Waves at surfactant-laden liquid-liquid crystal interface

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(Received 27 March 2007; published 20 July 2007)

A theoretical study is presented of surface waves at a monomolecular surfactant film between an isotropic liquid and a nematic liquid crystal for the case when the surfactant film is in the isotropic two-dimensional fluid phase and induces homeotropic (normal to the interface) orientation of the nematic director. The dispersion relation for the surface waves is obtained, and different surface modes are analyzed with account being taken of the anchoring induced by the surfactant layer, the curvature energy of the interface, and the anisotropy of the viscoelastic coefficients. The dispersion laws for capillary and dilatational surface modes retain structure similar to that in isotropic systems, but involve anisotropic viscosity coefficients. Additional modes are related to relaxation of the nematic director field due to anchoring at the interface. The results can be used to determine different properties of nematic-surfactant-isotropic interfaces from experimental data on surface light scattering.

I. INTRODUCTION

The presence of a surfactant film at a fluid-fluid interface alters the dynamics of the interface. This is manifested in behavior of the interfacial waves, induced either externally or by thermal fluctuations [1–3]. The interfacial dynamics can be probed by measuring the light scattered on such surface waves [4,5]. The scattering of light on surface waves is a powerful tool for probing the properties of surfactant films at fluid interfaces [5], and a variety of systems have been recently investigated using this method (e.g., Refs. [6–13]).

Recently, the application of surfactant films to modify the interfacial properties has been extended to the systems in which one of the fluids is in liquid-crystalline phase (e.g., liquid crystal colloids [14]). The presence of a liquid crystal as one of the fluids complicates the problem of probing the interfacial properties by studying the dynamics of the surface waves for the following reasons. First, there are additional degrees of freedom in the bulk of the liquid crystal phase due to its anisotropy. Secondly, the interaction with the surfactant film is more complicated due to anisotropic anchoring. Finally, the surfactant film in the anisotropic field created by the neighboring liquid crystal can itself show anisotropic behavior, even if it behaves as a two-dimensional isotropic fluid at the boundary between isotropic fluids.

A promising new direction for chemical and biological sensing devices has recently emerged which utilizes the properties of surfactant films self-assembled on the interface between water and a nematic liquid crystal. The surfactant film induces preferred orientation of the nematic director [15–17]. The adsorption of chemical or biological molecules at such interface can then lead to reorientation of the nematic director, enabling detection by an imaging system [18–22].

In these methods, easy detection is limited to the systems in which adsorption changes anchoring properties of the interface with respect to the adjacent liquid crystal phase quite considerably. Namely, the equilibrium anchoring angle should change in magnitude. The range of application of these systems could be made significantly broader, however, if a method were used that was sensitive to changes in the anchoring properties of the interface that did not necessarily result in nematic director reorientation. For example, the anchoring orientation may remain unchanged [14,18], the adsorption only changing the strength of the anchoring.

If a small amount of an analyte is present in the water it may be adsorbed at the surfactant layer, provided the surfactant molecules possess appropriate chemical properties. Generally, such adsorption will result in a change in the elastic and viscous properties of the interface. Hence sensitive experiments which are able to determine the interfacial properties will allow much more detailed experimental insight into the properties of the interaction between the surfactants and the analyte than has hitherto been available, and experimental study of surface waves is a possible technique for this purpose.

The theoretical description of surface waves at interfaces between nematic and isotropic liquids was made back in the 1970s [23–25]. The results demonstrated that the spectrum of surface waves has a more complicated structure than in the isotropic case, and allows the use of surface scattering experiments to determine properties of nematic interfaces [26–30]. Since then, several theoretical and experimental advances have been made, and presently these systems remain a subject of investigation [31–35].

The present paper presents a theoretical study of the dispersion of the surface waves at a monomolecular surfactant film between an isotropic liquid (e.g., water) and a nematic liquid crystal. The main distinguishing features of such interfaces are (i) the anchoring induced by the surfactant layer, (ii) the curvature energy of the interface, (iii) reduction of surface tension due to surfactant, and (iv) the anisotropy of the surface viscoelastic coefficients. We base our treatment on the mechanical model for anisotropic curved interfaces by Rey [36], which takes into account anchoring and bending properties of the surfactant. We consider the case of the insoluble surfactant film that is in its most symmetric phase (isotropic two-dimensional fluid), and induces homeotropic (normal to the surface) orientation of the director.

The paper is organized as follows. The continuum model used in the rest of the paper is set up in Sec. II. In Sec. III the dispersion relation for surface waves is derived. In Sec. IV

the numerical solution of the dispersion relation is solved with typical values of material parameters, and dispersion laws for different surface modes are analyzed in absence of the external magnetic field, and the influence of the magnetic field is discussed in Sec. V.

The explicit form of the dispersion relation is written in Appendix D.

II. MODEL

In this section we formulate the macroscopic model of the surfactant-laden interface between an isotropic liquid and a nematic liquid crystal, used in the present paper, and write down the governing equations.

The central equations in the present section are the conditions for the balance of forces [Eq. (1)] and torques [Eq. (5)] at the interface, written in Sec. II A. These equations will be used in section III to derive the dispersion relation for surface waves using standard techniques. The explicit form of the balance equations depends upon the chosen macroscopic model, and this section is devoted to formulation of the model used in the present paper.

We base the subsequent treatment of the surfactant-laden nematic-isotropic interface upon the models by Rey [36,37]. The theory of a compressible interface between nematic liquid crystals and isotropic viscous fluids, developed by Rey [37], provides general expressions for the interfacial anisotropic viscoelastic stress, and allows one to characterize the main elastic, viscous, and viscoelastic material properties of such interfaces. This theory allows one to describe in a consistent manner such features of these interfaces as anisotropic surface tension and anisotropic dissipative properties of the interface. The model for curved surfactant-laden liquid-liquid crystal interfaces, presented in Ref. [36], additionally takes into account the mechanical effects due to surface bending. The detailed discussion of these models is in the references cited above. We adopt Rey's results for elastic and viscous contributions to surface stresses and torques, as described below in Secs. II B and II C.

The model includes the effects of the nematic anchoring to the interface, and dependence of the energy of the surfactant film upon its curvature. The corresponding constitutive equations are presented in Sec. II D. Another important effect, which description is set up in Sec. II E, is the compressibility of a surfactant film, which is known to be responsible for appearance of longitudinal surface waves in an isotropic system.

In our model we use a number of assumptions about the properties of the system, which are the following.

We consider the case when the surfactant film induces homeotropic (normal to the surface) orientation of the nematic director, which is usually true in a range of the surfactant concentrations [14,18,38]. This case is the simplest to analyze, and, at the same time, the most important for biosensing applications where the direct change in anchoring angle cannot be always observed.

We assume that the system is far enough from any phase transitions both in the surfactant film [39] and in the nematic phase [40]. Thus we avoid complications related to the fluc-

tuations of the nematic and surfactant order parameters and the divergence of viscoelastic parameters near phase transitions.

The surfactant films can exhibit rich phase behavior [41], and the form of the surface stress tensor depends upon the symmetry of the interface. However, this does not normally influence much the dispersion laws of the surface modes compared to the isotropic case [2]. In the present paper we assume that the surfactant film is in the most symmetric phase (isotropic two-dimensional fluid). Although the symmetry of the film should break in the presence of the adjacent liquid-crystalline bulk phase, the film remains isotropic in equilibrium if the anchoring of the nematic is homeotropic, and symmetry breaking can occur only due to fluctuations of the director field. If we introduce the order parameter for the film, the corresponding anisotropic contributions to the interfacial stress tensor would be of higher order in the fluctuations of the dynamic variables than is required in our linearized treatment, so such contributions can be omitted.

We consider a surfactant layer at an interface between nematic and isotropic liquids to be macroscopically infinitely thin. We assume that the surfactant film is insoluble and Newtonian. This means that the model is applicable to systems in which the interchange of surfactant molecules between the interface and adjacent bulk fluids is small, and the relaxation of the orientation of surfactant molecules is fast compared to relaxation of surface waves. We also assume heat diffusion to be sufficiently fast so that the system is in thermal equilibrium. We do not consider systems where other effects, such as polarity, are important.

The linearized hydrodynamic description of isotropic liquids is well known [42], and summarized in Sec. II F. The nematic liquid crystal will be described in terms of the Eriksen-Leslie theory [40,43], which includes, in particular, the hydrodynamic coupling between the velocity and the nematic director fields. The linearized form of Eriksen-Leslie equations is summarized in Sec. II G.

With these assumptions, we write down the governing equations for the surfactant-laden nematic-isotropic interface in the rest of this section, to use them later to derive (Sec. III) and analyze (Sec. IV) the dispersion relation for surface waves.

In Sec. II H we include optional external magnetic field in our study, limiting our analysis by considering the direction of the magnetic field that does not change equilibrium orientation of the nematic director. The magnetic field tends to orient molecules of the nematic, resulting in the change of the effective interfacial properties, which, as we shall see in Sec. V, may affect the propagation of surface waves.

We shall 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 uniaxial nematic liquid crystal, and the half-space $z>0$ is filled by the isotropic liquid. Other details of the geometry used in the present paper are summarized in Appendix A.

A. Balance equations

The interfacial force balance equation is the balance between the interfacial force and the bulk stress jump:

$$\mathbf{F}^S + \mathbf{F}^N + \mathbf{F}^I = \mathbf{0}. \tag{1}$$

Here

$$\mathbf{F}^S = \nabla_s \cdot \mathbf{\Sigma}^S \tag{2}$$

is the force per unit area exerted by the interfacial stress $\mathbf{\Sigma}^S$,

$$\mathbf{F}^I = \mathbf{\Sigma}^I|_s \cdot \mathbf{k} \tag{3}$$

is the force per unit area exerted by the isotropic fluid,

$$\mathbf{F}^N = -\mathbf{\Sigma}^N|_s \cdot \mathbf{k} \tag{4}$$

is the force per unit area exerted by the nematic liquid crystal, the subscript s indicates that the bulk stress fields in the isotropic liquid, $\mathbf{\Sigma}^I$, and in the nematic, $\mathbf{\Sigma}^N$, are evaluated at the interface, $\mathbf{k}$ is the unit vector normal to the interface and directed into the isotropic liquid.

The interfacial torque balance equation can be cast as

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

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 explicit model for surface and bulk stresses and torques that enter Eqs. (1) and (5) is expanded in the remainder of this section.

B. Surface elastic stress and torque

In this and the following subsections we summarize the equations for the surface stress tensor $\mathbf{\Sigma}^S$ and surface torque vector $\mathbf{T}^S$. We represent these quantities as a sum of corresponding nondissipative (elastic) and dissipative (viscous) contributions:

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

$$\mathbf{T}^S = \mathbf{T}^{Se} + \mathbf{T}^{Sv}. \tag{7}$$

To describe the nondissipative contributions in the surface stress tensor, $\mathbf{\Sigma}^{Se}$, and surface torque vector, $\mathbf{T}^{Se}$, we use the equilibrium model proposed by Rey [36], which is summarized below.

Rey considered the interface with the Helmholtz free energy per unit mass $\mathcal{F}^S$ of the form

$$\mathcal{F}^S = \mathcal{F}^S(\rho^S, \mathbf{k}, \mathbf{b}), \tag{8}$$

where ρ^S is the surface mass density and $\mathbf{b}$ is the second fundamental tensor of the interface (see Appendix A). The corresponding differential was written as

$$d\mathcal{F}^S = -\frac{\sigma}{(\rho^S)^2} d\rho^S + \frac{\boldsymbol{\xi}_\|}{\rho} \cdot d\mathbf{k} + \frac{\mathbf{M}}{\rho} : d\mathbf{b}, \tag{9}$$

where

$$\sigma = \left[-(\rho^S)^2 \frac{\partial \mathcal{F}^S}{\partial \rho^S} \right]_{\mathbf{k}, \mathbf{b}} \tag{10}$$

is the interfacial tension,

$$\boldsymbol{\xi}_\| = \left(\rho^S \mathbf{I}_S \cdot \frac{\partial \mathcal{F}^S}{\partial \mathbf{k}} \right)_{\rho^S, \mathbf{b}} \tag{11}$$

is the tangential component of the capillary vector ($\mathbf{I}_S$ is the surface projector), and

$$\mathbf{M} = \left(\rho^S \frac{\partial \mathcal{F}^S}{\partial \mathbf{b}} \right)_{\rho^S, \mathbf{k}} \tag{12}$$

is the bending moment tensor. The elastic surface stress tensor was found to be

$$\mathbf{\Sigma}^{Se} = \sigma \mathbf{I}_S - \mathbf{M} \cdot \mathbf{b} + \mathbf{h}_\|^{Se} \mathbf{k}, \tag{13}$$

where the tangential surface molecular field is given by

$$\mathbf{h}_\|^{Se} = -\mathbf{I}_S \cdot \frac{\delta \mathcal{F}^S}{\delta \mathbf{k}} = -\boldsymbol{\xi}_\| - \mathbf{I}_S \cdot (\nabla_s \cdot \mathbf{M}), \tag{14}$$

∇_s is surface gradient operator, and $\delta/\delta\mathbf{k}$ denotes variational derivative with respect to $\mathbf{k}$. The elastic contribution to surface torque was written as

$$\mathbf{T}^{Se} = -\boldsymbol{\epsilon} : \mathbf{\Sigma}^{Se} + \nabla \cdot \mathbf{C}_S, \tag{15}$$

where

$$\mathbf{C}_S = -\mathbf{M} \cdot \boldsymbol{\epsilon}_S \tag{16}$$

is the surface couple stress, $\boldsymbol{\epsilon}$ is the Levi-Civita tensor, and $\epsilon_S = -\mathbf{I}_S \times \mathbf{k}$ is the surface alternator tensor.

C. Surface viscous stress and torque

The viscous properties of interfaces between an isotropic fluid and a nematic liquid crystal were considered in detail by Rey [37], and the results are summarized below.

The forces and fluxes that contribute to the dissipation function R were identified as follows:

$$R = \mathbf{\Sigma}_s^{Sv} : \mathbf{S}^S + \mathbf{\Sigma}_a^{Sv} : \mathbf{A}^S + \mathbf{h}_\|^{Sv} \cdot \left(\mathbf{I}_s \cdot \frac{d\mathbf{n}_\|}{dt} \right) + \mathbf{h}_\perp^{Sv} \cdot \left(\mathbf{k}\mathbf{k} \cdot \frac{d\mathbf{n}_\perp}{dt} \right), \tag{17}$$

where $\mathbf{\Sigma}_s^{Sv}$ and $\mathbf{\Sigma}_a^{Sv}$ are, correspondingly, symmetric and antisymmetric parts of the surface viscous stress tensor $\mathbf{\Sigma}^{Sv}$, $\mathbf{h}_\|^{Sv}$, and $\mathbf{h}_\perp^{Sv}$ are the components of the surface viscous molecular field tangential and normal to the surface,

$$\mathbf{S}^S = \frac{1}{2}[\nabla_s \mathbf{v}^S \cdot \mathbf{I}_s + \mathbf{I}_s \cdot (\nabla_s \mathbf{v}^S)^T] \tag{18}$$

is the surface rate-of-deformation tensor $[(\cdots)^T$ denotes the transposed tensor],

$$\mathbf{A}^S = \frac{1}{2}[\nabla_s \mathbf{v}^S \cdot \mathbf{I}_s - \mathbf{I}_s \cdot (\nabla_s \mathbf{v}^S)^T] \tag{19}$$

is the surface vorticity tensor, $\mathbf{v}^S$ is surface velocity,

$$\frac{d\mathbf{n}_\|}{dt} = \frac{\partial \mathbf{n}_\|}{\partial t} + \mathbf{v}^S \cdot \nabla_s \mathbf{n}_\| \tag{20}$$

and

$$\frac{d\mathbf{n}_\perp}{dt} = \frac{\partial \mathbf{n}_\perp}{\partial t} + \mathbf{v}^S \cdot \nabla_s \mathbf{n}_\perp \tag{21}$$

are the total time derivatives of the components $\mathbf{n}_\parallel = \mathbf{I}_s \cdot \mathbf{n}$ and $\mathbf{n}_\perp = \mathbf{kk} \cdot \mathbf{n}$ of the nematic director field $\mathbf{n}$, tangential and normal to the surface, correspondingly.

Generally, presence of the surfactant film at the interface complicates the form of the entropy production due to additional internal degrees of freedom of the surfactant, and to the anisotropy of the adjacent nematic liquid. However, if the surfactant film that is in its isotropic liquid phase and favors homeotropic anchoring of the nematic, the resulting anisotropic terms in the entropy production introduce corrections to the hydrodynamic equations of higher order than linear, and therefore can be neglected in the linearized treatment. Since this is the case we are considering, we shall adopt the form of the entropy production (17) in our model and use the form of the viscous contribution to the surface stress tensor derived by Rey [37], which is given by

$$\begin{aligned}\boldsymbol{\Sigma}^{Sv} = &\alpha_1^S \mathbf{S}^S {:} \mathbf{n}_\parallel \mathbf{n}_\parallel \mathbf{n}_\parallel \mathbf{n}_\parallel + \alpha_2^S \mathbf{n}_\parallel \mathbf{N}^S + \alpha_3^S \mathbf{N}^S \mathbf{n}_\parallel + \alpha_4^S \mathbf{S}^S + \alpha_5^S \mathbf{n}_\parallel \mathbf{n}_\parallel \cdot \mathbf{S}^S \\ &+ \alpha_6^S \mathbf{S}^S \cdot \mathbf{n}_\parallel \mathbf{n}_\parallel + \alpha_7^S \mathbf{n}_\parallel \mathbf{n}_\parallel (\mathbf{n}_\parallel \cdot \mathbf{N}^S) + \beta_1^S \mathbf{I}_s (\mathbf{I}_s {:} \mathbf{S}^S) \\ &+ \beta_2^S [\mathbf{n}_\parallel \mathbf{n}_\parallel (\mathbf{I}_s {:} \mathbf{S}^S) + \mathbf{I}_s (\mathbf{n}_\parallel \mathbf{n}_\parallel {:} \mathbf{S}^S)],\end{aligned} \tag{22}$$

where $\mathbf{N}^S$ is the surface Jaumann (corrotational) derivative [44] of the tangential component of the director $\mathbf{n}_\parallel$, and α_{1-7}^S, β_{1-2}^S are nine independent surface viscosity coefficients. In the isotropic case $\mathbf{n} = \mathbf{0}$, the expression for the surface viscous stress tensor reduces to the viscous stress tensor of Boussinesq-Schriven surface fluid [1,45] with the interfacial shear viscosity η_s given by

$$\eta_s = \frac{\alpha_4^S}{2}, \tag{23}$$

and dilatational viscosity ζ_s given by

$$\zeta_s = \frac{\alpha_4^S}{2} + \beta_1^S. \tag{24}$$

The surface viscous torque, corresponding to Eq. (17), is given by [37]

$$\mathbf{T}^{Sv} = -\mathbf{n} \times \mathbf{h}^{Sv}, \tag{25}$$

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

$$\begin{aligned}\mathbf{h}^{Sv} = &\gamma_2^S \mathbf{A} \cdot \mathbf{n}_\parallel + \gamma_1^S \mathbf{N}^S + \alpha_6^S \mathbf{n}_\parallel (\mathbf{n}_\parallel \mathbf{n}_\parallel {:} \mathbf{A}^S) + \frac{\gamma_2^S}{2} \mathbf{n}_\parallel (\mathbf{I}_s {:} \mathbf{S}^S) \\ &+ \gamma_{1\perp}^S \mathbf{kk} \cdot \frac{d\mathbf{n}_\perp}{dt}.\end{aligned} \tag{26}$$

The viscosity coefficients γ_i^S can be expressed in terms of quantities α_i^S. We shall need only the expression for the tangential rotational viscosity:

$$\gamma_1^S = \alpha_3^S - \alpha_2^S. \tag{27}$$

D. Anchoring and curvature energies

To calculate explicitly the interfacial tension σ [Eq. (10)], the tangential component of the capillary vector $\boldsymbol{\xi}_\parallel$ [Eq. (11)],

and the bending moment tensor $\mathbf{M}$ [Eq. (12)], we need to know the dependence of the surface free energy $\mathcal{F}^S$ on the orientation of the interface given by unit normal vector $\mathbf{k}$, and on its curvature described by second fundamental tensor $\mathbf{b}$. For small deviations of $\mathbf{k}$ and $\mathbf{b}$ from equilibrium, we can expand the free energy in powers of these quantities and truncate the series. The result can be represented as

$$\mathcal{F}^S(\rho^S, \mathbf{k}, \mathbf{b}) = \mathcal{F}_t^S(\rho^S) + \mathcal{F}_a^S(\mathbf{k}) + \mathcal{F}_c^S(\mathbf{b}), \tag{28}$$

each of the contribution described below.

The contribution $\mathcal{F}_t^S$ corresponds to the surface tension $\bar{\sigma}$ of the equilibrium interface (flat interface, adjacent nematic director normal to the interface):

$$\rho^S \mathcal{F}_t^S = \bar{\sigma}. \tag{29}$$

The anchoring contribution to the surface free energy density, $\mathcal{F}_a^S$, describes the energetics of the preferred alignment direction of the nematic director relative to the interface. For the homeotropic equilibrium anchoring, it can be written in terms of $\mathbf{n}_\parallel$ as follows:

$$\rho^S \mathcal{F}_a^S = \frac{1}{2} W \mathbf{n}_\parallel^2 + o(\mathbf{n}_\parallel^2). \tag{30}$$

Such expansion applied to the widely used Rapini-Papoular form of the anchoring free energy density [46]

$$\rho^S \mathcal{F}_{\mathrm{RP}} = \frac{W_{\mathrm{RP}}}{2} (\mathbf{n} \cdot \mathbf{k})^2, \tag{31}$$

shows that these definitions of the anchoring strength coefficient have opposite signs:

$$W = -W_{\mathrm{RP}}. \tag{32}$$

We shall use W as the anchoring strength coefficient to ensure that it is positive in the case of the homeotropic anchoring being considered.

The third contribution to the surface free energy density, $\mathcal{F}_c^S$, is caused by finite interface thickness, and is related to the difference of the curvature of a surfactant film from the locally preferred (spontaneous) value. The widely used form of this contribution is the Helfrich curvature expansion [47,48]

$$\rho^S \mathcal{F}_c^S = -2\kappa \bar{H}^2 + 2\kappa (H - \bar{H})^2 + \bar{\kappa} K + o((\nabla \mathbf{k})^2). \tag{33}$$

Here the geometry of the interface is described by the mean curvature H and the Gaussian curvature K, and the material parameters characterizing the interface are the bending rigidity κ, the saddle-splay (or Gaussian) rigidity $\bar{\kappa}$, and the spontaneous curvature $\bar{H}$. The term $-2\kappa \bar{H}^2$ guarantees that the curvature energy of a flat interface ($H=0$, $K=0$) is zero.

E. Surfactant concentration

To complete the description of the interface, we need the continuity equation for the surfactant concentration ν. For insoluble surfactants, the continuity equation reads

$$\frac{d\nu}{dt} + \nu \nabla_s \cdot \mathbf{v}^S = 0. \tag{34}$$

We shall extend the description of the dependence of the interfacial tension upon the concentration of surfactant, presented by Buzza [3], to other parameters characterizing the interface (surface tension $\bar{\sigma}$, anchoring strength W, bending rigidity κ, saddle-splay rigidity $\bar{\kappa}$, spontaneous curvature $\bar{H}$, and surface viscosities α_i^S, β_i^S). For small deviation $\delta\nu = \nu - \nu_0$ of the surfactant concentration ν from its equilibrium value ν_0, these coefficients can be written in the form

$$\bar{\sigma}(\nu) = \bar{\sigma}(\nu_0) + \frac{\partial\bar{\sigma}}{\partial\nu}\delta\nu, \tag{35}$$

and similarly for other quantities. Casting surface velocity $\mathbf{v}^S$ as the time derivative of the small surface displacement $\mathbf{u}$,

$$\mathbf{v}^S = \frac{d\mathbf{u}}{dt}, \tag{36}$$

we obtain from the continuity equation (34) that

$$\delta\nu = -\nu_0 \nabla_s \cdot \mathbf{u}. \tag{37}$$

This allows us to represent the material parameters of the interface as

$$\bar{\sigma}(\nu) = \sigma_0 + \epsilon_0 \nabla_s \cdot \mathbf{u}, \tag{38}$$

$$W(\nu) = W_0 + W_1 \nabla_s \cdot \mathbf{u}, \tag{39}$$

$$\kappa(\nu) = \kappa_0 + \kappa_1 \nabla_s \cdot \mathbf{u}, \tag{40}$$

$$\bar{H}(\nu) = \bar{H}_0 + \bar{H}_1 \nabla_s \cdot \mathbf{u}. \tag{41}$$

In these formulas $\sigma_0 = \bar{\sigma}(\nu_0)$, $W_0 = W(\nu_0)$, $\kappa_0 = \kappa(\nu_0)$, $\bar{H}_0 = \bar{H}(\nu_0)$ are, correspondingly, the interfacial tension, anchoring strength, bending rigidity, and spontaneous curvature in the unperturbed interface, $\epsilon_0 = -\nu_0 \partial\bar{\sigma}/\partial\nu$ is the static dilatational elasticity, $W_1 = -\nu_0 \partial W/\partial\nu$, $\kappa_1 = -\nu_0 \partial\kappa/\partial\nu$, and $\bar{H}_1 = -\nu_0 \partial\bar{H}/\partial\nu$ are coefficients in the first order term of the expansion of anchoring strength, bending rigidity, and spontaneous curvature in powers of $(\nabla_s \cdot \mathbf{u})$. There are similar expansions for Gaussian rigidity $\bar{\kappa}$ and surface viscosities α_i^S, β_i^S.

F. Isotropic liquid

We assume both the isotropic liquid and the nematic liquid crystal are incompressible, so that their densities ρ^I and ρ^N, are constant.

The linearized equations for the incompressible isotropic liquid are well known [42]. They are the continuity equation

$$\nabla \cdot \mathbf{v} = 0, \tag{42}$$

and Navier-Stokes equations

$$\rho^I \frac{\partial\mathbf{v}}{\partial t} = \nabla \cdot \mathbf{\Sigma}^I, \tag{43}$$

where the hydrodynamic stress tensor is given by

$$\mathbf{\Sigma}^I = -p\mathbf{I} + 2\eta\mathbf{S}, \tag{44}$$

where η is the shear viscosity of the isotropic liquid, $\mathbf{I}$ is the unit tensor, and

$$\mathbf{S} = \frac{1}{2}[\nabla\mathbf{v} + (\nabla\mathbf{v})^{\mathrm{T}}] \tag{45}$$

is the strain rate tensor.

We assume the nonslip boundary condition 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, $\mathbf{v}|_s$:

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

G. Nematic liquid crystal

To describe the dynamics of the nematic liquid crystal that is far from the isotropic-nematic transition and has small deviations from its equilibrium state, we shall use the linearized form of the Eriksen-Leslie theory [40,43,50]. The linearized equations for the incompressible nematic liquid crystal are the continuity equation (42), the equation for the velocity

$$\rho^N \frac{\partial\mathbf{v}}{\partial t} = \nabla \cdot \mathbf{\Sigma}^N, \tag{47}$$

and the equation for the director

$$\frac{\partial\delta\mathbf{n}}{\partial t} = \mathbf{n}_0 \cdot \mathbf{A} + \lambda(\mathbf{I} - \mathbf{n}_0\mathbf{n}_0) \cdot \mathbf{S} \cdot \mathbf{n}_0 + \frac{1}{\gamma_1}\mathbf{h}. \tag{48}$$

Here

$$\mathbf{A} = \frac{1}{2}[\nabla\mathbf{v} - (\nabla\mathbf{v})^{\mathrm{T}}] \tag{49}$$

is the antisymmetric vorticity tensor, λ is the reactive material parameter, γ_1 is the orientational viscosity, $\mathbf{h}$ is the molecular field which, assuming Frank form of the elastic free energy of a nematic liquid crystal in magnetic field $\mathcal{H}$ [40]

$$\mathcal{F}_F = \frac{K_1}{2}(\nabla \cdot \mathbf{n})^2 + \frac{K_2}{2}[\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 + \frac{K_3}{2}[\mathbf{n} \times (\nabla \times \mathbf{n})]^2$$

$$-\frac{1}{2}\chi_a(\mathbf{n} \cdot \mathcal{H})^2, \tag{50}$$

has the linearized form

$$\mathbf{h} = (\mathbf{I} - \mathbf{n}_0\mathbf{n}_0) \cdot \mathbf{h}^*, \tag{51}$$

where

$$\mathbf{h}^* = K_1 \nabla \nabla \cdot \delta\mathbf{n} - K_2 \nabla \times \{\mathbf{n}_0[\mathbf{n}_0 \cdot (\nabla \times \delta\mathbf{n})]\} \tag{52}$$

$$+ K_3 \nabla \times \{\mathbf{n}_0 \times [\mathbf{n}_0 \times (\nabla \times \delta\mathbf{n})]\} + \chi_a(\mathbf{n} \cdot \mathcal{H})\mathcal{H}, \tag{53}$$

K_1, K_2, and K_3 are the splay, twist, and bend Frank elastic constants, correspondingly, and χ_a is the difference of the

longitudinal and transversal magnetic susceptibilities [Eq. (63)].

The stress tensor can be represented as a sum of reactive and viscous (dissipative) contributions,

$$\mathbf{\Sigma}^N = \mathbf{\Sigma}^{Nr} + \mathbf{\Sigma}^{Nv}. \tag{54}$$

The linearized form of the reactive part is

$$\mathbf{\Sigma}^{Nr} = -p\mathbf{I} + \frac{1}{2}(\mathbf{n}_0\mathbf{h} - \mathbf{h}\mathbf{n}_0) - \frac{\lambda}{2}(\mathbf{n}_0\mathbf{h} + \mathbf{h}\mathbf{n}_0). \tag{55}$$

The linearized viscous stress tensor of incompressible nematic is

$$\mathbf{\Sigma}^{Nv} = 2\nu_2\mathbf{S} + 2(\nu_3 - \nu_2)(\mathbf{n}_0\mathbf{S}\cdot\mathbf{n}_0 + \mathbf{n}_0\cdot\mathbf{S}\mathbf{n}_0)$$
$$+ 2(\nu_1 + \nu_2 - 2\nu_3)\mathbf{n}_0\mathbf{n}_0\mathbf{n}_0\mathbf{n}_0{:}\mathbf{S}. \tag{56}$$

The quantities ν_1, ν_2, ν_3, γ_1, and λ can be expressed through more commonly used Leslie viscosity coefficients [50,51]. Note that equating $\eta \equiv \nu_1 = \nu_2 = \nu_3$ recovers the viscous stress tensor $2\eta\mathbf{S}$ of the isotropic incompressible fluid [last term in Eq. (44)].

H. Magnetic field

Magnetic field $\mathcal{H}$ in the isotropic and nematic regions satisfies Maxwell equations [24,49]

$$\nabla \times \mathcal{H} = \mathbf{0}, \tag{57}$$

$$\nabla \cdot (\mathcal{H} + 4\pi\mathcal{M}) = 0. \tag{58}$$

Neglecting magnetization of the interface, the boundary conditions read

$$\mathbf{I}_s \cdot \mathcal{H}|_N = \mathbf{I}_s \cdot \mathcal{H}|_I, \tag{59}$$

$$\mathbf{k} \cdot (\mathcal{H} + 4\pi\mathcal{M})|_N = \mathbf{k} \cdot (\mathcal{H} + 4\pi\mathcal{M})|_I. \tag{60}$$

Here the magnetization of the isotropic liquid is

$$\mathcal{M}|_I = \chi^I \mathcal{H}|_I, \tag{61}$$

where χ^I is the magnetic susceptibility of the isotropic liquid, the magnetization of the uniaxial nematic liquid crystal is [40]

$$\mathcal{M}|_N = \chi_\perp^N \mathcal{H} + \chi_a(\mathcal{H}\cdot\mathbf{n})\mathbf{n}|_N, \tag{62}$$

where χ_a is the difference of the longitudinal and transversal magnetic susceptibilities of the nematic:

$$\chi_a = \chi_\parallel^N - \chi_\perp^N. \tag{63}$$

III. DISPERSION RELATION

The aim of this section is to construct the dispersion relation for the surface waves on the basis of the model set up above. We consider a surface wave with frequency ω and wave vector $\mathbf{q} = (q,0,0)$ propagating along x axis, and solve force balance equation, Eq. (1), and torque balance equation,

Eq. (5), using a linearized form of the hydrodynamic equations written in Sec. II.

In order to linearize the hydrodynamic equations, we represent 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

$$p = p_0 + \delta p, \tag{64}$$

$$\mathbf{n} = \mathbf{n}_0 + \delta\mathbf{n}, \tag{65}$$

where δp and $\delta\mathbf{n}$ are the deviations of pressure and director from their equilibrium values p_0 and $\mathbf{n}_0$, correspondingly. The velocity $\mathbf{v} = \mathbf{v}(\mathbf{r},t)$ is itself the deviation from zero equilibrium velocity. Homeotropic anchoring corresponds to

$$\mathbf{n}_0 = (0,0,1). \tag{66}$$

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 vanish at $z \to \pm\infty$.

The magnetic field can also be represented as $\mathcal{H} = \mathcal{H}_0 + \delta\mathcal{H}$, where $\mathcal{H}_0 = (0,0,\mathcal{H}_0)$ is the equilibrium value, and the deviation $\delta\mathcal{H}$ can be found from the linearized form of the Maxwell equations (57) and (58). The terms in the final equations, containing $\delta\mathcal{H}$, are of higher order than linear, so we shall use only the equilibrium value, and skip the "0" subscript, so that $\mathcal{H} = (0,0,\mathcal{H})$.

Substituting the interfacial free energy density (28) into Eqs. (10)–(12) and (14), we find the contributions up to the first order in $\mathbf{u}$ (and its derivatives) and $\mathbf{n}_\parallel$ into surface tension

$$\sigma = \bar{\sigma} + \frac{W}{2}\mathbf{n}_\parallel^2 - 2\kappa\bar{H}^2 + 2\kappa(H - \bar{H})^2 + \bar{\kappa}K, \tag{67}$$

bending moment tensor

$$\mathbf{M} = 2[(\kappa + \bar{\kappa})H - \kappa\bar{H}]\mathbf{I}_s - \bar{\kappa}\mathbf{b}, \tag{68}$$

tangential component of the capillary vector

$$\boldsymbol{\xi}_\parallel = -W\mathbf{n}_\parallel, \tag{69}$$

and tangential surface molecular field

$$\mathbf{h}_\parallel^{Sv} = W\mathbf{n}_\parallel - 2\nabla_s[(\kappa + \bar{\kappa})H - \kappa\bar{H}] + \nabla_s \cdot (\bar{\kappa}\mathbf{b}). \tag{70}$$

The nonvanishing components of the surface viscous stress tensor (22) are

$$\mathbf{\Sigma}^{Sv} = 2\eta_s\mathbf{S}^S + (\zeta_s - \eta_s)(\mathbf{I}_s{:}\mathbf{S}^S)\mathbf{I}_s. \tag{71}$$

The total interfacial force $\mathbf{F}^S$ can be found by substituting Eqs. (6), (13), and (67)–(71), into Eq. (2), and has components

$$F_x^S = \epsilon_0\partial_x^2 u_x + (\eta_s + \zeta_s)\partial_x^2 v_x, \tag{72}$$

$$F_y^S = \eta_s\partial_x^2 v_y, \tag{73}$$

$$F_z^S = (\sigma_0 + W_0)\partial_x^2 u_z + W_0\partial_x\delta n_x + \psi\partial_x^3 u_x - \kappa_0\partial_x^4 u_z, \tag{74}$$

where

$$\psi \equiv 2(\kappa_0 \bar{H}_1 + \kappa_1 \bar{H}_0). \tag{75}$$

To write the explicit form of the force balance equations (1), we also need the expressions for the components of the force (3) exerted by the isotropic fluid,

$$F_x^I = \eta (\partial_x v_z + \partial_z v_x)_{z=+0}, \tag{76}$$

$$F_y^I = \eta (\partial_z v_y)_{z=+0}, \tag{77}$$

$$F_z^I = (2\eta \partial_z v_z - p)_{z=+0}, \tag{78}$$

and the components of the force (2) exerted by the nematic liquid crystal,

$$F_x^N = \left[\frac{1+\lambda}{2} h_x - \nu_3 (\partial_x v_z + \partial_z v_x) \right]_{z=-0}, \tag{79}$$

$$F_y^N = \left[\frac{1+\lambda}{2} h_y - \nu_3 \partial_z v_y \right]_{z=-0}, \tag{80}$$

$$F_z^N = (p - 2\nu_1 \partial_z v_z)_{z=-0}. \tag{81}$$

The hydrodynamic fields **v**, p, and **n** in the bulk isotropic and nematic liquids are found by solution of the hydrodynamic expressions. The explicit formulas are presented in Appendixes B and C.

Next we introduce Fourier transforms in the x coordinate and in time as

$$\mathbf{v}(\mathbf{r},t) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} d\omega \, e^{i\omega t - iqx} \tilde{\mathbf{v}}(q,z,\omega), \tag{82}$$

$$\delta p(\mathbf{r},t) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} d\omega \, e^{i\omega t - iqx} \tilde{p}(q,z,\omega), \tag{83}$$

$$\delta \mathbf{n}(\mathbf{r},t) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} d\omega \, e^{i\omega t - iqx} \tilde{\mathbf{n}}(q,z,\omega) \tag{84}$$

(for brevity we shall henceforth omit arguments of the transformed functions). Performing Fourier-transform of the force balance equation (1), and substituting $\tilde{\mathbf{u}} = \tilde{\mathbf{v}}/i\omega$, we obtain balance equations for the force components in form

$$- \epsilon_0^* q^2 \tilde{v}_x^S - i\omega \eta (m^I + q) \tilde{v}_x^S - \omega \eta (m^I - q) \tilde{v}_z^S$$
$$- \frac{\omega}{q} \nu_3 \sum_{i=1}^{3} [(m_i^{N\|})^2 + q^2] C_i^{N\|} + i\omega \frac{1+\lambda}{2} \sum_{i=1}^{3} [K_3 (m_i^{N\|})^2$$
$$- K_1 q^2 + \chi_a \mathcal{H}^2] B_i^\| C_i^{N\|} = 0, \tag{85}$$

$$- \eta_s q^2 \tilde{v}_y^S - \eta m^I \tilde{v}_y^S - \nu_3 \sum_{i=1}^{2} m_i^{N\perp} C_i^{N\perp} + \frac{1+\lambda}{2}$$
$$\times \sum_{i=1}^{2} [K_3 (m_i^{N\perp})^2 - K_2 q^2 + \chi_a \mathcal{H}^2] B_i^\perp C_i^{N\perp} = 0, \tag{86}$$

$$- (\sigma_0 + W_0) q^2 \tilde{v}_z^S + \omega q W_0 \tilde{n}_x^S - \kappa_0 q^4 \tilde{v}_z^S - i q^3 \psi \tilde{v}_x^S - 2\omega q \eta \tilde{v}_x^S$$
$$+ \frac{\omega^2 \rho^I}{q} \frac{i q \tilde{v}_x^S + m^I \tilde{v}_z^S}{m^I - q} + i\omega \sum_{i=1}^{3} (A_i - 2\nu_1 m_i^{N\|}) C_i^{N\|} = 0, \tag{87}$$

where $\epsilon_0^* = \epsilon_0 + i\omega (\eta_s + \zeta_s)$ is the complex dilatational modulus, m^I is defined in Appendix B by Eq. (B9), and the quantities $m_i^{N\|}$, $m_i^{N\perp}$, $C_i^{N\|}$, $C_i^{N\perp}$, $B_i^{N\|}$, $B_i^{N\perp}$, and A_i are defined in Appendix C by Eqs. (C22), (C11), (C29), (C28), (C21), (C10), and (C20), correspondingly.

To write the interfacial torque balance equation (5), we cast the torque exerted upon the interface by the nematic liquid crystal, $\mathbf{T}^N$, and the interfacial torque arising due to surface interactions, $\mathbf{T}^S$, entering the interfacial torque balance equation (5), in the form

$$\mathbf{T}^N = \mathbf{k} \times \mathbf{h}^N \tag{88}$$

and

$$\mathbf{T}^S = \mathbf{k} \times \mathbf{h}^S, \tag{89}$$

where the molecular field from the bulk

$$\mathbf{h}^N = -\mathbf{k} \cdot \left[\frac{\partial \mathcal{F}_F}{\partial (\nabla \mathbf{n})} \right]_S \tag{90}$$

has linearized components

$$h_x^N = -K_3 \partial_z \delta n_x^S, \tag{91}$$

$$h_y^N = -K_3 \partial_z \delta n_y^S, \tag{92}$$

and the surface molecular field $\mathbf{h}^S$ can be represented as a sum of elastic ($\mathbf{h}^{Se}$) and viscous ($\mathbf{h}^{Sv}$) contributions

$$\mathbf{h}^S = \mathbf{h}^{Se} + \mathbf{h}^{Sv}, \tag{93}$$

given by Eqs. (14) and (26), correspondingly, and can be represented in components as

$$h_x^{Se} = W_0 (\delta n_x^S + \partial_x u_z) - \kappa_0 \partial_x^3 u_z + \psi \partial_x^2 u_x, \tag{94}$$

$$h_y^{Se} = W_0 \delta n_y^S, \tag{95}$$

$$h_x^{Sv} = \gamma_{1\|}^S \frac{\partial (\delta n_x + \partial_x u_z)}{\partial t}, \tag{96}$$

$$h_y^{Sv} = \gamma_{1\|}^S \frac{\partial \delta n_y}{\partial t}. \tag{97}$$

Then the surface torque balance equations can be written as

$$- K_3 \partial_z \delta n_x^S + W_0 (\delta n_x + \partial_x u_z) - \kappa_0 \partial_x^3 u_z + \psi \partial_x^2 u_x$$
$$+ \gamma_{1\|}^S \frac{\partial (\delta n_x + \partial_x u_z)}{\partial t} = 0, \tag{98}$$

$$- K_3 \partial_z \delta n_y^S + W_0 \delta n_y + \gamma_{1\|}^S \frac{\partial \delta n_y}{\partial t} = 0, \tag{99}$$

or, substituting the expressions (C17), (C19), and (C9)

$$\sum_{i=1}^{3}\left[(K_3 m_i^{N\|} - W_0 - i\omega\gamma_1^S)B_i^{\|}\right.$$

$$\left. + \frac{q}{\omega}(W_0 + \kappa_0 q^2 - \psi m_i^{N\|} + i\omega\gamma_1^S)\right]C_i^{N\|} = 0, \quad (100)$$

$$\sum_{i=1}^{2}(K_3 m_i^{N\perp} - W_0 - i\omega\gamma_1^S)B_i^{\perp}C_i^{N\perp} = 0. \quad (101)$$

The interfacial force balance equations [Eqs. (85)–(87)] and the interfacial torque balance equations [Eqs. (100) and (101)] form, with account of Eqs. (C28) and (C29), a homogeneous system of linear algebraic equations in $\tilde{v}_x^S$, $\tilde{v}_y^S$, $\tilde{v}_z^S$, $\tilde{n}_x^S$, and $\tilde{n}_y^S$. The dispersion relation is obtained from the condition of existence of a solution to these equations, i.e., the requirement for the determinant $D(\omega,q)$ of the matrix of coefficients for this system to be zero

$$D(\omega,q) = 0. \quad (102)$$

Equations (86) and (101) in $\tilde{v}_y^S$ and $\tilde{n}_y^S$ decouple from Eqs. (85), (87), and (100) in $\tilde{v}_x^S$, $\tilde{v}_z^S$, and $\tilde{n}_z^S$. Therefore, the matrix of coefficients is block-diagonal, and the dispersion relation [Eq. (102)] is equivalent to a pair of relations for (x,z) and y directions:

$$D_{\|}(\omega,q) = 0, \quad (103)$$

$$D_{\perp}(\omega,q) = 0, \quad (104)$$

where $D_{\|}(\omega,q)$ is the determinant of the 3×3 matrix $M_{\|}$ of coefficients for Eqs. (85), (87), and (100), and $D_{\perp}(\omega,q)$ is the determinant of the 2×2 matrix of coefficients for Eqs. (86) and (101).

The explicit form of the dispersion relations is presented in Appendix D and can be readily used for the numerical analysis of surface modes.

IV. SURFACE MODES

In this section the dispersion equation, which is presented in Appendix D, is solved numerically, and surface modes of different types are analyzed. For simplicity, we assume the density of the isotropic liquid, ρ^I, to be small enough to be neglected (e.g., nematic-surfactant-air interface). We also assume that the magnetic field is absent.

The surface modes can be easily classified at low wave vectors q. Expansion of the dispersion relation in powers of the wave vector q is a straightforward exercise in algebra, and the resulting modes are described below.

First, there is a transverse capillary mode, which has the dispersion law similar to that in the case of an isotropic liquid-liquid interface [2,52]:

$$\omega_C(q) = \sqrt{\frac{\sigma_0 q^3}{\rho^N}} + o(q^{3/2}). \quad (105)$$

The principal contribution to this mode at large wavelengths arises due to the restoring influence of surface tension σ_0, and the predominant motion is in the direction normal to the

interface (z). The differences from the isotropic case, related to anisotropy of viscous dissipation in the nematic, appear in higher orders in q.

The dilatational (or compression) mode with predominant motion in the direction along wave propagation (x) arises in the presence of the surfactant layer due to the restoring force provided by the dilatational elastic modulus ϵ_0. The dispersion law for this mode can be written as

$$\omega_D(q) = \left[\frac{i\epsilon_0^2 q^4 \nu_3}{\rho^N(\eta_2^M)^2}\right]^{1/3} + o(q^{4/3}), \quad (106)$$

where the Miesowicz viscosity η_2^M is given by [50]

$$\eta_2^M = \nu_3 + \frac{(1+\lambda)^2}{4}\gamma_1. \quad (107)$$

The difference from the dispersion law for the dilatational mode in the case of a surfactant film at the interface between isotropic fluids, given by [2,52]

$$\omega_D^I(q) = \left(\frac{i\epsilon_0^2 q^4}{\rho^I \eta}\right)^{1/3} + o(q^{4/3}), \quad (108)$$

arises due to anisotropy of viscous dissipation in nematic.

A new mode, specific to the nematic, is driven by relaxation of the director field to equilibrium due to anchoring at the interface and has the disperion law

$$\omega_N(q) = \frac{iW_0}{\gamma_1^S} + o(q^0). \quad (109)$$

Such relaxation is present even in the absence of motion of the interface (e.g., when the interface is solid), so that $i\omega_N$ does not vanish at $q \to 0$. For nematic-isotropic interfaces, the corresponding motion of the interface is induced by backflow effects.

Finally, behavior of the in-plane shear mode, with motion in the y direction, is also governed by relaxation of the nematic director due to anchoring. The corresponding dispersion law

$$\omega_S(q) = \frac{iW_0}{\gamma_1^S} + o(q^0) \quad (110)$$

appears to be different from the isotropic case, where the damping of the in-plane shear mode in the absence of anchoring is governed by the surface viscosity η_s [52].

Gravity g, so far neglected in our analysis, becomes important at wave vectors

$$q \sim q_g = \sqrt{\frac{|\rho^N - \rho^I|g}{\sigma_0 + W_0}}, \quad (111)$$

and can be taken into account by adding the hydrostatic pressure term $-g|\rho^N-\rho^I|$ to Eq. (D28), which corresponds to the additional contribution $-g|\rho^N-\rho^I|u_z$ to the vertical component of the force, Eq. (74). The resulting dispersion law for transversal mode is given by the expression

$$\omega_G(q) = \sqrt{gq} + o(q^{1/2}), \quad (112)$$

which describes well-known gravity waves [42].

In the opposite case of large wave vectors, the curvature energy becomes important. Analysis of Eqs. (74) and (94) yields the characteristic values of q

$$q \sim q_\kappa = \sqrt{\frac{W_0}{\kappa_0}} \tag{113}$$

and

$$q \sim q_\psi = \frac{W_0}{|\kappa_0 \bar{H}_1 + \kappa_1 \bar{H}_0|} \tag{114}$$

below which one can neglect in the dispersion relation the terms containing bending rigidity κ and its derivatives with respect to surfactant concentration, given by ψ.

Usually $q_\psi > q_\kappa$, and the range of q in which both gravity and curvature contributions become small, given by

$$q_g \ll q \ll q_\kappa, \tag{115}$$

is rather wide. For typical values $|\rho^N - \rho^I| \sim 10$ kg/m^3, $g \sim 10$ m/s^2, $\sigma_0 \sim W_0 \sim 10^{-2}$ J/m^2, $\kappa_0 \sim 10^{-18}$ J, Eq. (115) reads 1 cm$^{-1} \ll q \ll 10^6$ cm^{-1}, which includes the range of wave vectors typically probed by surface light scattering experiments.

To obtain the dispersion laws for surface modes at larger values of the wave vector q, the dispersion equation must be solved numerically. The numerical solution presented below uses the following typical values of the material parameters when it is not indicated otherwise. For the nematic liquid crystal we use the parameters of 4-n-pentyl-4′-cyanobiphenyl (5CB) at 26 °C [53]: The density $\rho^N = 1021.5$ kg/m^3, the elastic constants $K_1 = 5.95 \times 10^{-12}$ N, $K_2 = 3.77 \times 10^{-12}$ N, $K_3 = 7.86 \times 10^{-12}$ N, the Leslie viscosities $\alpha_1 = -6.6 \times 10^{-3}$ kg/(m s), $\alpha_2 = -77.0 \times 10^{-3}$ kg/(m s), $\alpha_3 = -4.2 \times 10^{-3}$ kg/(m s), $\alpha_4 = 63.4 \times 10^{-3}$ kg/(m s), $\alpha_5 = 62.4 \times 10^{-3}$ kg/(m s), $\alpha_6 = -18.4 \times 10^{-3}$ kg/(m s). The viscosity coefficient used in the present paper can be calculated from the Leslie equations [50,51] and equal $\nu_1 = 50.4 \times 10^{-3}$ kg/(m s), $\nu_2 = 31.7 \times 10^{-3}$ kg/(m s), $\nu_3 = 19.96 \times 10^{-3}$ kg/(m s), $\gamma_1 = 72.8 \times 10^{-3}$ kg/(m s), $\lambda = 1.115$. We use the value of the bending rigidity $\kappa_0 = 10^{-19}$ J which is typical for surfactant layers [54]. For other parameters we use the following typical values: $\gamma_1^S \sim 5 \times 10^{-9}$ kg/s, $\bar{H}_0 = 0$, $\epsilon_0 = 10^{-3}$ N/m, $\eta_s = 10^{-8}$ N/m, $\sigma_0 = 5 \times 10^{-3}$ J/m^2, and $W_0 = 20 \times 10^{-3}$ J/m^2.

The dispersion law $\omega(q)$ for different surface modes in absence of gravity, obtained by solution of the dispersion relation (103) with the values of the parameters given above, is presented in Fig. 1. At low q the dispersion of modes C, D, N, as denoted in Fig. 1, is in good agreement with approximate formulas (105), (106), and (109), correspondingly. The noticeable discrepancy in behavior of capillary and dilatational modes appears at $q \sim 10$ cm^{-1}, and the damping of surface waves becomes large at larger q, which is qualitatively similar to the case of the interface between isotropic liquids.

The results presented in Fig. 1 suggest that in the typical range of q probed by surface light scattering experiments (100 cm$^{-1} \lesssim q \lesssim 2000$ cm^{-1}), the approximate expressions
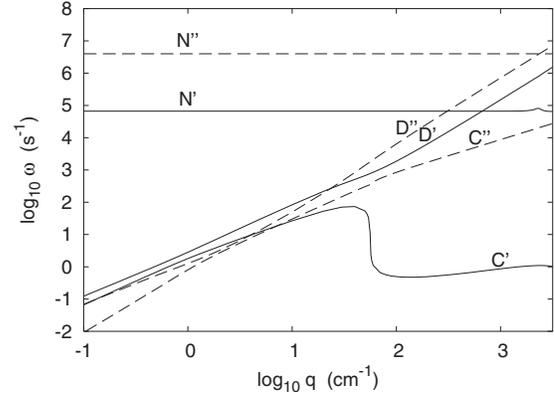

FIG. 1. Dispersion law $\omega(q)$ for different surface modes in the absence of gravity, obtained by solution of the dispersion relation (103) with the values of the parameters given in the text. Letters C, D, and N denote transverse (capillary), dilatational, and nematic director relaxation modes, correspondingly. Prime and double prime denote real (solid line) and imaginary (dashed line) parts of ω, correspondingly.

(105) and (106) do not describe well the dispersion curves, and accurate solution of the dispersion equation should be used instead.

Figure 2 presents the dispersion law $\omega(q)$ for different surface modes obtained by solution of the dispersion relation (103) in the presence of gravity $g = 9.8$ m/s^2. In agreement with the discussion above, the influence of gravity on the dispersion laws is small at $q \gg q_g$, where q_g is given by Eq. (111).

If the bending rigidity κ is large, its influence becomes noticeable, as it is demonstrated in Fig. 3. For $\kappa \sim kT$, typical for surfactant films, the value of q_κ, given by Eq. (113), corresponds to a wavelength close to atomic scales, and curvature energy can be neglected in typical surface light scattering experiments, in agreement with the discussion above.
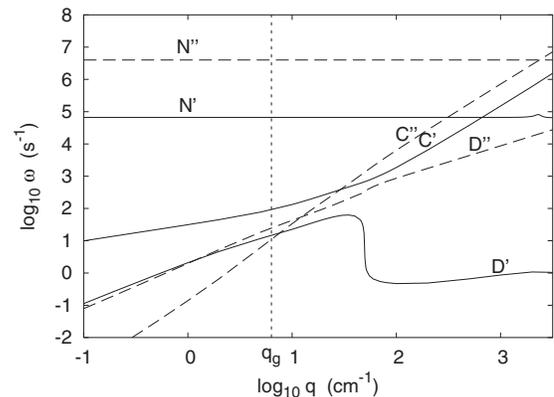

FIG. 2. Dispersion law $\omega(q)$ for different surface modes in the presence of gravity $g = 9.8$ m/s^2, obtained by solution of the dispersion relation (103) with the values of the parameters given in the text. Letters C, D, and N denote transverse, dilatational, and nematic director relaxation modes, correspondingly. Prime and double prime denote real (solid line) and imaginary (dashed line) parts of ω, correspondingly. Vertical dotted line corresponds to the value of q_g given by Eq. (111).
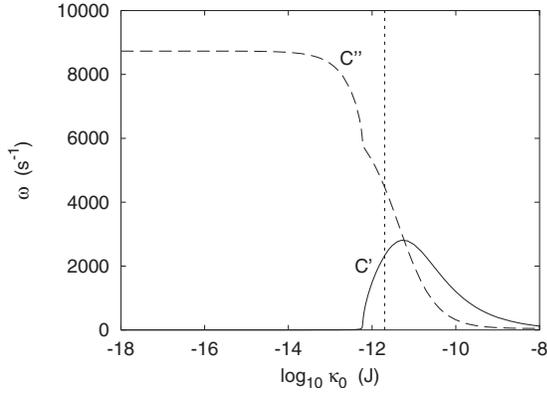
FIG. 3. Dependence of the real (solid line) and imaginary (dashed line) parts of the frequency of the transverse capillary mode upon the bending rigidity κ_0, calculated at $q=1000$ cm^{-1} in the absence of gravity. Vertical line corresponds to the value of κ_0 that satisfies Eq. (113).

The dispersion laws for the modes governed by relaxation of the nematic director field in x and y directions due to anchoring of the nematic director at the interface, obtained by numerical solution of the dispersion equation with the values of the parameters given above, are well described by Eqs. (109) and (110).

As the anchoring strength becomes smaller, other mechanisms start to take over, as demonstrated in Figs. 4 and 5. In particular, the frequencies ω_N and ω_S of these modes becomes dependent upon the wave vector q due to the elasticity of the nematic phase, which is characterized by the elastic constants K_1, K_2, K_3. We should also note that homeotropic anchoring strength as low as 10^{-6} J/m^2 has been observed giving rise to director instabilities [55,56]. Although the nature of the nematic director relaxation modes at small anchoring strengths requires further investigation, in the typical experiments the transversal displacement of the interface is measured. This is only weakly affected by oscillations of the director field through backflow effects.
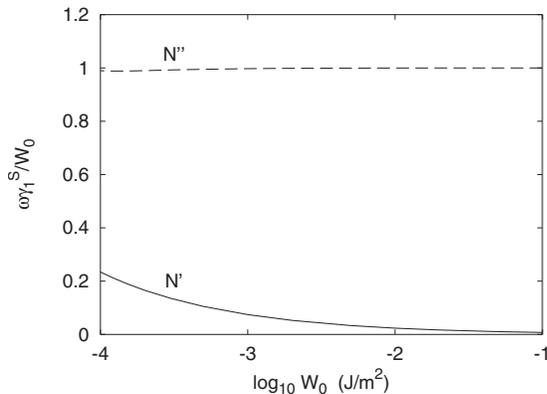

FIG. 4. Dependence of the real (solid line) and imaginary (dashed line) parts of the frequency ω of the nematic director relaxation mode, normalized by W_0/γ_1^S [see Eq. (109)], upon the anchoring strength W_0, calculated at $q=100$ cm^{-1} in absence of gravity.
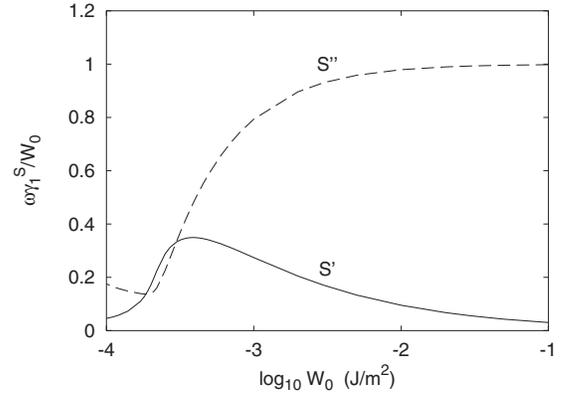

FIG. 5. Dependence of the real (solid line) and imaginary (dashed line) parts of the frequency ω of the in-plane shear mode, normalized by W_0/γ_1^S [see Eq. (110)], upon the anchoring strength W_0, calculated at $q=100$ cm^{-1} in absence of gravity.

V. INFLUENCE OF MAGNETIC FIELD

In this section we discuss how the surface modes described in Sec. IV are altered in the presence of the external magnetic field directed normally to the surface (along z axis).

The external magnetic field effectively acts on the nematic molecules as an additional molecular field [see Eq. (52)], and the primary counteracting mechanism is provided by orientational shear relaxation. Thus we may expect the influence of the magnetic field becomes noticeable at

$$\chi_a \mathcal{H}^2 \sim \gamma_1 \omega. \tag{116}$$

The results of the numerical solution of the dispersion equation in the presence of magnetic field, presented in Fig. 6, confirm that noticeable change in dispersion of capillary and dilatational modes arises only around the value of the field given by Eq. (116). The change due to magnetic field in
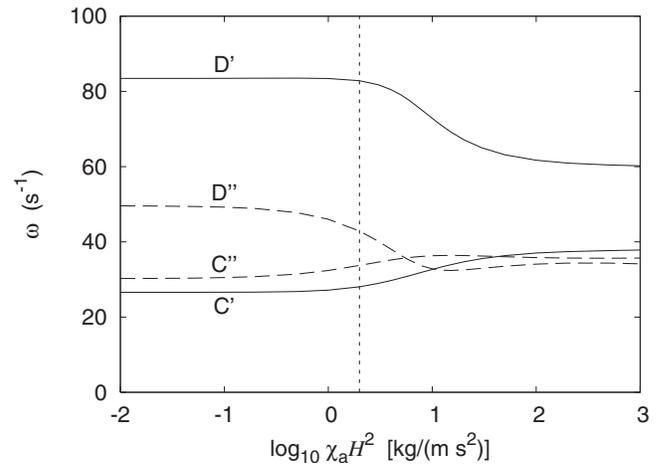

FIG. 6. Dependence of the real (solid lines) and imaginary (dashed lines) parts of the frequencies of the modes C and D (as defined on Fig. 1) upon the magnetic field, calculated at $q=10$ cm^{-1} in absence of gravity. Vertical dotted line corresponds to $\chi_a \mathcal{H}^2 = \gamma_1 \omega_C$ [see Eq. (116)].

modes governed by anchoring is found to be negligibly small.

At low q the dispersion of a capillary mode in strong magnetic field is different from the law (105) and is given by

$$\omega_C = \sqrt{\frac{(\sigma_0 + W_0)q^3}{\rho^N}} + o(q^{3/2}). \qquad (117)$$

The frequency of this mode becomes sensitive to the anchoring properties of the interface, because the nematic director tends to be oriented along the field rather than to be advected with the nematic liquid. The practical use of this effect is, however, limited, because at short wavelengths extremely large magnetic field is required, and at long wavelengths gravity becomes dominating [Eq. (112)]. For example, using the data in Fig. 6 we obtain the value $\chi_a \mathcal{H}^2 = \gamma_1 \omega_C \approx 2$ kg/m s^2, which corresponds to the transition between weak and strong field regimes. With the typical value of the anisotropy of the magnetic susceptibility $\chi_a \sim 10^{-7}$ [40], the required magnetic field is $\sim 10^4$ oersteds.

In principle, magnetic field can also influence surface waves through change in the properties of the interface (e.g. surface tension) due to the magnetization of the surfactant. A separate study is required to estimate the magnitude of this effect.

VI. CONCLUSION

We have obtained the dispersion relation for the surface waves at a surfactant-laden nematic isotropic interface for the case when the surfactant film induces homeotropic (normal to the surface) orientation of the director, and the surfactant film is in the isotropic two-dimensional fluid phase. We have analyzed the dispersion law of different surface modes analytically in long wavelength limit, and numerically in broader range of wave vectors, using typical values of the material parameters.

At long wavelengths the dispersion of capillary, dilatational (or compression), in-plane shear, and director relaxation modes is described by Eqs. (105) [or (112)], (106), (110), and (109), correspondingly. At smaller wavelength, the solution of the full dispersion relation should be used. Gravity influences the transversal mode at small wave vectors [Eq. (111)], and curvature energy of surfactant can be neglected if wave vector is not too large [Eq. (113)]. For all modes, the influence of the external magnetic field directed normally to the interface is small.

The influence of the magnetic field should be more pronounced if the direction of the field does not coincide with equilibrium nematic director. In this case the dispersion law for surface modes may be expected to be quantitatively different due to anisotropy of viscous dissipation in nematic, and different anchoring energy. The results of the present paper can be readily extended to the case of arbitrary direction of the external field and to other types of nematic anchoring.

A promising approach to experimental investigation of the propagating regime of capillary waves is the use of the external electric field, which is known to couple much more strongly with the nematic than the magnetic field [57]. The theoretical analysis of the nematic-surfactant-isotropic system may be more complicated than that undertaken in the present work because of the need to take into account polarizability of the interface, and the spontaneous dielectric polarization of a deformed nematic.

An alternative experimental technique which allows one to directly investigate the propagation of low-wave-number surface waves is the use of externally excited surface waves [58]. This technique provides data on the dependence of complex wavenumber q upon real frequency ω, which can be directly analyzed using the dispersion relation derived in the present paper.

Other possible developments, which may increase the range of accessible systems and conditions, is the extension of the results to wider range of the states of the surfactant film, and the study of the effects which may be caused by the phase transitions in the surfactant film and bulk liquid crystal.

Dependence of the dispersion waves upon the parameters of the interface suggests the surface light scattering on a surfactant-laden nematic-isotropic interface as a potential method for determining the properties of surfactant-laden nematic-isotropic interfaces, and as a possible candidate for a chemical or biological sensing technique.

APPENDIX A: DIFFERENTIAL GEOMETRY OF THE INTERFACE

The geometrical description we use is similar to those presented in works [3,36]. We choose the plane $z=0$ to coincide with the unperturbed interface, the half-space $z<0$ to be occupied by the uniaxial nematic liquid crystal, and the half-space $z>0$ to be filled by the isotropic liquid.

Let the position of a fluid particle at the interface be $\mathbf{r} = \mathbf{r}_0 + \mathbf{u}$, where $\mathbf{r}_0 = (x_0, y_0, 0)$ is its position on the undeformed interface ($z=0$), and $\mathbf{u} = \mathbf{u}(\mathbf{r}_0)$ is the displacement vector with components (u_x, u_y, u_z). We shall use x_0 and y_0 as surface coordinates and denote them as s^α, α and other Greek indices taking values 1 and 2.

The position $\mathbf{r}$ of fluid particles at the interface in 3D space can be cast as

$$\mathbf{r} = \mathbf{R}(s^\alpha). \qquad (A1)$$

The surface tangent base vectors $\mathbf{a}_\alpha = \partial \mathbf{r} / \partial s^\alpha$, corresponding to the chosen surface coordinates, can be written in terms of the components of the displacement vectors:

$$\mathbf{a}_1 = \frac{\partial \mathbf{r}}{\partial s^1} = (1 + \partial_x u_x, \ \partial_x u_y, \ \partial_x u_z) \qquad (A2)$$

and

$$\mathbf{a}_2 = \frac{\partial \mathbf{r}}{\partial s^2} = (\partial_y u_x, \ 1 + \partial_y u_y, \ \partial_y u_z). \tag{A3}$$

The surface metric tensor

$$a_{\alpha\beta} = \mathbf{a}_\alpha \cdot \mathbf{a}_\beta = \begin{pmatrix} 1 + 2\partial_x u_x & \partial_x u_y + \partial_y u_x \\ \partial_x u_y + \partial_y u_x & 1 + 2\partial_y u_y \end{pmatrix} + O(u^2), \tag{A4}$$

has determinant

$$a = \det(a_{\alpha\beta}) = 1 + 2(\partial_x u_x + \partial_y u_y) + O(u^2). \tag{A5}$$

The corresponding reciprocal base vectors $\mathbf{a}^\alpha$ and metric tensor $a^{\alpha\beta}$ take the form

$$\mathbf{a}^1 = \frac{\partial s^1}{\partial \mathbf{r}} = (1 - \partial_x u_x, \ -\partial_y u_x, \ \partial_x u_z) + O(u^2), \tag{A6}$$

$$\mathbf{a}^2 = \frac{\partial s^2}{\partial \mathbf{r}} = (-\partial_x u_y, \ 1 - \partial_y u_y, \ \partial_y u_z) + O(u^2), \tag{A7}$$

$$a^{\alpha\beta} = \mathbf{a}^\alpha \cdot \mathbf{a}^\beta = \begin{pmatrix} 1 - 2\partial_x u_x & -\partial_x u_y - \partial_y u_x \\ -\partial_x u_y - \partial_y u_x & 1 - 2\partial_y u_y \end{pmatrix} + O(u^2). \tag{A8}$$

The base and reciprocal base vectors satisfy

$$\mathbf{a}_\alpha \cdot \mathbf{a}^\beta = \delta_\alpha^\beta = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{A9}$$

We write the unit vector $\mathbf{k}$, normal to the interface and directed into the isotropic liquid, as

$$\mathbf{k} = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{|\mathbf{a}_1 \times \mathbf{a}_2|} = (-\partial_x u_z, \ -\partial_y u_z, \ 1) + O(u^2). \tag{A10}$$

We shall also define the dyadic surface idem factor

$$\mathbf{I}_s = \mathbf{a}_\alpha \mathbf{a}^\alpha = \begin{pmatrix} 1 & 0 & \partial_x u_z \\ 0 & 1 & \partial_y u_z \\ \partial_x u_z & \partial_y u_z & 0 \end{pmatrix} + O(u^2), \tag{A11}$$

the surface gradient operator

$$\nabla_s = \mathbf{I}_s \cdot \nabla = \begin{pmatrix} \partial_x + (\partial_x u_z)\partial_z \\ \partial_y + (\partial_y u_z)\partial_z \\ (\partial_x u_z)\partial_x + (\partial_y u_z)\partial_y \end{pmatrix} + O(u^2), \tag{A12}$$

and the second fundamental tensor

$$\mathbf{b} = -\nabla_s \mathbf{k} = \begin{pmatrix} \partial_x^2 u_z & \partial_x \partial_y u_z & 0 \\ \partial_x \partial_y u_z & \partial_y^2 u_z & 0 \\ 0 & 0 & 0 \end{pmatrix} + O(u^2). \tag{A13}$$

The mean curvature H and Gaussian curvature K are given by

$$H = \frac{1}{2}(\mathbf{I}_s : \mathbf{b}) = \frac{1}{2}(\partial_x^2 u_z + \partial_y^2 u_z) + O(u^2), \tag{A14}$$

$$K = \frac{1}{2}\epsilon^{\alpha\beta}\epsilon^{\gamma\delta}b_{\alpha\gamma}b_{\beta\delta} = O(u^2). \tag{A15}$$

Other useful identities include the surface projection $\mathbf{n}_\parallel$ of a nematic director field $\mathbf{n}$, Eqs. (65) and (66),

$$\mathbf{n}_\parallel = \mathbf{I}_S \cdot \mathbf{n} = \begin{pmatrix} \delta n_x + \partial_x u_z \\ \delta n_y + \partial_y u_z \\ 0 \end{pmatrix} + o(\nabla \mathbf{u}, \delta \mathbf{n}), \tag{A16}$$

and its surface divergence

$$\nabla_S \cdot \mathbf{n}_\parallel = \partial_x \delta n_x + \partial_y \delta n_y + \partial_x^2 u_z + \partial_y^2 u_z + o(\nabla \mathbf{u}, \delta \mathbf{n}). \tag{A17}$$

APPENDIX B: BULK SOLUTION FOR ISOTROPIC LIQUID

This appendix presents the solution to the linearized hydrodynamic equations in bulk isotropic liquid, obtained by Kramer [52].

Substitution of Eq. (82) into Eq. (42) yields

$$-iq\tilde{v}_x + \partial_z \tilde{v}_z = 0. \tag{B1}$$

Substituting Eqs. (82) and (83) into Eqs. (43)–(45), we obtain

$$[i\omega\rho^I + \eta(q^2 - \partial_z^2)]\tilde{v}_x = iq\tilde{p}, \tag{B2}$$

$$[i\omega\rho^I + \eta(q^2 - \partial_z^2)]\tilde{v}_y = 0, \tag{B3}$$

$$[i\omega\rho^I + \eta(q^2 - \partial_z^2)]\tilde{v}_z = -\partial_z \tilde{p}, \tag{B4}$$

where Eq. (B3) is decoupled from other equations. The general solution to Eqs. (B1)–(B4) vanishing at $z \to \infty$ can be written as

$$\tilde{v}_x = iC_1^{I\parallel}e^{-qz} + i\frac{m^I}{q}C_2^{I\parallel}e^{-m^I z}, \tag{B5}$$

$$\tilde{v}_y = C^{I\perp}e^{-m^I z}, \tag{B6}$$

$$\tilde{v}_z = C_1^{I\parallel}e^{-qz} + C_2^{I\parallel}e^{-m^I z}, \tag{B7}$$

$$\tilde{p} = \frac{i\omega\rho^I}{q}C_1^{I\parallel}e^{-qz}, \tag{B8}$$

with

$$m^I = \left(q^2 + \frac{i\omega\rho^I}{\eta}\right)^{1/2}, \quad \text{Re } m^I > 0. \tag{B9}$$

The quantities $C_1^{I\parallel}$, $C_2^{I\parallel}$, and $C^{I\perp}$ are functions of q and ω and are determined by the boundary conditions at the interface as follows:

$$C_1^{I\parallel} = \frac{iq\tilde{v}_x^S + m^I \tilde{v}_z^S}{m^I - q}, \tag{B10}$$

$$C^{I\perp} = \tilde{v}_y^S, \tag{B11}$$

$$C_2^{I\parallel} = -\frac{iq\tilde{v}_x^S + q\tilde{v}_z^S}{m^I - q}, \tag{B12}$$

where the superscript S indicates that the values of the corresponding dynamic variables are taken at $z \to 0$.

APPENDIX C: BULK SOLUTION FOR NEMATIC LIQUID CRYSTAL

In this appendix the solution is presented to the linearized hydrodynamic equations in bulk nematic liquid crystal.

For the equilibrium director along z axis [Eq. (66)], the Fourier transform, similar to Eqs. (82)–(84), of the linearized molecular field [Eq. (51)], $\tilde{\mathbf{h}}$, has nonzero components

$$\tilde{h}_x = -K_1 q^2 \tilde{n}_x + K_3 \partial_z^2 \tilde{n}_x + \chi_a \mathcal{H}^2 \tilde{n}_x, \tag{C1}$$

$$\tilde{h}_y = -K_2 q^2 \tilde{n}_y + K_3 \partial_z^2 \tilde{n}_y + \chi_a \mathcal{H}^2 \tilde{n}_y. \tag{C2}$$

Substituting them into Eqs. (47) and (54)–(56), we obtain the following linear differential equations,

$$[i\omega\rho^N + (2\nu_2 - \nu_3)q^2 - \nu_3\partial_z^2]\tilde{v}_x - \frac{1-\lambda}{2}\partial_z\tilde{h}_x = iq\tilde{p}, \tag{C3}$$

$$[i\omega\rho^N + \nu_2 q^2 - \nu_3\partial_z^2]\tilde{v}_y - \frac{1-\lambda}{2}\partial_z\tilde{h}_y = 0, \tag{C4}$$

$$[i\omega\rho^N + \nu_3 q^2 - (2\nu_1 - \nu_3)\partial_z^2]\tilde{v}_z - iq\frac{1+\lambda}{2}\tilde{h}_x = -\partial_z\tilde{p}, \tag{C5}$$

which are analogous to Eqs. (B2)–(B4) for isotropic liquids. Equation (48) for the director after Fourier transform gives two equations,

$$i\omega\tilde{n}_x = \frac{1+\lambda}{2}\partial_z\tilde{v}_x + \frac{1-\lambda}{2}iq\tilde{v}_z + \frac{1}{\gamma_1}\tilde{h}_x \tag{C6}$$

and

$$i\omega\tilde{n}_y = \frac{1+\lambda}{2}\partial_z\tilde{v}_y + \frac{1}{\gamma_1}\tilde{h}_y, \tag{C7}$$

where $\tilde{h}_x$ and $\tilde{h}_y$ are given by Eqs. (C1) and (C2).

Thus we have six linear differential equations [Eqs. (B1) and (C3)–(C7)] for six dynamic variables (pressure, three components of velocity, and two components of director). Equations (C4) and (C7) for $\tilde{v}_y$ and $\tilde{n}_y$ decouple from the others, their general solution vanishing at $z \to -\infty$ can be cast as

$$\tilde{v}_y = \sum_{i=1}^{2} C_i^{N\perp} e^{m_i^{N\perp} z}, \tag{C8}$$

$$\tilde{n}_y = \sum_{i=1}^{2} B_i^{\perp} C_i^{N\perp} e^{m_i^{N\perp} z}, \tag{C9}$$

where

$$B_i^{\perp} = \frac{(1+\lambda)\gamma_1 m_i^{N\perp}}{2[i\omega\gamma_1 + K_2 q^2 - K_3(m_i^{N\perp})^2 - \chi_a\mathcal{H}^2]}, \tag{C10}$$

$$m_i^{N\perp} = (\mu_i^{\perp})^{1/2}, \quad \operatorname{Re} m_i^{N\perp} > 0, \tag{C11}$$

and $\mu_i^{\perp}$, $i=1,2$, are the roots of the quadratic equation

$$a_2^{\perp}(\mu^{\perp})^2 + a_1^{\perp}\mu^{\perp} + a_0^{\perp} = 0, \tag{C12}$$

where

$$a_2^{\perp} = \left(\frac{1-\lambda^2}{4}\gamma_1 - \nu_3\right)K_3, \tag{C13}$$

$$a_1^{\perp} = (i\omega\gamma_1 + K_2 q^2 - \chi_a\mathcal{H}^2)\nu_3 + (i\omega\rho^N + \nu_2 q^2)K_3$$
$$-\frac{1-\lambda^2}{4}\gamma_1(K_2 q^2 - \chi_a\mathcal{H}^2), \tag{C14}$$

$$a_0^{\perp} = -(i\omega\rho^N + \nu_2 q^2)(i\omega\gamma_1 + K_2 q^2 - \chi_a\mathcal{H}^2). \tag{C15}$$

The general solution to the equations (B1), (C3), (C5), and (C6) vanishing at $z \to -\infty$ can be cast as

$$\tilde{v}_x = -\frac{i}{q}\sum_{i=1}^{3} m_i^{N\parallel} C_i^{N\parallel} e^{m_i^{N\parallel} z}, \tag{C16}$$

$$\tilde{v}_z = \sum_{i=1}^{3} C_i^{N\parallel} e^{m_i^{N\parallel} z}, \tag{C17}$$

$$\tilde{p} = \sum_{i=1}^{3} A_i C_i^{N\parallel} e^{m_i^{N\parallel} z}, \tag{C18}$$

$$\tilde{n}_x = \sum_{i=1}^{3} B_i^{\parallel} C_i^{N\parallel} e^{m_i^{N\parallel} z}, \tag{C19}$$

where

$$A_i = -\frac{1}{m_i^{N\parallel}}\left\{ iq\frac{1+\lambda}{2} \times [K_1 q^2 - K_3(m_i^{N\parallel})^2 - \chi_a\mathcal{H}^2]B_i^{\parallel} \right.$$
$$\left. + [i\omega\rho^N + \nu_3 q^2 - (2\nu_1 - \nu_3)(m_i^{N\parallel})^2] \right\}, \tag{C20}$$

$$B_i^{\parallel} = \frac{i\gamma_1}{2q}\frac{(1-\lambda)q^2 - (1+\lambda)(m_i^{N\parallel})^2}{i\omega\gamma_1 + K_1 q^2 - K_3(m_i^{N\parallel})^2 - \chi_a\mathcal{H}^2}, \tag{C21}$$

$$m_i^{N\parallel} = (\mu_i^{\parallel})^{1/2}, \quad \operatorname{Re} m_i^{N\parallel} > 0, \tag{C22}$$

and $\mu_i^{\parallel}$, $i=1,2,3$, are the roots of the cubic equation

$$a_3^{\parallel}(\mu^{\parallel})^3 + a_2^{\parallel}(\mu^{\parallel})^2 + a_1^{\parallel}\mu^{\parallel} + a_0^{\parallel} = 0, \tag{C23}$$

where

$$a_3^{\parallel} = \left(\frac{1-\lambda^2}{4}\gamma_1 - \nu_3\right)K_3, \qquad (C24)$$

$$a_2^{\parallel} = i\omega\gamma_1\nu_3 - \left(\frac{1-\lambda^2}{4}\gamma_1 - \nu_3\right)(K_1q^2 - \chi_a\mathcal{H}^2)$$
$$+ \left\{i\omega\rho^N - \left[\frac{1+\lambda^2}{2}\gamma_1 - 2(\nu_1+\nu_2-\nu_3)\right]q^2\right\}K_3, \qquad (C25)$$

$$a_1^{\parallel} = -i\omega\gamma_1[i\omega\rho^N + 2(\nu_1+\nu_2-\nu_3)q^2]$$
$$- \left\{i\omega\rho^N - \left[\frac{1+\lambda^2}{2}\gamma_1 - 2(\nu_1+\nu_2-\nu_3)\right]q^2\right\}$$
$$\times (K_1q^2 - \chi_a\mathcal{H}^2)$$
$$- \left[i\omega\rho^N - \left(\frac{1-\lambda^2}{4}\gamma_1 - \nu_3\right)q^2\right]K_3q^2, \qquad (C26)$$

$$a_0^{\parallel} = i\omega\gamma_1q^2(i\omega\rho^N + \nu_3q^2) + \left[i\omega\rho^N - \left(\frac{1-\lambda^2}{4}\gamma_1 - \nu_3\right)q^2\right]$$
$$\times (K_1q^2 - \chi_a\mathcal{H}^2)q^2. \qquad (C27)$$

The quantities $C_i^{N\parallel}$ and $C_i^{N\perp}$ are functions of q and ω and are determined by the boundary conditions at the interface as

$$C_1^{N\perp} = \frac{B_2^{\perp}\tilde{v}_y^S - \tilde{n}_y^S}{B_2^{\perp} - B_1^{\perp}}, \qquad (C28)$$

$$C_1^{N\parallel} = [iq(B_3^{\parallel} - B_2^{\parallel})\tilde{v}_x^S + (m_2^{N\parallel} - m_3^{N\parallel})\tilde{n}_x^S$$
$$+ (m_3^{N\parallel}B_2^{\parallel} - m_2^{N\parallel}B_3^{\parallel})\tilde{v}_z^S]/\Delta, \qquad (C29)$$

where

$$\Delta = (B_3^{\parallel} - B_2^{\parallel})m_1^{N\parallel} + (B_1^{\parallel} - B_3^{\parallel})m_2^{N\parallel} + (B_2^{\parallel} - B_1^{\parallel})m_3^{N\parallel}, \qquad (C30)$$

and expressions for $C_2^{N\perp}$, $C_2^{N\parallel}$, and $C_3^{N\parallel}$ are obtained from Eqs. (C28) and (C29) by cyclic permutation of subscript indices

APPENDIX D: EXPLICIT FORM OF DISPERSION RELATION

To write the explicit form of the dispersion relations (103) and (104), we recast Eq. (C28) and (C29) in the form

$$C_i^{N\perp} = L_i^{(vy)}\tilde{v}_y + L_i^{(ny)}\tilde{n}_y, \qquad (D1)$$

$$C_i^{N\parallel} = L_i^{(vx)}\tilde{v}_x + L_i^{(vz)}\tilde{v}_z, + L_i^{(nx)}\tilde{n}_x, \qquad (D2)$$

where

$$L_1^{(vy)} = \frac{B_2^{\perp}}{B_2^{\perp} - B_1^{\perp}}, \qquad (D3)$$

$$L_2^{(vy)} = \frac{B_1^{\perp}}{B_1^{\perp} - B_2^{\perp}}, \qquad (D4)$$

$$L_1^{(ny)} = \frac{1}{B_1^{\perp} - B_2^{\perp}}, \qquad (D5)$$

$$L_2^{(ny)} = \frac{1}{B_2^{\perp} - B_1^{\perp}}, \qquad (D6)$$

$$L_1^{(vx)} = \frac{iq(B_3^{\parallel} - B_2^{\parallel})}{\Delta}, \qquad (D7)$$

$$L_2^{(vx)} = \frac{iq(B_1^{\parallel} - B_3^{\parallel})}{\Delta}, \qquad (D8)$$

$$L_3^{(vx)} = \frac{iq(B_2^{\parallel} - B_1^{\parallel})}{\Delta}, \qquad (D9)$$

$$L_1^{(vz)} = \frac{m_3^{N\parallel}B_2^{\parallel} - m_2^{N\parallel}B_3^{\parallel}}{\Delta}, \qquad (D10)$$

$$L_2^{(vz)} = \frac{m_1^{N\parallel}B_3^{\parallel} - m_3^{N\parallel}B_1^{\parallel}}{\Delta}, \qquad (D11)$$

$$L_3^{(vz)} = \frac{m_2^{N\parallel}B_1^{\parallel} - m_1^{N\parallel}B_2^{\parallel}}{\Delta}, \qquad (D12)$$

$$L_1^{(nx)} = \frac{m_2^{N\parallel} - m_3^{N\parallel}}{\Delta}, \qquad (D13)$$

$$L_2^{(nx)} = \frac{m_3^{N\parallel} - m_1^{N\parallel}}{\Delta}, \qquad (D14)$$

$$L_3^{(nx)} = \frac{m_1^{N\parallel} - m_2^{N\parallel}}{\Delta}, \qquad (D15)$$

Δ is given by Eq. (C30), $B_i^{\perp}$ and $B_i^{\parallel}$ are given by Eqs. (C10) and (C21), and $m_i^{N\perp}$ and $m_i^{N\parallel}$ are given by Eqs. (C22) and (C11), correspondingly.

Then the dispersion relation (104) can be written as

$$\det M^{\perp} = 0, \qquad (D16)$$

where $M^{\perp}$ is 2×2 matrix of coefficients for Eqs. (86) and (101)

$$M^{\perp} = \begin{pmatrix} M_{11}^{\perp} & M_{12}^{\perp} \\ M_{21}^{\perp} & M_{22}^{\perp} \end{pmatrix} \qquad (D17)$$

with the following components:

$$M_{11}^{\perp} = -\eta_s q^2 - \eta m^I + \sum_{i=1}^{2}\left\{-\nu_3 m_i^{N\perp} + \frac{1+\lambda}{2}\right.$$
$$\times [K_3(m_i^{N\perp})^2 - K_2q^2 + \chi_a\mathcal{H}^2]B_i^{\perp}\left.\right\}L_i^{(vy)}, \qquad (D18)$$

$$M_{12}^{\perp} = \sum_{i=1}^{2} \left\{ -\nu_3 m_i^{N\perp} + \frac{1+\lambda}{2} \right.$$

$$\left. \times [K_3(m_i^{N\perp})^2 - K_2 q^2 + \chi_a \mathcal{H}^2]B_i^{\perp} \right\} L_i^{(ny)}, \quad (D19)$$

$$M_{21}^{\perp} = \sum_{i=1}^{2} (K_3 m_i^{N\perp} - W_0 - i\omega\gamma_1^S)B_i^{\perp} L_i^{(vy)}, \quad (D20)$$

$$M_{22}^{\perp} = \sum_{i=1}^{2} (K_3 m_i^{N\perp} - W_0 - i\omega\gamma_1^S)B_i^{\perp} L_i^{(ny)}. \quad (D21)$$

The dispersion relation (103) can be written as

$$\det M^{\parallel} = 0, \quad (D22)$$

where $M^{\parallel}$ is 3×3 matrix of coefficients for Eqs. (85), (87), and (100),

$$M^{\parallel} = \begin{pmatrix} M_{11}^{\parallel} & M_{12}^{\parallel} & M_{13}^{\parallel} \\ M_{21}^{\parallel} & M_{22}^{\parallel} & M_{23}^{\parallel} \\ M_{31}^{\parallel} & M_{32}^{\parallel} & M_{33}^{\parallel} \end{pmatrix} \quad (D23)$$

with the following components:

$$M_{11}^{\parallel} = -\epsilon_0^* q^2 - i\omega\eta(m^I + q) - \frac{\omega}{q}\nu_3 \sum_{i=1}^{3} [(m_i^{N\parallel})^2 + q^2]L_i^{(vx)}$$

$$+ i\omega\frac{1+\lambda}{2} \times \sum_{i=1}^{3} [K_3(m_i^{N\parallel})^2 - K_1 q^2 + \chi_a\mathcal{H}^2]B_i^{\parallel}L_i^{(vx)}, \quad (D24)$$

$$M_{12}^{\parallel} = -\omega\eta(m^I - q) - \frac{\omega}{q}\nu_3 \sum_{i=1}^{3} [(m_i^{N\parallel})^2 + q^2]L_i^{(vz)} + i\omega\frac{1+\lambda}{2}$$

$$\times \sum_{i=1}^{3} [K_3(m_i^{N\parallel})^2 - K_1 q^2 + \chi_a\mathcal{H}^2]B_i^{\parallel}L_i^{(vz)}, \quad (D25)$$

$$M_{13}^{\parallel} = -\frac{\omega}{q}\nu_3 \sum_{i=1}^{3} [(m_i^{N\parallel})^2 + q^2]L_i^{(nx)} + i\omega\frac{1+\lambda}{2}$$

$$\times \sum_{i=1}^{3} [K_3(m_i^{N\parallel})^2 - K_1 q^2 + \chi_a\mathcal{H}^2]B_i^{\parallel}L_i^{(nx)}, \quad (D26)$$

$$M_{21}^{\parallel} = -iq^3\psi - 2\omega q\eta + \frac{i\omega^2\rho^I}{m^I - q} + i\omega\sum_{i=1}^{3} (A_i - 2\nu_1 m_i^{N\parallel})L_i^{(vx)}, \quad (D27)$$

$$M_{22}^{\parallel} = -g|\rho^N - \rho^I| - (\sigma_0 + W_0)q^2 - \kappa_0 q^4 + \frac{\omega^2\rho^I m^I}{q(m^I - q)}$$

$$+ i\omega\sum_{i=1}^{3} (A_i - 2\nu_1 m_i^{N\parallel})L_i^{(vz)}, \quad (D28)$$

$$M_{23}^{\parallel} = \omega q W_0 + i\omega\sum_{i=1}^{3} (A_i - 2\nu_1 m_i^{N\parallel})L_i^{(nx)}, \quad (D29)$$

$$M_{31}^{\parallel} = \sum_{i=1}^{3} \left\{ (K_3 m_i^{N\parallel} - W_0 - i\omega\gamma_1^S)B_i^{\parallel} \right.$$

$$\left. + \frac{q}{\omega}[W_0 + \kappa_0 q^2 - \psi m_i^{N\parallel} + i\omega\gamma_1^S] \right\} L_i^{(vx)}, \quad (D30)$$

$$M_{32}^{\parallel} = \sum_{i=1}^{3} \left\{ (K_3 m_i^{N\parallel} - W_0 - i\omega\gamma_1^S)B_i^{\parallel} \right.$$

$$\left. + \frac{q}{\omega}[W_0 + \kappa_0 q^2 - \psi m_i^{N\parallel} + i\omega\gamma_1^S] \right\} L_i^{(vz)}, \quad (D31)$$

$$M_{33}^{\parallel} = \sum_{i=1}^{3} \left\{ (K_3 m_i^{N\parallel} - W_0 - i\omega\gamma_1^S)B_i^{\parallel} \right.$$

$$\left. + \frac{q}{\omega}[W_0 + \kappa_0 q^2 - \psi m_i^{N\parallel} + i\omega\gamma_1^S] \right\} L_i^{(nx)}. \quad (D32)$$

Note that gravity g has been incorporated into the dispersion relation by adding the hydrostatic pressure term $-g|\rho^N - \rho^I|$ to $M_{22}^{\parallel}$ [Eq. (28)].

By setting $\nu_1 = \nu_2 = \nu_3$, and setting to zero quantities K_1, K_2, K_3, λ, γ_1, $\gamma_{1\parallel}^S$, and χ_a, specific to nematic, and neglecting curvature contributions by setting to zero κ_0 and ψ, the dispersion relation is reduced to the well studied form for the case of isotropic liquids [2,3,52,59].

[1] L. E. Schriven, Chem. Eng. Sci. **12**, 98 (1960).

[2] E. I. Kats and V. V. Lebedev, Sov. Phys. JETP **67**, 940 (1988).

[3] D. M. A. Buzza, Langmuir **18**, 8418 (2002).

[4] J. C. Earnshaw, Adv. Colloid Interface Sci. **68**, 1 (1996).

[5] *Light Scattering by Liquid Surfaces and Complementary Techniques*, edited by D. Langevin (Dekker, New York, 1992).

[6] A. J. Milling, L. R. Hutchings, and R. W. Richards, Langmuir **17**, 5305 (2001).

[7] Z. H. Yang and R. Sharma, Langmuir **17**, 6254 (2001).

[8] J. Eastoe, A. Rankin, R. Wat, C. D. Bain, D. Styrkas, and J. Penfold, Langmuir **19**, 7734 (2003).

[9] Y. Y. Wang, Y. H. Dai, L. Zhang, L. Luo, Y. P. Chu, S. Zhao, M. Z. Li, E. J. Wang, and J. Y. Yu, Macromolecules **37**, 2930 (2004).

[10] K. Sakai, H. Honda, and Y. Hiraoka, Rev. Sci. Instrum. **76**, 063908 (2005).

[11] O. J. Rojas, R. D. Neuman, and P. M. Claesson, J. Phys. Chem. B **109**, 22440 (2005).

[12] C. Kim, A. R. Esker, F. E. Runge, and H. Yu, Macromolecules **39**, 4889 (2006).

[13] P. Cicuta and I. Hopkinson, Colloids Surf., A **233**, 97 (2004).

[14] P. Poulin and H. Stark, Science **275**, 1770 (1997).

[15] G. P. Crawford, R. J. Ondris-Crawford, J. W. Doane, and S. Žumer, Phys. Rev. E **53**, 3647 (1996).

[16] V. S. U. Fazio, F. Nannelli, and L. Komitov, Phys. Rev. E **63**, 061712 (2001).

[17] C. Bahr, Phys. Rev. E **73**, 030702(R) (2006).

[18] J. M. Brake and N. L. Abbott, Langmuir **18**, 6101 (2002).

[19] J. M. Brake, A. D. Mezera, and N. L. Abbott, Langmuir **19**, 6436 (2003).

[20] B. H. Clare and N. L. Abbott, Langmuir **21**, 6451 (2005).

[21] N. A. Lockwood and N. L. Abbott, Curr. Opin. Colloid Interface Sci. **10**, 111 (2005).

[22] N. A. Lockwood, J. J. de Pablo, and N. L. Abbott, Langmuir **21**, 6805 (2005).

[23] D. Langevin and M. A. Bouchiat, J. Phys. (France) **33**, 101 (1972).

[24] C. F. Hayes, J. Colloid Interface Sci. **53**, 115 (1975).

[25] J. D. Parsons and C. F. Hayes, Phys. Rev. A **10**, 2341 (1974).

[26] D. Langevin, J. Phys. (France) **33**, 249 (1972).

[27] D. Langevin and M. A. Bouchiat, Mol. Cryst. Liq. Cryst. **22**, 317 (1973).

[28] D. H. McQueen and V. K. Singhal, J. Phys. D **7**, 1983 (1974).

[29] D. Langevin, J. Phys. (France) **7–8**, 745 (1975).

[30] C. H. Sohl, K. Miyano, J. B. Ketterson, and G. Wong, Phys. Rev. A **22**, 1256 (1980).

[31] V. Popa-Nita and T. J. Sluckin, Phys. Rev. E **66**, 041703 (2002).

[32] V. Popa-Nita and P. Oswald, Phys. Rev. E **68**, 061707 (2003).

[33] V. Popa-Nita, T. J. Sluckin, and S. Kralj, Phys. Rev. E **71**, 061706 (2005).

[34] J. Elgeti and F. Schmid, Eur. Phys. J.: Appl. Phys. **18**, 407 (2005).

[35] S. Wolfsheimer, C. Tanase, K. Shundyak, R. van Roij, and T. Schilling, Phys. Rev. E **73**, 061703 (2006).

[36] A. D. Rey, Langmuir **22**, 219 (2006).

[37] A. D. Rey, Phys. Rev. E **61**, 1540 (2000).

[38] V. K. Gupta, J. J. Skaife, T. B. Dubrovsky, and N. L. Abbott, Science **279**, 2077 (1998).

[39] V. M. Kaganer, H. Möhwald, and P. Dutta, Rev. Mod. Phys. **71**, 779 (1999).

[40] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).

[41] A. D. Price and D. K. Schwartz, J. Phys. Chem. B **111**, 1007 (2007).

[42] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, Course of Theoretical Physics Vol. 6 (Pergamon, Oxford, 1987).

[43] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, Course of Theoretical Physics Vol. 7 (Pergamon, Oxford, 1986).

[44] J.-L. Thiffeault, J. Phys. A **34**, 5875 (2001).

[45] R. Aris, *Vectors, Tensors, and the Basic Equations of Fluid Mechanics* (Dover Publications, New York, 1989).

[46] A. Rapini and M. Papoular, J. Phys. (Paris), Colloq. **30**, C4 (1969).

[47] W. Helfrich, Z. Naturforsch. C **28c**, 693 (1973).

[48] S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Addison-Wesley, Redwood City, CA, 1994).

[49] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Course of Theoretical Physics Vol. 8 (Pergamon, Oxford, 1984).

[50] D. Forster, T. C. Lubensky, P. C. Martin, J. Swift, and P. S. Pershan, Phys. Rev. Lett. **26**, 1016 (1971).

[51] H. Pleiner and H. R. Brand, Continuum Mech. Thermodyn. **14**, 297 (2002).

[52] L. Kramer, J. Chem. Phys. **55**, 2097 (1971).

[53] T. Börzsönyi, Á. Buka, A. P. Krekhov, and L. Kramer, Phys. Rev. E **58**, 7419 (1998).

[54] D. Marsh, Chem. Phys. Lipids **144**, 146 (2006).

[55] I. Lelidis and G. Barbero, Europhys. Lett. **61**, 646 (2003).

[56] G. Barbero, L. R. Evangelista, and I. Lelidis, Phys. Rev. E **67**, 051708 (2003).

[57] I. Lelidis and G. Durand, Phys. Rev. Lett. **73**, 672 (1994).

[58] K. Miyano, Ref. [5], Chap. 16.

[59] J. C. Earnshaw and E. McCoo, Langmuir **11**, 1087 (1995).