant film induces homeotropic anchoring of the nematic director. The result can be used for determination of the surface tension, compressional modulus, and a combination of the surface viscosity coefficients from the experimental SQELS data.

Keywords Nematic-isotropic interface; SQELS; Surface waves; Surfactant; Thermal fluctuations

Introduction

Currently, there is a growing interest in the study of surfactant films adsorbed at interfaces between nematic and isotropic fluids. Surfactant-laden liquid-liquid crystal interfaces demonstrate interesting phase behavior (Price and Schwartz, 2007; Gupta et al., 2008), anchoring (Brake and Abbott, 2002; Brake et al., 2003; Lockwood et al., 2005; Kadivar et al., 2007), and wetting (Bahr, 2006) properties. Surfactants play an important role in the formation and stability of liquid-crystal emulsions (Kim et al., 1998; Park and Lee, 1999; Yamamoto and Tanaka, 2001; Caggioni et al., 2005). Nematic-surfactant-isotropic interfaces are also promising candidates for use in biosensing due to the possibility of synthesizing surfactant molecules able to specifically bind to biomolecules such as proteins (Clare and Abbott, 2005; Lockwood and Abbott, 2005) or DNA (Xu et al., 2005). In view of potential applications, it is important to develop techniques that allow accurate determination of the properties of such systems.

A powerful noninvasive experimental technique for studying viscoelastic properties of fluid-fluid interfaces is surface quasi-elastic light scattering (SQELS) (Langevin, 1992). It relies on the fact that the free surface of a liquid is not perfectly planar because of thermal fluctuations. The temporal evolution of surface waves is governed by surface tension and the viscoelastic properties of the liquid surface and bulk liquid (Kramer, 1971; Kats and Lebedev, 1988; Earnshaw, 1996; Buzza, 2002). The analysis of the data obtained in SQELS experiments provides information on the values of the surface tension and bulk and surface viscoelastic

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coefficients of surfactant films on fluid interfaces (Milling et al., 2001; Cicuta and Hopkinson, 2004; Rojas et al., 2005; Kim et al., 2006).

The theoretical description of surface waves at interfaces between nematic and isotropic liquids was first given by Langevin and Bouchiat (1972b) and successfully applied to investigate the properties of nematic-isotropic interfaces by surface light scattering (Langevin, 1972, 1975; Langevin and Bouchiat, 1972a, 1973; McQueen, 1973; McQueen and Singhal, 1974; Shih et al., 1983). Since then, several advances have been made in the study of capillary waves at nematic-isotropic interfaces (Parsons and Hayes, 1974; Hayes, 1975; Popa-Nita and Sluckin, 2002; Popa-Nita and Oswald, 2003; Popa-Nita et al., 2005; Elgeti and Schmid, 2005) that elucidate the role of the anisotropic structure of liquid crystal for the spectrum of surface waves.

The present article is devoted to the study of the power spectrum of light scattered from the surfactant film between nematic and isotropic fluids. The surfactant film at the nematic-isotropic interface reduces surface tension (Kim et al., 2004) and induces anchoring of the nematic liquid (Brake and Abbott, 2002; Brake et al., 2003; Lockwood et al., 2005; Kadivar et al., 2007). The presence of the adjacent nematic phase results in the anisotropy of the surface viscoelastic coefficients (Rey, 2000). An additional effect of the surfactant is related to the nonzero curvature energy of the interface (Helfrich, 1973; Rey, 2006a).

The influence of the above effects upon the surface waves at a surfactant-laden nematic-isotropic interface was investigated before (Lishchuk, 2007) for the case when the surfactant film is in the isotropic fluid state and induces homeotropic anchoring of the nematic director. This case corresponds to a wide range of experimental conditions and is especially simple to investigate theoretically due to the symmetry of the problem. It was shown that there are four surface modes, which correspond to capillary, compression, in-plane shear, and director relaxation modes.

In the present study the model developed in the previous work (Lishchuk, 2007) is used to derive the power spectrum of surface light scattering. We shall see that in the range of wave vector and frequencies used in SQELS experiments the expression for power spectrum can be considerably simplified. As a result, it depends upon only three material parameters of the interface (assuming the bulk properties of the fluids known): the interfacial tension, compressional modulus, and sum of interfacial shear and dilatational viscosities. The fitting of the model predictions to the experimental SQELS power spectra should make it possible to determine these quantities for surfactant-laden nematic interfaces.

The article is organized as follows. The general expression of the SQELS power spectrum in terms of the force-displacement linear response function is given next. Then there is a summary of the model of the surfactant-laden nematic interface used in the present article. The explicit expression for the force-displacement linear response function is derived in the following section and used to investigate the dependence of the SQELS power spectrum upon material parameters of the interface.

Surface Light Scattering

A detailed overview of the surface light scattering technique is given in a book by Langevin (1992). In a typical SQELS experiment the incident laser beam of wavelength λ is sent to the fluid surface at the angle θ_0 with the surface normal. Due to thermal fluctuations, the surface of the fluid is not perfectly planar, and surface waves of different wavelengths are excited. As a result, part of the beam is scattered in directions different from specular reflection. The intensity of the scattered light is measured as a function of the deviation $\delta\theta$ of the angle from the specular reflection.

Let unperturbed fluid surface lie in the X-Y plane. The measured intensity of a scattered light is proportional to the power spectrum $\langle|u_z(q,\omega)|^2\rangle$ of the surface vertical displacement $u_z(q,\omega)$ (i.e., amplitude of the surface waves in the Z direction normal to the surface). Here angular brackets denote thermal average, ω is the frequency of a surface wave, and q is the wavenumber, which in the limit of small scattering angles is related to $\delta\theta$ by

$$q = \frac{2\pi\cos\theta_0}{\lambda}\delta\theta \tag{1}$$

Typical values of q investigated in SQELS experiment lie in the interval 100–$2000\,\mathrm{cm}^{-1}$.

In the linear response regime the surface displacement $\mathrm{u}(q,\omega)$ can be cast as

$$u_i(q,\omega) = \chi_{ij}(q,\omega)F_j^{\mathrm{ext}}(q,\omega) \tag{2}$$

where $\mathrm{F}^{\mathrm{ext}}(q,\omega)$ is the external force (per unit area) applied to the interface, and $\chi_{ij}(q,\omega)$ is the force-displacement linear response function. The power spectrum $\langle|u_z(q,\omega)|^2\rangle$ can be found using the fluctuation-dissipation theorem, which in the classical form reads

$$\langle|u_z(q,\omega)|^2\rangle = -\frac{2k_BT}{\omega}\chi''_{zz}(q,\omega) \tag{3}$$

Here double prime denotes the imaginary part.

In this study we shall derive the explicit expression for $\chi_{ij}(q,\omega)$ for the surfactant-laden interface between the nematic liquid crystal and the isotropic fluid, using a model equivalent to one used in the previous work (Lishchuk, 2007) and summarized in the following section.

Model

In this section we summarize the macroscopic model of the surfactant-laden interface between an isotropic liquid and a nematic liquid crystal (Lishchuk, 2007) used in the present article and present the governing equations.

We assume that the temperature of the system and surface concentration of a surfactant are within the range in which the surfactant film is in the most symmetric phase (isotropic two-dimensional fluid). We also assume that the system is far from any phase transitions both in the surfactant film and in the bulk nematic phase. The surfactant layer is assumed to be insoluble in both bulk fluids, Newtonian, and macroscopically infinitely thin. We also assume heat diffusion to be sufficiently fast so that the system is in thermal equilibrium.

The surface dynamics of the compressible surfactant-laden interface between nematic and isotropic fluids is described using the theory of a compressible interface between nematic liquid crystals and isotropic viscous fluids (Rey, 2000) and the model for curved surfactant-laden liquid-liquid crystal interfaces (Rey, 2006a). Both bulk fluids (isotropic and nematic) are assumed incompressible. The orientational order in the nematic liquid crystal is described by the unit director vector $\mathbf{n}$, and the dynamics is described in terms of linearized Eriksen-Leslie theory (De Gennes and Prost, 1993; Landau and Lifshitz, 1986).

In order to determine the linear response function χ_{ij} using Equation (2), we write the interfacial force balance equation in the form

$$\mathbf{F}^S + \mathbf{F}^N + \mathbf{F}^I + \mathbf{F}^{\text{ext}} = 0 \tag{4}$$

where $\mathbf{F}^S = \nabla_s \cdot \Sigma^S$ is the force per unit area exerted by the interfacial stress Σ^S, $\mathbf{F}^I = \Sigma^I|_s \cdot \mathbf{k}$ is the force per unit area exerted by the isotropic fluid, $\mathbf{F}^N = \Sigma^N|_s \cdot \mathbf{k}$ is the force per unit area exerted by the nematic liquid crystal, $\mathbf{k}$ is the unit vector normal to the interface and directed into the isotropic fluid, and the subscript s indicates that the bulk stress fields in the isotropic fluid, Σ^I, and in the nematic, Σ^N, are evaluated at the interface. We also need the interfacial torque balance equation

$$\mathbf{T}^S + \mathbf{T}^N = 0 \tag{5}$$

where $\mathbf{T}^S$ is the interfacial torque arising due to surface interactions, and $\mathbf{T}^N$ is the torque exerted upon the interface by the adjacent nematic liquid crystal.

The surface stress tensor $\boldsymbol{\Sigma}^S$ is represented as a sum of corresponding nondissipative (elastic) contribution $\boldsymbol{\Sigma}^{Se}$ and dissipative (viscous) contribution Σ^{Sv}:

$$\boldsymbol{\Sigma}^S = \boldsymbol{\Sigma}^{Se} + \boldsymbol{\Sigma}^{Sv} \tag{6}$$

We describe the elastic surface stress tensor using the expression proposed by Rey (2006a) for the surfactant-laden nematic-isotropic interfaces:

$$\Sigma^{Se} = \sigma \mathbf{I}_s + \mathbf{h}_{\|}^{Se}\mathbf{k} - \mathbf{M} \cdot \mathbf{b} \tag{7}$$

Here

$$\sigma = \left[-\left(\rho^S\right)^2 \frac{\partial \mathcal{F}^S}{\partial \rho^S} \right]_{\mathbf{k},\mathbf{b}} \tag{8}$$

is the interfacial tension,

$$\mathbf{h}_{\|}^{Se} = -\left(\rho^S \mathbf{I}_s \cdot \frac{\partial \mathcal{F}^S}{\partial \mathbf{k}} \right)_{\rho^S,\mathbf{b}} - \mathbf{I}_s \cdot (\nabla_s \cdot \mathbf{M}) \tag{9}$$

is the tangential surface molecular field,

$$\mathbf{M} = \left(\rho^S \frac{\partial \mathcal{F}^S}{\partial \mathbf{b}} \right)_{\rho^S,\mathbf{k}} \tag{10}$$

is the bending moment tensor, $\mathcal{F}^S$ is the Helmholtz free energy of the interface per unit mass, ρ^S is the surface mass density, $\mathbf{I}_s = \mathbf{I} - \mathbf{kk}$ is the surface projector ($\mathbf{I}$ is the unit tensor), $\nabla_s = \mathbf{I}_s \cdot \nabla$ is the surface gradient operator, and $\mathbf{b} = -\nabla_s \mathbf{k}$ is the second fundamental tensor of the interface.

We describe the viscous surface stress tensor using the expression proposed by Rey (2000) for the nematic-isotropic interfaces:

$$\begin{aligned} \Sigma^{Sv} = {} & \alpha_1^s \mathbf{S}^S : \mathbf{n}_{\|}\mathbf{n}_{\|}\mathbf{n}_{\|}\mathbf{n}_{\|} + \alpha_2^s \mathbf{n}_{\|}\mathbf{N}^S + \alpha_3^s \mathbf{N}^S \mathbf{n}_{\|} + \alpha_4^s \mathbf{S}^S \\ & + \alpha_5^s \mathbf{n}_{\|}\mathbf{n}_{\|} \cdot \mathbf{S}^S + \alpha_6^s \mathbf{S}^S \cdot \mathbf{n}_{\|}\mathbf{n}_{\|} + \alpha_7^s \mathbf{n}_{\|}\mathbf{n}_{\|}\left(\mathbf{n}_{\|} \cdot \mathbf{N}^S\right) \\ & + \beta_1^s \mathbf{I}_s\left(\mathbf{I}_s : \mathbf{S}^S\right) + \beta_2^s \left[\mathbf{n}_{\|}\mathbf{n}_{\|}\left(\mathbf{I}_s : \mathbf{S}^S\right) + \mathbf{I}_s\left(\mathbf{n}_{\|}\mathbf{n}_{\|} : \mathbf{S}^S\right)\right] \end{aligned} \tag{11}$$

where $\mathbf{S}^S = \frac{1}{2}[\nabla_s \mathbf{I}_s \cdot \mathbf{v}^S + \mathbf{I}_s \cdot (\nabla_s \mathbf{v}^S)^{\mathrm{T}}]$ is the surface rate-of-deformation tensor ($(\cdots)^{\mathrm{T}}$ denotes the transposed tensor), is the surface vorticity tensor, $\mathbf{v}^S$ is surface velocity, $\mathbf{n}_{\|} = \mathbf{I}_s \cdot \mathbf{n}$ is the component of the nematic director $\mathbf{n}$ tangential to the surface,

$$\mathbf{N}^S = \mathbf{I}_s \cdot \frac{d\mathbf{n}_{\|}}{dt} + \mathbf{A}^S \cdot \mathbf{n}_{\|} \tag{12}$$

is its surface Jaumann (corrotational) derivative, $\mathbf{A}^S = \frac{1}{2}[\nabla_s \mathbf{I}_s \cdot \mathbf{v}^S - \mathbf{I}_s \cdot (\nabla_s \mathbf{v}^S)^{\mathrm{T}}]$ and $\alpha^S_{1-7}, \beta^S_{1-2}$ are nine independent surface viscosity coefficients.

Generally, there are additional dissipative contributions to the stress tensor, related to bending and torsion (Rey, 2006b). It becomes small for small displacements of the interface from equilibrium (Gurkov and Kralchevsky, 1990), and therefore will be neglected in this study.

The surface torque vector $\mathbf{T}^S$ is also represented as a sum of corresponding nondissipative (elastic) contribution $\mathbf{T}^{Se}$ and dissipative (viscous) contribution $\mathbf{T}^{Sv}$:

$$\mathbf{T}^S = \mathbf{T}^{Se} + \mathbf{T}^{Sv} \tag{13}$$

The elastic contribution to surface torque is

$$\mathbf{T}^{Se} = -\boldsymbol{\epsilon} : \Sigma^{Se} + \nabla \cdot \mathbf{C}_s \tag{14}$$

where $\mathbf{C}_s = -\mathbf{M} \cdot \boldsymbol{\epsilon}_s$ is the surface couple stress, $\boldsymbol{\epsilon}$ is the Levi-Civita tensor, and $\boldsymbol{\epsilon}_s = -\mathbf{I}_s \times \mathbf{k}$ is the surface alternator tensor. The surface viscous torque is given by

$$\mathbf{T}^{Sv} = -\mathbf{n} \times \mathbf{h}^{Sv} \tag{15}$$

where the surface viscous molecular field $\mathbf{h}^{Sv}$ is

$$\begin{aligned}\mathbf{h}^{Sv} = {} & \left(\alpha^S_3 + \alpha^S_2\right)\left[\mathbf{S}^S \cdot \mathbf{n}_{\|} + \frac{1}{2}\left(\mathbf{I}_s : \mathbf{S}^S\right)\mathbf{n}_{\|}\right] \\ & + \left(\alpha^S_3 - \alpha^S_2\right)\mathbf{N}^S + \alpha^S_6 \mathbf{n}_{\|}\left(\mathbf{n}_{\|}\mathbf{n}_{\|} : \mathbf{S}^S\right) + \gamma^S_{1\perp}\mathbf{k}\mathbf{k} \cdot \frac{d\mathbf{n}_{\perp}}{dt}\end{aligned} \tag{16}$$

$\gamma^S_{1\perp}$ is the normal rotational viscosity.

The surface free energy $\mathcal{F}^S$, which enters Equations (8)–(10), depends upon the orientation and curvature of the interface. We expand the free energy in powers of small deviations of the unit normal vector $\mathbf{k}$ and on the second fundamental tensor $\mathbf{b}$ from equilibrium, and represent the truncated series as a sum of three contributions:

$$\mathcal{F}^S\left(\rho^S, \mathbf{k}, \mathbf{b}\right) = \mathcal{F}^s_t\left(\rho^S\right) + \mathcal{F}^s_a(\mathbf{k}) + \mathcal{F}^s_c(\mathbf{b}) \tag{17}$$

Explicitly, the surface tension contribution has the form

$$\rho^S \mathcal{F}^S_t = \bar{\sigma} \tag{18}$$

where $\bar{\sigma}$ is the surface tension of the unperturbed interface. The anchoring contribution can be written as

$$\rho^S \mathcal{F}^S_a = \frac{1}{2} W\left(\delta n^2_{\|} + \delta n^2_{\perp}\right) \tag{19}$$

where W determines the zenithal anchoring strength, $\delta n_{\|} = \left|\mathbf{n}_{\|} - \mathbf{n}_{0\|}\right|$ and $\delta n_{\perp} = \left|\mathbf{n}_{\perp} - \mathbf{n}_{0\perp}\right|$ are the deviations of the tangential ($\mathbf{n}_{\|} = \mathbf{I}_s \cdot \mathbf{n}$) and normal

($\mathbf{n}_\perp = \mathbf{n} - \mathbf{n}_\parallel$) components of the director from the corresponding equilibrium values $\mathbf{n}_{0\parallel}$ and $\mathbf{n}_{0\perp}$. The curvature contribution to the surface free energy density, $\mathcal{F}_c^S$, becomes negligible at wavenumbers q that satisfy the condition (Buzza, 2002; Lishchuk, 2007)

$$q \ll \sqrt{\sigma/\kappa} \tag{20}$$

The typical value of the bending rigidity κ for surfactant films is of the order 10^{-21} J (Marsh, 2006), so the inequality (20) is well satisfied for the wavenumbers used in typical surface light scattering experiments. For this reason, the curvature contribution $\mathcal{F}_c^S$ will be henceforth neglected, and the surface free energy density takes the form

$$\rho^S \mathcal{F}^S = \bar{\sigma} + \frac{1}{2} W\left(\delta n_\parallel^2 + \delta n_\perp^2\right) \tag{21}$$

The continuity equation for the insoluble surfactant reads

$$\frac{d\nu}{dt} + \nu \nabla_s \cdot \mathbf{v}^S = 0 \tag{22}$$

where ν is the surfactant concentration, $\mathbf{v}^S = d\mathbf{u}/dt$ is the surface velocity, and $\mathbf{u}$ is the surface displacement. For small deviation $\delta\nu = \nu - \nu_0$ of the surfactant concentration from its equilibrium value ν_0, the dependence of the parameters characterizing the interface (surface tension $\bar{\sigma}$, anchoring strength W, and surface viscosities α_i^S, β_i^S) upon ν can be cast, using Equation (22), in the following form (Buzza, 2002; Lishchuk, 2007):

$$\sigma(\nu) = \sigma_0 + \epsilon_0 \nabla_s \cdot \mathbf{u} \tag{23}$$

$$W(\nu) = W_0 + W_1 \nabla_s \cdot \mathbf{u} \tag{24}$$

In these formulas $\sigma_0 = \bar{\sigma}(\nu_0)$ and $W_0 = W(\nu_0)$ are, correspondingly, the interfacial tension and the anchoring strength of the unperturbed interface, $\epsilon_0 = -\nu_0 \partial\bar{\sigma}/\partial\nu$ is the static compressional modulus, and $W_1 = -\nu_0 \partial W/\partial\nu$ is the coefficient in the first-order term of the expansion of anchoring strength in powers of $(\nabla_s \cdot \mathbf{u})$. There are similar expansions for surface viscosities α_I^S, β_I^S.

Power Spectrum

In this section the model described above is used to derive the explicit form of the force balance equation (4).

We choose a coordinate system in such a way that the unperturbed interface lies at a plane $z = 0$, the half-space $z < 0$ is occupied by the nematic liquid crystal, and the half-space $z > 0$ is filled by the isotropic liquid. We shall consider a surface wave with frequency ω and wave vector $\mathbf{q} = (q, 0, 0)$ propagating along x axis, and write the force balance equation using a linearized form of the hydrodynamic equations. We consider the case where the nematic director is normal to the interface, and represent the equilibrium director in the form

$$\mathbf{n}_0 = (0, 0, 1) \tag{25}$$

In order to linearize the hydrodynamic equations, we write pressure $p = p(\mathbf{r}, t)$ and the nematic director $\mathbf{n} = \mathbf{n}(\mathbf{r}, t)$, where $\mathbf{r} = (x, y, z)$ is the position in space, t is time, in the form

$$p = p_0 + \delta p \tag{26}$$

$$\mathbf{n} = \mathbf{n}_0 + \delta\mathbf{n} \tag{27}$$

where δp and $\delta\mathbf{n}$ are the deviations of pressure and director from their equilibrium values p_0 and $\mathbf{n}_0$, correspondingly. For small deviations from the equilibrium, we shall use the hydrodynamic equations linearized in $\mathbf{v}$, δp, and $\delta\mathbf{n}$. We shall assume these quantities to be independent of the coordinate y ($\partial_y \equiv \partial/\partial y = 0$), and to vanish at $z \to \pm\infty$.

Substituting the interfacial free energy density (21) into Equations (8)–(10), we find the following expressions for the surface tension:

$$\sigma = \bar{\sigma} + \frac{W}{2}\delta n_{\|}^2 \tag{28}$$

tangential surface elastic molecular field:

$$\mathbf{h}_{\|}^{Se} = W\delta\mathbf{n}_{\|} \tag{29}$$

and bending moment tensor:

$$\mathbf{M} = 0 \tag{30}$$

The x and z components of the interfacial force $\mathbf{F}^S$ reduce, in linear approximation, to the following expressions:

$$F_x^S = \epsilon_0\partial_x^2 u_x + (\eta_s + \zeta_s)\,\partial_x^2 v_x^S \tag{31}$$

$$F_z^S = \sigma_0\partial_x^2 u_z + W_0\partial_x\,(\delta n_x + \partial_x u_z) \tag{32}$$

Here

$$\eta_s = \frac{\alpha_4^S}{2} \tag{33}$$

is interfacial shear viscosity, and

$$\zeta_s = \frac{\alpha_4^S}{2} + \beta_1^S \tag{34}$$

is dilatational viscosity.

The x component of the surface torque balance equation can be written as

$$\left(W_0 + \gamma_{1\|}^S\frac{\partial}{\partial t}\right)(\delta n_x + \partial_x u_z) = K_3\partial_z\delta n_x^S \tag{35}$$

The right-hand side of this equation can be neglected if $s \equiv K_3 q/W_0 \ll 1$. Substituting typical values $K_3 \sim 10^{-12}$ N, $W_0 \sim 10^{-2}$ J/m^2, and $q \sim 10^4$ m^{-1}, we obtain $s \sim 10^{-6}$. The smallness of this value allows us to write $\delta n_x + \partial_x u_z = 0$ and use it to write Equation (32) as

$$F_z^S = \sigma_0\partial_x^2 u_z \tag{36}$$

As a result, there is no dependence upon the anchoring strength, and the interfacial force (Equations (31) and (35)) has the same form as in the case of isotropic fluids.

To write the explicit form of the force balance equation (4), we need to add forces $\mathbf{F}^N$ and $\mathbf{F}^I$, exerted upon the interface by adjacent nematic and isotropic fluids. These are derived in Appendix A. Introducing Fourier transforms in the x coordinate and in time as

$$\mathbf{v}(\mathbf{r}, t) = \frac{1}{2\pi^2} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} d\omega e^{i\omega t - iqx} \tilde{\mathbf{v}}\,(q, z, \omega) \tag{37}$$

$$\delta p(\mathbf{r}, t) = \frac{1}{2\pi^2} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} d\omega e^{i\omega t - iqx} \tilde{p}\,(q, z, \omega) \tag{38}$$

and performing Fourier transform of the force balance equation, we obtain balance equations for the force components in the form

$$\begin{aligned} \tilde{F}_x^{\text{ext}} &= \epsilon_0^* q^2 \tilde{u}_x^S + \eta(m^I + q)\tilde{v}_x^S - i\eta(m^I - q)\tilde{v}_z^S \\ &\quad - \frac{i\nu_3}{q} \sum_{i=1}^{2} \left[(m_i^N)^2 + q^2 \right] C_i^N \end{aligned} \tag{39}$$

$$\begin{aligned} \tilde{F}_z^{\text{ext}} &= \sigma_0 q^2 \tilde{\nu}_z^S - -2i\eta q \tilde{\nu}_x^S + \frac{i\omega\rho^I}{q} \frac{iq\tilde{u}_x^S + m^1 \tilde{u}_z^S}{m^1 - q} \\ &\quad - \sum_{i=1}^{2} \left(A_i - 2\nu_1 m_i^N \right) C_i^N \end{aligned} \tag{40}$$

where

$$\epsilon_0^* = \epsilon_0 + i\omega\,(\eta_s + \zeta_s) \tag{41}$$

is the complex compressional modulus, and the quantities m^I, m_i^N, C_i^N, and A_i are defined in Appendix A. Note that in the considered case of homeotropic anchoring the x and z components of the force balance equations are decoupled from the y component.

In fact, Equations (38)—(40) constitute the inverse of Equation (2):

$$\tilde{F}_i^{\text{ext}} = (\chi^{-1})_{ij\tilde{u}_j} \tag{42}$$

where $\tilde{\mathbf{u}}_i = \tilde{\mathbf{v}}_i / i\omega$, and the elements of the inverse linear response matrix are:

$$\begin{aligned} (\chi^{-1})_{xx} &= \epsilon_0^* q^2 + i\eta\omega(m^I + q) + i\nu_3\omega\,(m_1^N + m_2^N) \\ (\chi^{-1})_{xz} &= -(\chi^{-1})_{zx} = \eta\omega(m^I - q) - \nu_3\omega\left(\frac{m_1^N m_2^N}{q} - q\right) \\ (\chi^{-1})_{zz} &= \sigma_0 q^2 + i\eta\omega \frac{m^I(m^I + q)}{q} + i\nu_3\omega \frac{m_1^N m_2^N \left(m_1^N + m_2^N\right)}{q^2} \end{aligned} \tag{43}$$

To calculate the power spectrum of the vertical displacement of the interface given by Equation (3), we need the component $\chi_{zz}(q, \omega)$ of the force-displacement linear response function, which is given in terms of $(\chi^{-1})_{ij}$ by

$$\chi_{zz}(q,\omega) = \frac{(\chi^{-1})_{xx}}{(\chi^{-1})_{xx}(\chi^{-1})_{zz} - (\chi^{-1})_{xz}(\chi^{-1})_{zx}} \tag{44}$$

Equation (3) together with Equations (43) and (44) can be directly used to calculate the power spectrum of the vertical displacement of the interface $\left\langle |u_z(q,\omega)|^2 \right\rangle$. The fitting of the experimental spectrum by Equation (3) should allow determination of three surface viscoelastic parameters: the surface tension (σ_0), compressional modulus (ϵ_0), and a sum of surface shear and dilatational viscosities ($\eta_s + \zeta_s$), provided densities and viscosities of bulk isotropic liquid and nematic liquid crystal are known.

We shall demonstrate the behavior of the spectrum by calculating it numerically using typical values of the material parameters. For the nematic liquid crystal we use the following parameters of *p*-azoxyanisole (PAA) at 122°C: the density $\rho^N = 1168\,\mathrm{kg}/m^3$ (Hoyer and Nolle, 1956) and the viscosities $\nu_1 = 3.2 \times 10^{-3}\,\mathrm{kg}/(\mathrm{m}\cdot\mathrm{s})$, $\nu_2 = 3.4 \times 10^{-3}\,\mathrm{kg}(\mathrm{m}\cdot\mathrm{s})$, and $\nu_3 = 2.4 \times 10^{-3}\,\mathrm{kg}/(\mathrm{m}\cdot\mathrm{s})$ (Kemp and Letcher, 1971). We assume the density ρ^I of the isotropic fluid to be negligible, which is true for the nematic-air interfaces. We adopt the value of the surface tension of PAA measured without surfactant film $\sigma_0 = 0.050\,\mathrm{Nm}$ (McQueen and Singhal, 1974). For surface viscoelastic coefficients we use the following typical values: $\epsilon_0 = 10^{-2}$ N/m, $\eta_s = \zeta_s = 10^{-7}\,\mathrm{kg/s}$.

The power spectrum of surface vertical displacement calculated with these parameters for the typical wavenumber $q = 400\,\mathrm{cm}^{-1}$ is shown in Figure 1. Figure 2 presents the q-dependence of the maximum position ($\omega_{\max}$) and half-width ($\Gamma_{1/2}$) of the peak, normalized by the quantity

$$\omega_c = \sqrt{\frac{\sigma_0 q^3}{\rho^N}} \tag{45}$$

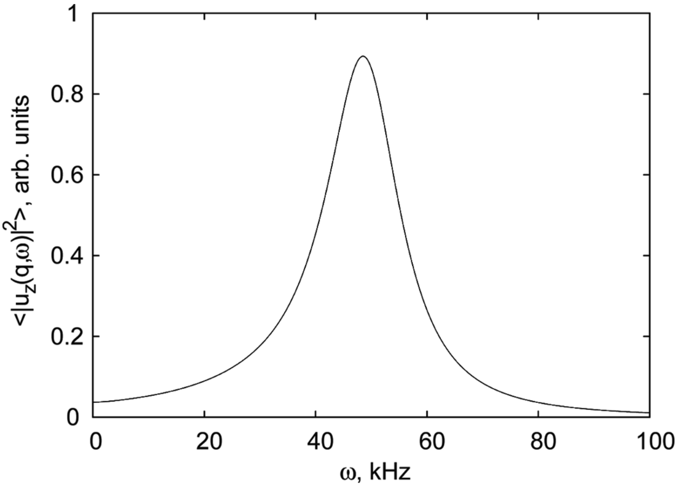

Figure 1. Power spectrum of vertical displacement of surfactant-laden nematic interface for $q = 400\,\mathrm{cm}^{-1}$, calculated with the help of Equations (3), (44), and (43). Material parameters are given in the text.

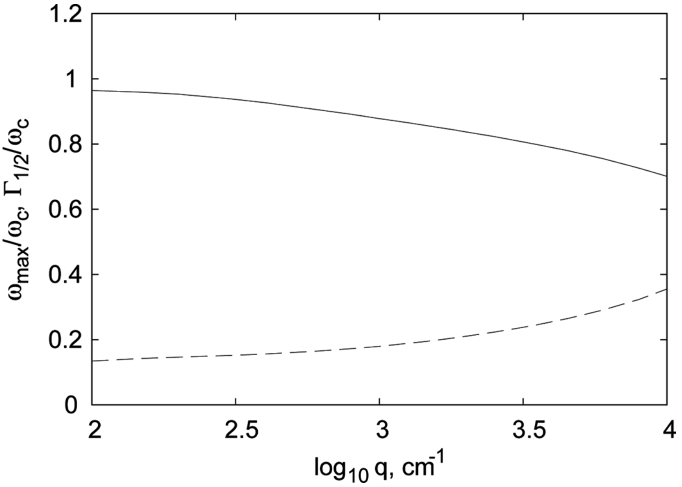

Figure 2. Dependence of maximum position $\omega_{\max}$ (solid line) and half-width $\Gamma_{1/2}$ (dashed line) of the peak in the power spectrum of surface vertical displacement upon wavenumber q. The quantity ω_c is defined by Equation (45).

which corresponds to the frequency of the capillary mode in the absence of dissipation. Qualitatively, the behavior of the spectrum is similar to the simpler case of isotropic fluids (Langevin, 1992). However, quantitative details of the spectrum depend upon the surface tension and viscosities of the interface, as demonstrated in Figure 3. This should allow determination of the surface tension, compressional modulus, and a sum of the isotropic surface viscosity coefficients by fitting experimental SQELS data by Equations (3), (43), and (44).

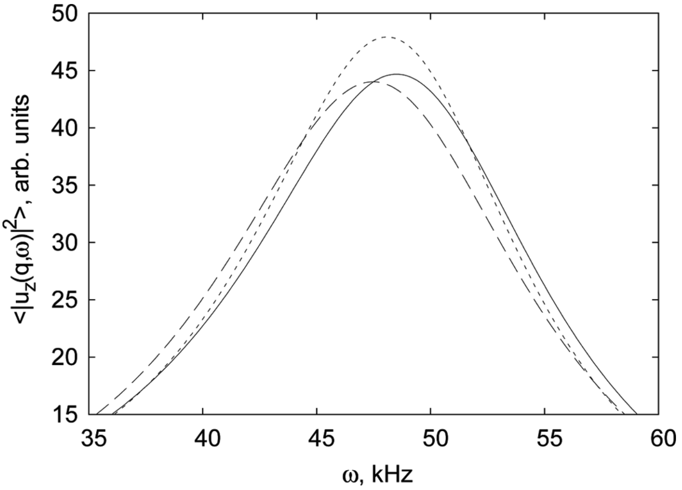

Figure 3. Dependence of the power spectrum of vertical displacement for $q = 400\,\mathrm{cm}^{-1}$ upon material parameters of the interface. Solid line corresponds to the values of parameters given in the text, in particular $\epsilon_0 = 10^{-2}\,\mathrm{N/m}$, $\eta_s = \zeta_s = 10^{-7}\,\mathrm{kg/s}$. Dashed line corresponds to $\epsilon_0 = 2 \times 10^{-2}\,\mathrm{N/m}$, dotted line corresponds to $\eta_s = \zeta_s = 2 \times 10^{-7}\,\mathrm{kg/s}$.

Conclusion

We have derived the expressions for the spectrum of surface quasi-elastic light scattering on a surfactant-laden interface between nematic liquid crystal and isotropic fluid for the case when the surfactant film is in the fluid state and induces homeotropic anchoring of the nematic director. The symmetry of this case allows considerable simplification of the resulting equations. The spectrum depends only upon three material parameters of the interface: surface tension coefficient, compressional modulus, and a sum of surface shear and dilatational viscosity coefficients. The obtained formulas can be used for determination of these quantities by fitting the experimental SQELS data.

The case described in the present study is accessible in wide range of the system states and may provide a fruitful route to experimental determination of some of the properties of the surfactant-laden interface between nematic liquid crystal and isotropic fluid. The generalization of the result to the case of tilted anchoring is straightforward. However, the expression for power spectrum becomes much more complicated and is dependent upon the larger set of parameters describing the interface. For example, even in the case in which the equilibrium nematic director lies in a plane perpendicular to the direction of wave propagation, the resulting formulas involve three independent combinations of anisotropic surface viscosities (see Appendix B). The situation becomes even more complicated if the surfactant film itself is in one of its anisotropic phases or in the vicinity of the phase transition. The procedure of fitting the experimental spectrum by formulas with a larger number of parameters is of limited use due to uncertainties in experimental spectra. This may be remedied by further developments of the experimental techniques for investigation of surface waves.

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Appendix A. Hydrodynamic Fields in Bulk Fluids

In this appendix the solutions to linearized hydrodynamic equations in bulk isotropic and nematic fluids are summarized. The perturbations to equilibrium dynamic fields are assumed to vanish at $z \to \pm\infty$. The non-slip boundary condition is assumed for the velocities of bulk fluids adjacent to the interface, which means the equality of the velocity of surfactant, $\mathbf{v}^S$, and that of the bulk fluids at an interface, $\mathbf{v}|_s$:

$$\mathbf{v}^S = \mathbf{v}|_s \tag{46}$$

Isotropic Liquid

The linearized equations for the incompressible isotropic liquid are well known (Landau and Lifshitz, 1987). They are the continuity equation

$$\nabla \cdot \mathbf{v} = 0 \tag{47}$$

and Navier-Stokes equations

$$\rho^I \frac{\partial \mathbf{v}}{\partial t} = \nabla \cdot \boldsymbol{\Sigma}^I \tag{48}$$

where $\boldsymbol{\Sigma}^I = -p\mathbf{I} + 2\eta\mathbf{S}$ is the hydrodynamic stress tensor, η is the shear viscosity of the isotropic liquid, $\mathbf{I}$ is the isotropic tensor, and $\mathbf{S} = \frac{1}{2}[\nabla\mathbf{v} + (\nabla\mathbf{v})^{\mathrm{T}}]$ is the strain rate tensor.

The general solution to the linearized form of these equations vanishing at $z \to \infty$ can be written as (Kramer, 1971)

$$\tilde{v}_x = iC_1^I e^{-qz} + i\frac{m^I}{q} C_2^I e^{-m^I z} \tag{49}$$

$$\tilde{v}_z = C_1^I e^{-qz} + C_2^I e^{-m^I z} \tag{50}$$

$$\tilde{p} = \frac{i\omega\rho^I}{q} C_1^I e^{-qz} \tag{51}$$

with

$$m^I = \left(q^2 + \frac{i\omega\rho^I}{\eta}\right)^{1/2}, \qquad \mathrm{Re}\, m^I > 0 \tag{52}$$

The quantities C_1^I and C_2^I are functions of q and ω and are determined by the boundary conditions at the interface as follows:

$$C_1^I = \frac{iq\tilde{v}_x^S + m^I \tilde{v}_z^S}{m^I - q}, \qquad C_2^I = -\frac{iq\tilde{v}_x^S + q\tilde{v}_z^S}{m^I - q} \tag{53}$$

To write the explicit form of the force balance equations, we need the following expressions for the components of the force $\mathbf{F}^I$ exerted by the isotropic liquid:

$$\tilde{F}_x^I = \eta(\partial_z \tilde{v}_x - iq\tilde{v}_z)_{z=+0} \tag{54}$$

$$\tilde{F}_z^I = (2\eta\partial_z \tilde{v}_z - \tilde{p})_{z=+0} \tag{55}$$

Nematic Liquid Crystal

To describe the dynamics of the nematic liquid crystal we shall use the linearized form of the Eriksen-Leslie theory (De Gennes and Prost, 1993; Forster et al., 1971). The hydrodynamic fields in the incompressible uniaxial nematic liquid crystal are velocity $\mathbf{v}(\mathbf{r}, t)$, pressure $p(\mathbf{r}, t)$, and director $\mathbf{n}(\mathbf{r}, t)$. They satisfy the continuity equation, the equation for the acceleration, and the equation for the rate of change of the director.

The continuity equation has the same form as for isotropic liquid and is given by Equation (47).

The equation for the acceleration has the form

$$\rho^N \frac{\partial \mathbf{v}}{\partial t} = \nabla \cdot \mathbf{\Sigma}^N \tag{56}$$

where the stress tensor can be represented as a sum of reactive and viscous dissipative contributions,

$$\mathbf{\Sigma}^N = \mathbf{\Sigma}^{Nr} + \mathbf{\Sigma}^{Nv} \tag{57}$$

The linearized form of the reactive contribution is given by

$$\mathbf{\Sigma}^{Nr} = -p\mathbf{I} + \frac{1}{2}(\mathbf{n}_0\mathbf{h} - \mathbf{h}\mathbf{n}_0) - \frac{\lambda}{2}(\mathbf{n}_0\mathbf{h} + \mathbf{h}\mathbf{n}_0) \tag{58}$$

where **h** is the molecular field, and λ is the reactive material parameter. The linearized form of the viscous contribution is given by

$$\begin{aligned}\mathbf{\Sigma}^{Nv} &= 2\nu_2\mathbf{S} + 2(\nu_3 - \nu_2)(\mathbf{n}_0\mathbf{S}\cdot\mathbf{n}_0 + \mathbf{n}_0\cdot\mathbf{S}\mathbf{n}_0) \\ &\quad + 2(\nu_1 + \nu_2 - 2\nu_3)\mathbf{n}_0\mathbf{n}_0\mathbf{n}_0\mathbf{n}_0 : \mathbf{S}\end{aligned} \tag{59}$$

where ν_1, ν_2, and ν_3 are nematic viscosities.

Let us compare the magnitude of contributions from the molecular field in Equation (58) to viscous contributions in Equation (59). The molecular field is by an order of magnitude $\mathbf{h} \sim Kq^3v/\omega$, K being the order of magnitude of the elastic constants of a nematic. Since $\lambda \sim 1$, the corresponding contribution into $\mathbf{\Sigma}^{Nr}$ is of the same order. Taking its ratio to the viscous contributions, which have the order νvq (ν being the order of the nematic viscosity coefficients), we obtain the relative magnitude of the molecular field contribution being $r \sim Kq^2/\nu\omega$. Substituting typical values $K \sim 10^{-12}\,\mathrm{N}$, $\nu \sim 10^{-2}\,\mathrm{kg/(m\cdot s)}$, $q \sim 10^4\,\mathrm{m}^{-1}$, and $\omega \sim 10^4\,\mathrm{s}^{-1}$, we obtain $r \sim 10^{-2}$. The smallness of this value allows us to neglect the molecular field in Equation (58) and write

$$\mathbf{\Sigma}^{Nr} = -p\mathbf{I} \tag{60}$$

Finally, the equation for the director becomes not necessary for our purposes because Equations (47) and (56) form a closed system with respect to pressure and velocity fields.

Fourier-transforming the linearized form of Equations (47) and (56), we obtain

$$-iq\tilde{v}_x + \partial_z\tilde{v}_z = 0 \tag{61}$$

$$[i\omega\rho^N + (2\nu_2 - \nu_3)q^2 - \nu_3\partial_z^2]\,\tilde{v}_x = iq\tilde{p} \tag{62}$$

$$[i\omega\rho^N - \nu_3q^2 + (2\nu_1 - \nu_3)\partial_z^2]\,\tilde{v}_z = -\partial_z\tilde{p} \tag{63}$$

The general solution to these equations vanishing at $z \to -\infty$ can be cast as

$$\tilde{v}_x = -\frac{i}{q}\sum_{i=1}^{2} m_i^N C_i^N e^{m_i^N z} \tag{64}$$

$$\tilde{v}_z = \sum_{i=1}^{2} C_i^N e^{m_i^N z} \tag{65}$$

$$\tilde{p} = \sum_{i=1}^{2} A_i C_i^N e^{m_i^N z} \tag{66}$$

where

$$C_1^N = -\frac{iq\tilde{v}_x^S - m_2^N \tilde{v}_z^S}{m_2^N - m_1^N}, \qquad C_2^N = \frac{iq\tilde{v}_x^S - m_1^N \tilde{v}_z^S}{m_2^N - m_1^N}, \tag{67}$$

$$A_i = -\frac{i\omega\rho^N + \nu_3 q^2 - (2\nu_1 - \nu_3)(m_i^N)^2}{m_i^N} \tag{68}$$

and m_i^N, $i = 1$, 2 are given by formulas

$$m_i^N = (\mu_i)^{1/2}, \quad \mathrm{Re}\, m_i^N > 0 \tag{69}$$

where

$$\mu_i = \frac{i\omega\rho^N + 2(\nu_1 + \nu_2 - \nu_3)q^2 \pm \sqrt{D}}{2\nu_3} \tag{70}$$

$$D = -\omega^2(\rho^N)^2 + 4(\nu_1 + \nu_2 - 2\nu_3)q^2\,[i\omega\rho^N + (\nu_1 + \nu_2)q^2] \tag{71}$$

To write the explicit form of the force balance equations, we need the following expressions for the components of the force $\mathbf{F}^N$ exerted by the nematic liquid crystal:

$$\tilde{F}_x^N = \nu_3(iq\tilde{v}_z - \partial_z\tilde{v}_x)_z = -0 \tag{72}$$

$$\tilde{F}_z^N = (\tilde{p} - 2\nu_1\partial_z\tilde{v}_z)_z = -0 \tag{73}$$

Appendix B. Tilted Anchoring

This appendix presents, without derivation, the explicit expressions for the inverse susceptibility matrix $(\chi^{-1})_{ij}$ for the case of tilted nematic anchoring. We consider the geometry in which the nematic director lies in a plane normal to the direction of propagation of the surface wave and represent the equilibrium director in the form

$$\mathbf{n}_0 = (0, n_{0y}, n_{0z}) \tag{74}$$

Here $n_{0y} = \sin\vartheta_0$, $n_{0z} = \cos\vartheta_0$, where ϑ_0 is the angle between the director and the interface in equilibrium. The value $\vartheta = \pi/2$ corresponds to the homeotropic anchoring (Equation (25)). The SQELS power spectrum can be obtained by inverting matrix $(\chi^{-1})_{ij}$, given below, and substituting the element χ_{zz} into Equation (3).

The elements of the inverse susceptibility matrix are the following:

$$(\chi^{-1})_{xx} = \epsilon_0^* q^2 + i\omega\eta(m^I - q) + \frac{\omega}{q}\nu_3\sum_{i=1}^{3}[(m_i^N)^2 + q^2]L_i^{(x)} \tag{75}$$

$$(\chi^{-1})_{xy} = \frac{\omega}{q}\nu_3\sum_{i=1}^{3}[(m_i^N)^2 + q^2]L_i^{(y)} \tag{76}$$

$$(\chi^{-1})_{xz} = \omega\eta(m^I - q) + \frac{\omega}{q}\nu_3 \sum_{i=1}^{3}[(m_i^N)^2 + q^2]L_i^{(z)} \tag{77}$$

$$(\chi^{-1})_{yx} = i\omega(\nu_3 + 2iqn_{0y}^2\alpha_3^S)\sum_{i=1}^{3} m_i^N B_i L_i^{(x)} \tag{78}$$

$$(\chi^{-1})_{yy} = i\omega\left[\frac{1}{2}(\alpha_4^S + n_{0y}^2\alpha_6^S)q^2 + \eta m^I + (\nu_3 + 2iqn_{0y}^2\alpha_3^S)\sum_{i=1}^{3} m_i^N B_i L_i^{(y)}\right] \tag{79}$$

$$(\chi^{-1})_{yz} = i\omega\left[2n_{0y}n_{0z}\alpha_3^S q^2 + (\nu_3 + 2iqn_{0y}^2\alpha_3^S)\sum_{i=1}^{3} m_i^N B_i L_i^{(z)}\right] \tag{80}$$

$$(\chi^{-1})_{zx} = 2\omega q\eta - \frac{i\omega^2\rho}{m^I - q} + i\omega\sum_{i=1}^{3}(2\nu_1 m_i^N - A_i)L_i^{(x)} \tag{81}$$

$$(\chi^{-1})_{zy} = i\omega\sum_{i=1}^{3}(2\nu_1 m_i^N - A_i)L_i^{(x)} \tag{82}$$

$$(\chi^{-1})_{zz} = \sigma_0 q^2 - \frac{\omega^2\rho^I m^I}{q(m^I - q)} + i\omega\sum_{i=1}^{3}(2\nu_1 m_i^N - A_i)L_i^{(x)} \tag{83}$$

In these expressions the following notations are used:

$$L_1^{(x)} = \frac{iq(B_3 - B_2)}{\Delta} \tag{84}$$

$$L_2^{(x)} = \frac{iq(B_1 - B_3)}{\Delta} \tag{85}$$

$$L_3^{(x)} = \frac{iq(B_2 - B_1)}{\Delta} \tag{86}$$

$$L_1^{(y)} = \frac{m_2^N - m_3^N}{\Delta} \tag{87}$$

$$L_2^{(y)} = \frac{m_3^N - m_1^N}{\Delta} \tag{88}$$

$$L_3^{(y)} = \frac{m_1^N - m_2^N}{\Delta} \tag{89}$$

$$L_1^{(z)} = \frac{B_2 m_3^N - B_3 m_2^N}{\Delta} \tag{90}$$

$$L_2^{(z)} = \frac{B_3 m_1^N - B_1 m_3^N}{\Delta} \tag{91}$$

$$L_3^{(z)} = \frac{B_1 m_2^N - B_2 m_1^N}{\Delta} \tag{92}$$

$$\Delta = B_1(m_2^N - m_3^N) + B_2(m_3^N - m_1^N) + B_3(m_1^N - m_2^N) \tag{93}$$

$$\begin{aligned} A_i = -\frac{2m_i}{q^2}&\left\{ i\omega\rho^N - [(m_i^N)^2 - q^2]\nu_2 - n_{0z}^2(m_i^N)^2\nu_{32} \right\} \\ &\times \left\{ 1 - \frac{n_{0z}^2(m_i^N)^2\nu_{123}}{[(m_i^N)^2 - q^2]\nu_{32} + 2n_{0z}^2(m_i^N)^2\nu_{123}} \right\} \end{aligned} \tag{94}$$

$$B_i = \frac{n_{0y}n_{0z}[(\nu_{32} + 2n_{0z}^2\nu_{123})(m_i^N)^2 - \nu_{32}q^2]}{i\omega\rho^N + (n_{0y}^2\nu_3 + n_{0z}^2\nu_2)q^2 - (\nu_3 + 2n_{0y}^2n_{0z}^2\nu_{123}(m_i^N)^2}, \tag{95}$$

$$\nu_{32} \equiv \nu_3 - \nu_2, \qquad \nu_{123} \equiv \nu_1 + \nu_2 - 2\nu_3 \tag{96}$$

The quantities m_i^N, $i = 1, 2, 3$, are given by formulas

$$m_i^N = (\mu_i)^{1/2}, \quad \mathrm{Re}\, m_i^N > 0 \tag{97}$$

where

$$\mu_1 = \frac{i\omega\rho^N + \nu_2 q^2}{\nu_2 + n_{0z}^2(\nu_3 - \nu_2)} \tag{98}$$

$$\begin{aligned} \mu_{2,3} = &\frac{1}{2(\nu_3 + 2n_{0y}^2n_{0z}^2\nu_{123})}\Big[i\omega\rho^N + 2(\nu_3 + n_{0z}^2\nu_{123})q^2 \\ &\pm \sqrt{-\omega^2(\rho^N)^2 + 4n_{0z}^2[(2n_{0z}^2 - 1)i\omega\rho^N + n_{0z}^2(\nu_1 + \nu_2)q^2]\nu_{123}q^2} \Big] \end{aligned} \tag{99}$$

In contrast to the case of homeotropic anchoring considered in the main text, the SQELS spectrum now depends upon three combinations of surface viscosity coefficients, namely, $(\alpha_4^S + \beta_1^S)$, α_3^S, and $(\alpha_4^S + n_{0y}^2\alpha_6^S)$, which together with surface tension σ_0 and compressional modulus ϵ_0 make the total number of the parameters of the interface equal to five.