

Viscoelastic theory for nematic interfaces

Alejandro D. Rey

Department of Chemical Engineering, McGill University, 3610 University Street, Montreal, Quebec, Canada H3A 2B2

(Received 17 June 1999)

A complete macroscopic theory for compressible nematic-viscous fluid interfaces is developed and used to characterize the interfacial elastic, viscous, and viscoelastic material properties. The derived expression for the interfacial stress tensor includes elastic and viscous components. Surface gradients of the interfacial elastic stress tensor generates tangential Marangoni forces as well as normal forces. The latter may be present even in planar surfaces, implying that in principle static planar interfaces may accommodate pressure jumps. The asymmetric interfacial viscous stress tensor takes into account the surface nematic ordering and is given in terms of the interfacial rate of deformation and interfacial Jaumann derivative. The material function that describes the anisotropic viscoelasticity is the dynamic interfacial tension, which includes the interfacial tension and dilational viscosities. Viscous dissipation due to interfacial compressibility is described by the anisotropic dilational viscosity, and it is shown to describe the Boussinesq surface fluid appropriate for Newtonian interfaces when the director is homeotropic. Three characteristic interfacial shear viscosities are defined according to whether the surface orientation is along the velocity direction, the velocity gradient, or the unit normal. In the last case the expression reduces to the interfacial shear viscosity of the Boussinesq surface fluid. The theory provides a theoretical framework to study interfacial stability, thin liquid film stability and hydrodynamics, and any other interfacial rheology phenomena.

PACS number(s): 64.70.Md, 68.10.Et, 61.30.Cz

I. INTRODUCTION

Interfacial viscoelasticity is one of the foundational elements of interfacial dynamics and interfacial rheology [1–5]. For interfaces between viscous Newtonian fluids it has been found that the main interfacial material properties are the interfacial tension, the interfacial dilational viscosity, and the interfacial shear viscosity. These material properties enter into the description of a wide range of interfacial phenomena such as interfacial stability, thin liquid film hydrodynamics, thin liquid film stability, emulsion and foam rheology [1].

The surface physics of nematic liquid crystals is currently an active area of research [6–10] since many applications of liquid crystalline materials involve multiphase systems, where interfaces play significant roles. The description of dynamical interfacial phenomena involving nematic liquid crystal phases requires, as in interfaces between Newtonian fluids, viscoelastic models that describe material properties such as the dynamic interfacial tension and interfacial viscosities. Interfacial orientation phenomena and orientational transitions are well characterized experimentally [7–9] and theoretically [7–9,11–14]. On the other hand, knowledge of interfacial dissipative phenomena is less developed. A theory of the role of interfacial rotational viscosity on hydrodynamic out-of-plane orientational instabilities during shear flow of nematic liquid crystals has been given [15]. The role of interfacial rotational dissipation on the wave length selection mechanism that occurs during magnetic reorientation of thin films of nematic polymers has been studied [16] and found to be consistent with experimental data. The interfacial rotational viscosity of a lyotropic liquid crystal in contact with a glass substrate and subjected to a magnetic field has been measured by postulating gliding of the director at the surface [17]. Certain measurements of the power spectrum of thermal fluctuations of the free surface of a nematic liquid

crystal in a magnetic field taking into account the competition of molecular order in the bulk and at the surface were interpreted using the concept of translational surface viscosity [18]. Thus no systematic theoretical characterization of the viscoelasticity of deforming and translating nematic interfaces has been performed. Such a theory is a prerequisite to study capillary phenomena involving nematic liquid crystal phases and will be presented in this paper.

For the so-called Newtonian interface the appropriate model is the Boussinesq surface fluid [1,5] whose physical predictions are embodied in the expression of interfacial stress tensor. As is well known [1,5] the interfacial linear momentum balance equation involves the surface gradient of the interfacial stress tensor, and its normal component determines the shape of the deforming interface, while its tangential component enters into the description of Marangoni flows such as those present in thermocapillarity, diffusocapillarity, and electrocapillarity. The Boussinesq interfacial stress tensor is a 2×2 symmetric, tangential tensor [1,5,19] and as such it is unable to describe the anisotropic viscoelasticity of nematic interfaces that arises due to the liquid crystalline orientational order [20].

A hallmark of the bulk mechanical behavior of nematic liquid crystalline materials is the anisotropic character of the viscoelastic modes [21,22]. The anisotropic Frank elasticity is now well established and responsible for many pattern selection phenomena in the presence of external fields [23]. A well-known example is the splay-avoidance mechanism active in deformations of nematic polymers. Viscous anisotropies are also well-characterized experimentally [20,22] and theoretically [22,24]. One prominent example here is the ordering in magnitude of the three Miesowicz shear viscosities, where the largest flow resistance is obtained when the average molecular orientation is fixed along the velocity gradient direction and the smallest when the

average molecular orientation is fixed along the vorticity. In addition, the shear flow-alignment properties that dictate whether the average orientation is close to the flow direction depends in part on the difference between two Miesowicz shear viscosities. These few examples show the prominence of anisotropic viscoelasticity in the bulk behavior of nematic liquid crystals.

It is expected that anisotropic viscoelasticity may play a similarly prominent role in the interfacial behavior of interfaces involving nematic liquid crystals. The anisotropic elastic nature of nematic interfaces is well understood [7–9,13,14] but its consequences in the presence of deforming interfaces has not been systematically studied. Elastic models for deforming nematic-viscous fluid interfaces have already been proposed [25–29] and used to describe nemato-capillarity phenomena such as bending stresses and Marangoni flows [28,29]. In these previous models the interface was considered to be incompressible and purely elastic. The presence of interfacial viscous modes and compressibility is now well established [1,5] and thus a more comprehensive model for nematic interfaces including compressibility and anisotropic viscous dissipation is in order. The present paper builds on previous work on incompressible elastic nematic interface models [25–29] and adds the required compressibility and dissipative elements to build a general viscoelastic model appropriate for compressible nematic-isotropic viscous fluid interfaces, denoted below as N/I . It should be mentioned that a related rigorous thermodynamic theory for two dimensional liquid crystals has been presented by Papenfuss and Muschik [30,31].

The objectives of this paper are (1) to derive a general expression for the interfacial anisotropic viscoelastic stress tensor for compressible interfaces between nematic liquid crystals and isotropic viscous fluids, and (2) define and characterize the main elastic, viscous, and viscoelastic material properties of such interfaces.

The organization of this paper is as follows. Section II defines the geometric properties of the N/I interface, and the objective kinematic measures that include the surface rate of deformation tensor and the surface Jaumann derivative of the nematic orientation field. It also presents the interfacial torque balance equation and the interfacial linear momentum balance equation. It presents and discusses the interfacial free energy density and defines the easy axis of N/I . Section III presents a concise derivation of the interfacial elastic stress tensor, identifies the tension (normal) and bending stress components, and identifies the principal orientation at which the bending stresses vanish for all possible parametric cases. Section IV presents a characterization and discussion of the nematic Marangoni and normal forces for all possible parametric cases. It identifies the normal forces acting a N/I interface of zero curvature. Section V presents a derivation of constitutive equations for the interfacial extra stress tensor and interfacial viscous molecular field. Thermodynamic restrictions on viscosity parameters are derived and consistency with the Bussinesq surface fluid is proved. Section VI presents a derivation of the dynamical interfacial tension and includes the development of an expression for its anisotropy. Section VII presents a derivation of the interfacial dilational viscosity and includes the development of an expression for its anisotropy. Section VIII presents the three interfacial

shear viscosities when the average molecular orientation is fixed along the surface velocity direction, the surface velocity gradients, or the unit normal to the N/I interface. Section IX presents the main conclusions.

II. INTERFACIAL BALANCE EQUATIONS

In this section we consider the interfacial torque balance equation and interfacial linear momentum balance equations that govern the dynamics of the interfacial director orientation, and the shape of the deforming interface between a nematic liquid crystal (N) and an isotropic viscous fluid (I), under isothermal conditions.

A. Nematic-isotropic fluid interface

The N/I interface is characterized by a unit normal \mathbf{k} , directed from the nematic phase into the isotropic phase, whose mean curvature is given by [1]

$$H = -\frac{1}{2}\nabla_S \cdot \mathbf{k} = \frac{1}{2}\mathbf{I}_S : \mathbf{b} = -\frac{1}{2}\mathbf{I}_S : \nabla_S \mathbf{k} = \frac{1}{2}(k_1 + k_2), \quad (1a)$$

$$\mathbf{b} = -\nabla_S \mathbf{k} = k_1 \mathbf{e}_1 + k_2 \mathbf{e}_2, \quad (1b)$$

where $\nabla_S = \mathbf{I}_S \cdot \nabla$ is the surface gradient, \mathbf{I}_S is the 2×2 unit surface dyadic, \mathbf{b} is the 2×2 symmetric surface curvature dyadic, and where $\{\kappa_i\}$ and $\{\mathbf{e}_i\}$, $i=1,2$ are the eigenvalues and eigenvectors of \mathbf{b} . The divergence of \mathbf{I}_S is a normal vector: $\nabla_S \cdot \mathbf{I}_S = 2H\mathbf{k}$.

At the N/I interface the nematic ordering is defined by the three-component orientation vector known as the director [20], $\mathbf{n} = \mathbf{n}(\mathbf{x}_S)$, where $\mathbf{n} \cdot \mathbf{n} = 1$, and \mathbf{x}_S is the surface position vector. A useful decomposition, used below, of the surface director field into tangential and normal components is: $\mathbf{n}_\parallel = \mathbf{I}_S \cdot \mathbf{n}$ and $\mathbf{n}_\perp = \mathbf{k}\mathbf{k} \cdot \mathbf{n}$.

B. Kinematics of deforming interfaces

The kinematic tensors needed to describe the N/I interfacial dynamics are the 2×2 symmetric surface rate of deformation tensor \mathbf{A}^S and the 2×2 antisymmetric surface vorticity tensor \mathbf{W}^S , given by [1,5,19]

$$\mathbf{A}^S = \frac{1}{2}(\nabla_S \mathbf{v}^0 \cdot \mathbf{I}_S + \mathbf{I}_S \cdot [\nabla_S \mathbf{v}^0]^T), \quad (2a)$$

$$\mathbf{W}^S = \frac{1}{2}(\nabla_S \mathbf{v}^0 \cdot \mathbf{I}_S - \mathbf{I}_S \cdot [\nabla_S \mathbf{v}^0]^T), \quad (2b)$$

where \mathbf{v}^0 is the surface velocity field, and the superscript T denotes the transpose. The decomposition of the velocity surface gradient tensor $\nabla_S \mathbf{v}^0$ into its symmetric \mathbf{A}^S and antisymmetric parts \mathbf{W}^S is

$$\nabla_S \mathbf{v}^0 \cdot \mathbf{I}_S = \mathbf{A}^S + \mathbf{W}^S, \quad (3)$$

where the unit surface dyadic is needed since $\nabla_S \mathbf{v}^0$ is a 2×3 tensor, while $(\mathbf{A}^S, \mathbf{W}^S)$ are 2×2 tensors. The surface rate of deformation \mathbf{A}^S and the surface vorticity tensor \mathbf{W}^S obey the following relations:

$$\mathbf{A}^S = \mathbf{I}_S \cdot \mathbf{A}^S = \mathbf{A}^S \cdot \mathbf{I}_S = \mathbf{I}_S \cdot \mathbf{A}^S \cdot \mathbf{I}_S, \quad (4a)$$

$$\mathbf{A}^S \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{A}^S = 0, \quad (4b)$$

$$\mathbf{W}^S = \mathbf{I}_S \cdot \mathbf{W}^S = \mathbf{W}^S \cdot \mathbf{I}_S = \mathbf{I}_S \cdot \mathbf{W}^S \cdot \mathbf{I}_S, \quad (5a)$$

$$\mathbf{W}^S \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{W}^S = 0. \quad (5b)$$

The surface vorticity vector $\boldsymbol{\omega}^S$ is related to the surface vorticity tensor \mathbf{W}^S by

$$\boldsymbol{\omega}^S = -\boldsymbol{\epsilon} : \mathbf{W}^S \quad (6)$$

and is a vector orthogonal to the interface: $\mathbf{I}_S \cdot \boldsymbol{\omega}^S = 0$.

The kinematic vector needed to describe director dynamics is the surface Jaumann derivative of the tangential component of the director \mathbf{N}^S [32]:

$$\mathbf{N}^{S'} = \mathbf{I}_S \cdot \frac{d\mathbf{n}_\parallel}{dt} - \boldsymbol{\omega}^S \times \mathbf{n}_\parallel, \quad (7a)$$

$$\mathbf{n}_\parallel = \mathbf{I}_S \cdot \mathbf{n}, \quad (7b)$$

which is a two-component tangential vector: $\mathbf{N}^S = \mathbf{I}_S \cdot \mathbf{N}^S$. In the general case $\mathbf{N}^S \cdot \mathbf{n}_\parallel = \mathbf{n}_\parallel \cdot d\mathbf{n}_\parallel/dt \neq 0$. The surface Jaumann derivative measures the rotation of the tangential component of the director relative to the background fluid. Since the only background fluid rotations are in the tangent plane, the only director rotations included in the Jaumann derivative are those of the \mathbf{n}_\parallel component. Director rotations around a tangential axis are excluded from the surface Jaumann derivative, and as a consequence the restriction $\mathbf{n} \cdot \mathbf{N} = 0$ that holds in the bulk case does not apply in the surface case.

The director surface Jaumann derivative defined above is an objective tensor that obeys the following transformation [32]:

$$\bar{\mathbf{N}}^S = \mathbf{Q}_S \cdot \mathbf{N}^S \quad (8)$$

where \mathbf{Q}_S is an orthogonal tangential transformation. Since \mathbf{A}^S and \mathbf{N}^S are objective they will appear in the constitutive equations for the surface extra stress tensor and the viscous molecular field, as discussed below.

C. Interfacial torque balance equation

The interfacial director torque balance equation is given by the balance of the surface elastic torque Γ^{se} and the surface viscous torque Γ^{sv} :

$$\mathbf{\Gamma}^{se} + \mathbf{\Gamma}^{sv} = 0, \quad (9)$$

$$\mathbf{\Gamma}^{se} = \mathbf{n} \times \mathbf{h}_e^s, \quad (10a)$$

$$\mathbf{\Gamma}^{sv} = -\mathbf{n} \times \mathbf{h}_v^s \quad (10b)$$

where \mathbf{h}_e^s is the surface elastic molecular field, and \mathbf{h}_v^s is the surface viscous molecular field. The elastic and viscous molecular fields ($\mathbf{h}_e^s, \mathbf{h}_v^s$) are three component vectors, with tangential ($\mathbf{h}_{e\parallel}^s, \mathbf{h}_{v\parallel}^s$) and normal ($\mathbf{h}_{e\perp}^s, \mathbf{h}_{v\perp}^s$) components with respect to the surface. The surface elastic molecular field \mathbf{h}^{se} given by

$$h_{ei}^s = -\frac{\partial F_s}{\partial n_i} - \frac{\partial F_b}{\partial n_{i,j}} k_j, \quad (11)$$

where F_S is the surface free energy density, and F_b is the well-known Frank energy density [20]. We next summarize

the relevant features of F_S for the present work. For a discussion of F_b please see Ref. [20].

The surface free energy density F_S is given by [11–14]

$$F_S(\mathbf{n} \cdot \mathbf{k}, T) = \tau_0(T) + \tau_{an}(\mathbf{n} \cdot \mathbf{k}, T),$$

$$\tau_{an}(\mathbf{n} \cdot \mathbf{k}, T) = \tau_2(T)[\mathbf{n} \cdot \mathbf{k}]^2 + \tau_4(T)[\mathbf{n} \cdot \mathbf{k}]^4, \quad (12)$$

where T is the temperature, τ_0 is the isotropic interfacial tension, and τ_{an} is the anisotropic contribution to the surface free energy, known as the anchoring energy. For low molar mass nematic liquid crystals the isotropic surface interfacial tension τ_0 is of the order of 10 ergs/cm², while the anchoring energy τ_{an} varies from 10⁻⁴ to 1 erg/cm² [7]. The nematic-isotropic interface of low-molar mass materials has a τ_0 of the order of 10⁻² erg/cm² and appears to be of similar magnitude than the anchoring energy [33–34]. No comprehensive data on interfacial energies and anchoring energies seems to be available for nematic main-chain and side-chain polymers. The director orientation that absolutely minimizes the surface free energy density is known as the easy axis of the interface. For Eq. (12) the easy axes are [13] the following:

(i) $\tau_2/2\tau_4 > 0$ and $\tau_2 > 0$, the easy axis is along the surface and the orientation is known as planar;

(ii) $\tau_2/2\tau_4 > 0$ and $\tau_2 < 0$, the easy axis is perpendicular to the surface and the orientation is known as homeotropic;

(iii) $-1 < \tau_2/2\tau_4 < 0$ and $\tau_2 < 0$, the easy axis is at an oblique angle given by $\cos(\mathbf{n} \cdot \mathbf{k}) = \sqrt{-\tau_2/2\tau_4}$;

(iv) $-1 < \tau_2/2\tau_4 < 0$ and $\tau_2 > 0$, the easy axis is along the surface, while the homeotropic orientation is a local minimum of F_S . The expression (12) for F_S is sufficient to explain all the interfacial orientations and transitions observed in experiments [13].

D. Interfacial linear momentum balance equation

At the N/I interface the linear momentum balance equation, that generalizes the Laplace equation to nonequilibrium cases, is given by [1,5],

$$-\mathbf{k} \cdot (\mathbf{t}^I - \mathbf{t}^N) = \nabla_S \cdot \mathbf{t}_e^S + \nabla_S \cdot \mathbf{t}_v^S, \quad (13)$$

where \mathbf{t}^N is the total stress tensor in the nematic phase at N/I , \mathbf{t}^I is the total stress tensor in the isotropic fluid phase at N/I , \mathbf{t}_e^S is the elastic surface stress tensor, and \mathbf{t}_v^S is the viscous ‘‘extra’’ surface stress tensor. The surface stress tensors are functions of the following fields:

$$\mathbf{t}_e^S = \mathbf{t}_e^S(\mathbf{I}_S, \mathbf{n}, \mathbf{k}); \quad \mathbf{t}_v^S = \mathbf{t}_v^S(\mathbf{I}_S, \mathbf{n}, \mathbf{A}^S, \mathbf{N}^S). \quad (14)$$

As shown below, in the general case the elastic stress tensor \mathbf{t}_e^S is a 2×3 tensor whose gradients represent tangential and normal elastic forces. The elastic tensor \mathbf{t}_e^S obeys: $\mathbf{t}_e^S = \mathbf{I}_S \cdot \mathbf{t}_e^S$. On the other hand, \mathbf{t}_v^S is a 2×2 tensor [5,19] The viscous surface stress tensor \mathbf{t}_v^S obeys: $\mathbf{t}_v^S = \mathbf{I}_S \cdot \mathbf{t}_v^S = \mathbf{t}_v^S \cdot \mathbf{I}_S = \mathbf{I}_S \cdot \mathbf{t}_v^S \cdot \mathbf{I}_S$; $\mathbf{t}_v^S \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{t}_v^S = 0$. The decomposition of the interfacial momentum balance equation leads to the following tangential and normal force balances:

$$-\mathbf{k} \cdot (\mathbf{t}^I - \mathbf{t}^N) \cdot \mathbf{I}_S = (\nabla_S \cdot \mathbf{t}_e^S) \cdot \mathbf{I}_S + (\nabla_S \cdot \mathbf{t}_v^S) \cdot \mathbf{I}_S, \quad (15)$$

$$-\mathbf{k} \cdot (\mathbf{t}^1 - \mathbf{t}^N) \cdot \mathbf{k} \mathbf{k} = (\nabla_S \cdot \mathbf{t}_e^S) \cdot \mathbf{k} \mathbf{k} + (\nabla_S \cdot \mathbf{t}_v^S) \cdot \mathbf{k} \mathbf{k}, \quad (16)$$

where the first balance equation (tangential stress) describes interfacial tangential Marangoni flows, and the second (normal stress) balance equation is used to find the shape of the deforming interface. For N/I interfaces the torque balance equation is coupled to the linear momentum balance equation since \mathbf{k} and \mathbf{n} appear in both equations. The viscoelasticity of N/I is represented by $(\mathbf{t}_e^S, \mathbf{t}_v^S)$.

In partial summary, Sec. II shows that the interfacial torque and linear momentum balance equations that describe orientation and shape dynamics are coupled through the director and the unit normal. The anchoring energy contributes to both surface forces and surfaces torques. The easy axis of the surface depends on the relative sign and magnitudes of the anchoring coefficients. The objective kinematic tensor that describes surface distortions is the 2×2 symmetric rate of deformation tensor \mathbf{A}^S , and the objective vector that describes the relative rotation of the director with respect to the surface motion is the surface Jaumann derivative \mathbf{N}^S . These basic results are used below to develop the expressions of the components of the viscoelastic stress tensor.

III. NEMATIC ELASTIC SURFACE STRESS TENSOR

The expression of the elastic surface stress tensor is found basically by noting that $F_S = F_S(\mathbf{n} \cdot \mathbf{k})$ and by using the identity $\mathbf{t}_e^S = \mathbf{I}_S \cdot \mathbf{t}_e^S$. The surface elastic stress tensor is given by the usual 2×2 symmetric interfacial tension contribution \mathbf{t}_{en}^S (normal stresses) and the 2×3 anisotropic contribution \mathbf{t}_{eb}^S (bending stresses):

$$\mathbf{t}_e^S = \mathbf{t}_{en}^S + \mathbf{t}_{eb}^S, \quad (17a)$$

$$\mathbf{t}_{en}^S = F_S \mathbf{I}_S. \quad (17b)$$

To find the expression for the bending stresses we can use the principle of virtual work. The change in surface free energy δF_t due to a displacement \mathbf{u} is

$$\delta F_t = \int \mathbf{t}_{eb}^S : (\nabla_S \mathbf{u})^T dS = \int \frac{\partial \tau_{an}}{\partial \mathbf{k}} \delta \mathbf{k} dS. \quad (18)$$

Using the fact that

$$\delta \mathbf{k} = -\mathbf{k} \cdot (\nabla_S \mathbf{u})^T, \quad (19)$$

we find that the bending stresses are given by [24–29]

$$\mathbf{t}_{eb}^S = -\mathbf{I}_S \cdot \left[\frac{\partial \tau_{an}}{\partial \mathbf{k}} \mathbf{k} \right] = -\mathbf{I}_S \cdot \left[\left(\frac{d\tau_{an}}{d(\mathbf{n} \cdot \mathbf{k})} \right) \mathbf{n} \mathbf{k} \right]. \quad (20)$$

Parametrizing the N/I interface with orthonormal unit surface base vectors (i_1, i_2) , the normal and bending stresses become

$$\mathbf{t}_{en}^S = F_S [i_1 i_1 + i_2 i_2], \quad (21a)$$

$$\mathbf{t}_{eb}^S = B_{13} i_1 \mathbf{k} + B_{23} i_2 \mathbf{k}, \quad (21b)$$

where the bending coefficients $[B_{13}, B_{23}]$ are given by

$$B_{13} = -i_1 \cdot (d\tau_{an}/d\mathbf{k}), \quad (22a)$$

$$B_{23} = -i_2 \cdot (d\tau_{an}/d\mathbf{k}), \quad (22b)$$

$$d\tau_{an}/d\mathbf{k} = [2\tau_2(\mathbf{k} \cdot \mathbf{n}) + 4\tau_2(\mathbf{k} \cdot \mathbf{n})^3] \mathbf{n}. \quad (23)$$

The bending coefficients $[B_{13}, B_{23}]$ are the projections of the derivative of the interfacial free energy with respect to the unit normal onto the unit surface vectors (i_1, i_2) . The bending coefficients $[B_{13}, B_{23}]$ are proportional to the amount of surface energy storage when the director deviates from its easy axis and to the orientation of the director with respect to the interface.

Two important properties of the elastic surface stress tensor, to be frequently used in the rest of the paper, are (i) the principal orientations at which bending stresses vanish, and (ii) the orientations corresponding to the extrema in bending stresses, as follows.

A. Principal orientations

The principal orientations of the elastic surface stress tensor are defined as the surface director orientations at which the surface stress tensor is diagonal, that is, the elastic stress tensor has only normal (tension) components. It turns out that for nematic interfaces bending stresses vanish when normal stresses achieve their extrema. This is a consequence of the fact that the magnitudes of the normal stresses are τ_{an} while the magnitudes of the bending stresses are proportional to $d(\tau_{an})/d\mathbf{k}$. From the above discussion it follows that the principal orientations occur at the following surface director orientations.

$$(a) \tau_2/2\tau_4 > 0, \tau_2 < 0 \text{ and } \tau_2/2\mu_4 > 0, \tau_2 > 0$$

$$\mathbf{n} \cdot \mathbf{k} = 1, \quad (24a)$$

$$\mathbf{n} \cdot \mathbf{k} = 0. \quad (24b)$$

For these two sets of parametric conditions, normal stresses extrema and zero bending stresses occur at planar and homeotropic director orientation.

$$(b) -1 < \tau_2/2\tau_4 < 0, \tau_2 < 0 \text{ and } -1 < \tau_2/2\tau_4 < 0, \tau_2 > 0$$

$$\mathbf{n} \cdot \mathbf{k} = 1, \quad \mathbf{n} \cdot \mathbf{k} = 0, \quad (25a)$$

$$\mathbf{k} \cdot \mathbf{n} = \pm \sqrt{-\frac{\tau_2}{2\tau_4}}. \quad (25b)$$

For these two sets of parametric conditions, normal stress extrema and zero bending stresses occur at the planar, homeotropic, and oblique director orientations.

B. Bending stress extrema

The extrema in bending stresses is found by solving $d^2(\tau_{an})/d^2\mathbf{k} = 0$,

$$(a) \tau_2/2\tau_4 > 0, \tau_2 < 0, \text{ and } \tau_2/2\tau_4 > 0, \tau_2 > 0$$

$$(\mathbf{k} \cdot \mathbf{n})^2 = \left\{ -\left(\frac{\tau_2}{\tau_4} - 3\right) + \left[\left(\frac{\tau_2}{\tau_4} - 3\right)^2 - 8\frac{\tau_2}{\tau_4} \right]^{1/2} \right\} / 8. \quad (26)$$

In this case there is only one stress extremum at a director angle lying between the planar and homeotropic orientations.

(b) $-1 < \tau_2/2\tau_4 < 0$, $\tau_2 < 0$ and $-1 < \tau_2/2\tau_4 < 0$, $\tau_2 > 0$

$$(\mathbf{k}^{N\alpha} \cdot \mathbf{n})^2 = \left\{ -\left(\frac{\tau_2}{\tau_4} - 3\right) \pm \left[\left(\frac{\tau_2}{\tau_4} - 3\right)^2 - 8\frac{\tau_2}{\tau_4} \right]^{1/2} \right\} / 8. \quad (27)$$

There are two director orientations of zero bending stress between their three extrema.

In partial summary, Sec. III provides a concise derivation of the surface elastic stress tensor, and characterizes the tension and bending components for the different anchoring cases. The principal directions of the surface elastic stress tensor are derived and discussed.

IV. ANISOTROPIC INTERFACIAL ELASTICITY: MARANGONI AND NORMAL FORCES

The physical significance of the normal and bending components of the surface stress tensor is clear and evident when one considers the net surface forces engendered by their surface gradients:

$$\mathbf{f} = \nabla_S \cdot \mathbf{t} = \underbrace{\left\{ \left[\frac{d\tau_{an}}{d\mathbf{n} \cdot \mathbf{k}} \right] \mathbf{k} \cdot (\nabla_S \mathbf{n})^T \right\}}_{\text{surface gradients in normal stresses}} \cdot \mathbf{I}_S + \underbrace{\left\{ -2H \left(\frac{d\tau_{an}}{d\mathbf{k}} \cdot \mathbf{k} \right) - \nabla_S \cdot \left(\frac{d\tau_{an}}{d\mathbf{k}} \right) \right\}}_{\text{surface gradients in bending stresses}} \mathbf{k}. \quad (28)$$

The normal stresses (t_{11}, t_{22}) generate tangential Marangoni forces $\mathbf{f}_{N\parallel}$:

$$\mathbf{f}_{N\parallel} = \left\{ \left[\frac{d\tau_{an}}{d\mathbf{n} \cdot \mathbf{k}} \right] \mathbf{k} \cdot (\nabla_S \mathbf{n})^T \right\} \cdot \mathbf{I}_S, \quad (29)$$

as well as the usual normal forces $\mathbf{f}_{n\perp}$

$$\mathbf{f}_{n\perp} = \{2HF_S\} \mathbf{k}. \quad (30)$$

The tangential forces $\mathbf{f}_{N\parallel}$ are the nematic Marangoni forces [28,29] caused by surface gradients of the director and are independent of curvature. The normal forces $\mathbf{f}_{n\perp}$ exist only in the presence of curvature, as for isotropic materials. For the anchoring energy τ_{an} given in Eq. (12) the Marangoni force $\mathbf{f}_{N\parallel}$ is given by

$$\begin{aligned} \mathbf{f}_{N\parallel} &= \left\{ \left[\frac{d\tau_{an}}{d\mathbf{n} \cdot \mathbf{k}} \right] \mathbf{k} \cdot (\nabla_S \mathbf{n})^T \right\} \cdot \mathbf{I}_S \\ &= \{(2\tau_2[\mathbf{n} \cdot \mathbf{k}] + 4\tau_4[\mathbf{n} \cdot \mathbf{k}]^3) \mathbf{k} \cdot (\nabla_S \mathbf{n})^T\} \cdot \mathbf{I}_S. \end{aligned} \quad (31)$$

Assuming that $\mathbf{n} = \mathbf{n}(x_1)$, and that as x_1 increases by a distance L the director rotates from planar to homeotropic, the following Marangoni force phenomenology arises.

(i) $\tau_2/2\tau_4 > 0$ and $\tau_2 > 0$, the Marangoni force is directed from the planar to homeotropic orientation region.

(ii) $\tau_2/2\tau_4 > 0$ and $\tau_2 < 0$, the Marangoni force is directed from the homeotropic to the planar orientation region.

(iii) $-1 < \tau_2/2\tau_4 < 0$ and $\tau_2 < 0$, the Marangoni force is directed from the homeotropic and planar orientation regions towards the oblique $[\cos(\mathbf{n} \cdot \mathbf{k}) = \sqrt{-\tau_2/2\tau_4}]$ region.

(iv) $-1 < \tau_2/2\tau_4 < 0$ and $\tau_2 > 0$, the Marangoni force is directed from the oblique $[\cos(\mathbf{n} \cdot \mathbf{k}) = \sqrt{-\tau_2/2\tau_4}]$ orientation region towards the homeotropic and planar orientation regions.

As the name implies bending stresses generate only normal forces $\mathbf{f}_{b\perp}$,

$$\mathbf{f}_{b\perp} = \left\{ -2H \left(\frac{d\tau_{an}}{d\mathbf{k}} \cdot \mathbf{k} \right) - \nabla_S \cdot \left(\frac{d\tau_{an}}{d\mathbf{k}} \right) \right\} \mathbf{k} \quad (32)$$

and exists because nematics have an anisotropic surface tension

$$\begin{aligned} \mathbf{f}_{b\perp} &= \frac{d\tau_{an}}{d(\mathbf{n} \cdot \mathbf{k})} [-\nabla_S \cdot \mathbf{n} - 2H(\mathbf{n} \cdot \mathbf{k})] \mathbf{k} \\ &\quad - \frac{d^2\tau_{an}}{d(\mathbf{n} \cdot \mathbf{k})^2} [\mathbf{kn} : \nabla_S \mathbf{n} - \mathbf{nn} : \mathbf{b}] \mathbf{k}. \end{aligned} \quad (33)$$

In the presence of interfacial director gradients the normal force $\mathbf{f}_{b\perp}$ exists even in the absence of curvature ($H=0, \mathbf{b}=\mathbf{0}$), and its magnitude $f_{b\perp}|_{\text{planar}}$ in this case is

$$f_{b\perp}|_{\text{planar}} = -\frac{d\tau_{an}}{d(\mathbf{n} \cdot \mathbf{k})} (\nabla_S \cdot \mathbf{n}) - \frac{d^2\tau_{an}}{d(\mathbf{n} \cdot \mathbf{k})^2} (\mathbf{kn} : \nabla_S \mathbf{n}). \quad (34)$$

Thus we find the surprising result planar interfaces ($H=0, \mathbf{b}=\mathbf{0}$) between nematics and isotropic materials may have a normal pressure jump if the surface director orientation is space-dependent. A similar observation has been presented previously by Papenfuss and Muschik [35] who note that normal stresses may not vanish even in the case of planar interfaces.

In partial summary, Sec. V shows the main characteristics of the tangential and normal elastic forces. It is shown that the tangential Marangoni forces arise due to interfacial director gradients. Normal forces may persist even in planar interfaces if interfacial director gradients exist. Thus even a planar N/I interface may accommodate pressure jumps.

V. INTERFACIAL ENTROPY PRODUCTION AND CONSTITUTIVE EQUATIONS

In this section constitutive equations for the surface extra stress tensor \mathbf{t}_v^S and the surface viscous molecular field \mathbf{h}_v^S are derived for isothermal, compressible N/I interfaces. As noted in the literature [1], incompressible interfaces are rare or non-existent and surface dilational effects must be taken into account. To find expressions for the surface extra stress tensor \mathbf{t}_v^S and the surface viscous molecular field \mathbf{h}_v^S we identify the forces and fluxes that contribute to the product of temperature times the surface rate of entropy production, Δ , as follows

$$\Delta = \mathbf{t}_{vs}^S : \mathbf{A}^S + \mathbf{t}_{va}^S : \mathbf{W}^S + \mathbf{h}_{v\parallel}^S \cdot \left(\mathbf{I}_S \cdot \frac{d\mathbf{n}_{\parallel}}{dt} \right) + \mathbf{h}_{v\perp}^S \cdot \left(\mathbf{kk} \cdot \frac{d\mathbf{n}_{\perp}}{dt} \right), \quad (35)$$

where \mathbf{t}_{vs}^s is the surface symmetric extra stress tensor, \mathbf{t}_{va}^s is the surface asymmetric extra stress tensor, $\mathbf{h}_{v\parallel}^s$ is the parallel component of the surface viscous molecular field, $d\mathbf{n}_{\parallel}/dt$ is the total derivative of the parallel director component,

$$\frac{d\mathbf{n}_{\parallel}}{dt} = \frac{\partial \mathbf{n}_{\parallel}}{\partial t} + \mathbf{v}^s \cdot \nabla_s \mathbf{n}_{\parallel}, \quad (36a)$$

$$\mathbf{n}_{\parallel} = \mathbf{I}_s \cdot \mathbf{n}. \quad (36b)$$

$\mathbf{h}_{v\perp}^s$ is the normal component of the surface viscous molecular field, $d\mathbf{n}_{\perp}/dt$ is the total derivative of the normal director component,

$$\frac{d\mathbf{n}_{\perp}}{dt} = \frac{\partial \mathbf{n}_{\perp}}{\partial t} + \mathbf{v}^s \cdot \nabla_s \mathbf{n}_{\perp}, \quad (37a)$$

$$\mathbf{n}_{\perp} = \mathbf{kk} \cdot \mathbf{n}. \quad (37b)$$

The 2×2 anisymmetric extra stress tensor \mathbf{t}_{va}^s can be written in terms of the tangential viscous molecular field $\mathbf{h}_{v\parallel}^s$:

$$\mathbf{t}_{va}^s = \frac{1}{2} [\mathbf{h}_{v\parallel}^s \mathbf{n}_{\parallel} - \mathbf{n}_{\parallel} \mathbf{h}_{v\parallel}^s], \quad (38)$$

which shows that when $\mathbf{n} = \mathbf{k}$, the interface is Newtonian and $\mathbf{t}_{va}^s = 0$. Eliminating \mathbf{t}_{va}^s , Δ becomes

$$\Delta = \mathbf{t}_{vs}^s : \mathbf{A}^s + \mathbf{h}_{v\parallel}^s \cdot \mathbf{N}^s + \mathbf{h}_{v\perp}^s \cdot \mathbf{kk} \cdot \frac{d\mathbf{n}_{\perp}}{dt}, \quad (39)$$

which shows that only the tangential fluxes ($\mathbf{t}_{vs}^s, \mathbf{h}_{v\parallel}^s$) are coupled. Expanding the tangential fluxes ($\mathbf{t}_{vs}^s, \mathbf{h}_{v\parallel}^s$) in terms of the tangential forces ($\mathbf{A}^s, \mathbf{N}^s$)

$$\mathbf{t}_{vs}^s = H_{ijkl}^s \mathbf{A}_{lk}^s + G_{ijk}^{sl} \mathbf{N}_k^s, \quad (40)$$

$$\mathbf{h}_{v\parallel}^s = G_{ijk}^{s2} \mathbf{A}_{kj}^s + M_{ij}^s \mathbf{N}_j^s, \quad (41)$$

where by Onsager reciprocal relations the matrix coefficients satisfy $H_{ijkl}^s = H_{klij}^s$; $G_{ijk}^{s1} = G_{kij}^{s2}$, and $M_{ij}^s = M_{ji}^s$. Imposing symmetry restrictions of forces and fluxes gives: $H_{ijkl}^s = H_{jikl}^s = H_{ijlk}^s$, $G_{ijk}^{s1} = G_{jik}^{s1}$, $G_{ijk}^{s2} = G_{ikj}^{s2}$. Expressing the matrix coefficients in terms of \mathbf{n}_{\parallel} and \mathbf{I}_s we find

$$\begin{aligned} \mathbf{t}_{vs}^s &= \alpha_1^s \mathbf{A}^s : \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} + \frac{1}{2} \gamma_2^s [\mathbf{N}^s \mathbf{n}_{\parallel} + \mathbf{n}_{\parallel} \mathbf{N}^s + \mathbf{I}_s (\mathbf{N}^s \cdot \mathbf{n}_{\parallel})] \\ &+ \alpha_4^s \mathbf{A}^s + \frac{1}{2} (\alpha_5^s + \alpha_6^s) (\mathbf{A}^s \cdot \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} + \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} \cdot \mathbf{A}^s) \\ &+ \alpha_7^s \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} (\mathbf{n}_{\parallel} \cdot \mathbf{N}^s) + \beta_1^s (\mathbf{I}_s : \mathbf{A}^s) + \beta_2^s [\mathbf{n}_{\parallel} \mathbf{n}_{\parallel} (\mathbf{I}_s : \mathbf{A}^s) \\ &+ \mathbf{I}_s (\mathbf{n}_{\parallel} \mathbf{n}_{\parallel} : \mathbf{A}^s)], \end{aligned} \quad (42)$$

$$\mathbf{h}_{v\parallel}^s = \gamma_2^s \mathbf{A}^s \cdot \mathbf{n}_{\parallel} + \gamma_{1\parallel}^s \mathbf{N}^s + \alpha_7^s \mathbf{n}_{\parallel} (\mathbf{n}_{\parallel} \mathbf{n}_{\parallel} : \mathbf{A}^s) + \frac{\gamma_2^s}{2} \mathbf{n}_{\parallel} (\mathbf{I}_s : \mathbf{A}^s). \quad (43)$$

The expression for \mathbf{t}_{vs}^s satisfies the restrictions on the symmetric component of the surface stress tensor, namely: $\mathbf{t}_{vs}^s = \mathbf{I}_s \cdot \mathbf{t}_{vs}^s = \mathbf{t}_{vs}^s \cdot \mathbf{I}_s = \mathbf{I}_s \cdot \mathbf{t}_{vs}^s \cdot \mathbf{I}$. The expression for $\mathbf{h}_{v\parallel}^s$ also satisfies the restriction $\mathbf{h}_{v\parallel}^s = \mathbf{I}_s \cdot \mathbf{h}_{v\parallel}^s$. The coefficients $\{\alpha_1^s; i = 1, \dots, 7\}, \{\gamma_2^s, \gamma_{1\parallel}^s\}, \{\beta_1^s, \beta_2^s\}$ have units of surface viscosi-

ties and are analogous to the Leslie coefficients [20]. The coefficient $\gamma_{1\parallel}^s$ is the tangential rotational viscosity already discussed in the literature [15–17].

The normal component of the molecular field $\mathbf{h}_{v\perp}^s$ is uncoupled to the tangential viscous flow process

$$\mathbf{h}_{v\perp}^s = \gamma_{1\perp}^s \mathbf{kk} \cdot \frac{d\mathbf{n}_{\perp}}{dt}, \quad (44)$$

where $\gamma_{1\perp}^s$ is the normal rotational viscosity. The use of two different rotational viscosities ($\gamma_{1\parallel}^s, \gamma_{1\perp}^s$) was also part of the Kleman-Pikin mode [15] for surface dissipation. The anti-symmetric part of the extra stress tensor \mathbf{t}_{va}^s computed from $\mathbf{t}_{va}^s = [\mathbf{h}_{v\parallel}^s \mathbf{n}_{\parallel} - \mathbf{n}_{\parallel} \mathbf{h}_{v\parallel}^s]/2$ is

$$\mathbf{t}_{va}^s = \frac{\gamma_2^s}{2} (\mathbf{A}^s \cdot \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} - \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} \cdot \mathbf{A}^s) + \frac{\gamma_{1\parallel}^s}{2} (\mathbf{N}^s \mathbf{n}_{\parallel} - \mathbf{n}_{\parallel} \mathbf{N}^s). \quad (45)$$

Using the relations

$$\gamma_{1\parallel}^s = \alpha_3^s - \alpha_2^s, \quad (46a)$$

$$\gamma_2^s = \alpha_3^s + \alpha_2^s = \alpha_6^s - \alpha_5^s, \quad (46b)$$

where the second inequality follows from Onsager's relation, the total surface extra stress tensor \mathbf{t}_v^s and surface viscous molecular field \mathbf{h}_v^s become

$$\begin{aligned} \mathbf{t}_v^s &= \alpha_1^s \mathbf{A}^s : \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} + \alpha_2^s \mathbf{n}_{\parallel} \mathbf{N}^s + \alpha_3^s \mathbf{N}^s \mathbf{n}_{\parallel} + \alpha_4^s \mathbf{A}^s + \alpha_5^s \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} \cdot \mathbf{A}^s \\ &+ \alpha_5^s \mathbf{A}^s \cdot \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} + \alpha_7^s \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} (\mathbf{n}_{\parallel} \cdot \mathbf{N}^s) + \beta_1^s \mathbf{I}_s (\mathbf{I}_s : \mathbf{A}^s) \\ &+ \beta_2^s [\mathbf{n}_{\parallel} \mathbf{n}_{\parallel} (\mathbf{I}_s : \mathbf{A}^s) + \mathbf{I}_s (\mathbf{n}_{\parallel} \mathbf{n}_{\parallel} : \mathbf{A}^s)], \end{aligned} \quad (47)$$

$$\begin{aligned} \mathbf{h}_v^s &= \gamma_2^s \mathbf{A}^s \cdot \mathbf{n}_{\parallel} + \gamma_{1\parallel}^s \mathbf{N}^s + \alpha_6^s \mathbf{n}_{\parallel} (\mathbf{n}_{\parallel} \mathbf{n}_{\parallel} : \mathbf{A}^s) + \frac{\gamma_2^s}{2} \mathbf{n}_{\parallel} (\mathbf{I}_s : \mathbf{A}^s) \\ &+ \gamma_{1\perp}^s \mathbf{kk} \cdot \frac{d\mathbf{n}_{\perp}}{dt}. \end{aligned} \quad (48)$$

The total number of independent surface viscosity coefficients is nine. For incompressible interfaces ($\mathbf{I}_s : \mathbf{A}^s = 0$) the number reduces to seven. For incompressible interfaces and planar orientation ($\mathbf{n}_{\parallel} \cdot \mathbf{N}^s = 0$) the number reduces to five as for the bulk nematodynamics equations. Equations (47) and (48) contain the necessary information to solve dynamical problems involving deforming N/I interfaces.

The surface rate of entropy production is positive definite if the following inequalities are obeyed:

$$\frac{1}{4} (\alpha_1^s + 2\alpha_4^s + \alpha_5^s + \alpha_6^s) + \beta_1^s + \beta_2^s \geq 0, \quad (49)$$

$$\frac{\alpha_4^s}{2} + \beta_1^s \geq 0, \quad (50)$$

$$2\alpha_4^s + \alpha_5^s + \alpha_6^s \geq 0, \quad (51)$$

$$\gamma_{1\parallel}^s \geq 0, \quad (52)$$

$$\gamma_{1\perp}^s \geq 0, \quad (53)$$

$$(2\alpha_4^S + \alpha_5^S + \alpha_6^S)\gamma_{1\parallel}^S - (\gamma_2^S)^2 \geq 0, \quad (54)$$

$$\alpha_4^S \geq 0, \quad (55)$$

where to obtain the inequalities we used a previously given methodology [36]. The thermodynamic inequalities (50) and (55) of the Boussinesq surface fluid [1,5] are recovered when all coefficients except of α_4^S and β_1^S are set to zero. The inequalities are also consistent with those of bulk incompressible nematics where $\mathbf{n} \cdot \mathbf{N} = 0$, $\text{tr} \mathbf{A} = 0$, and $\beta_1^S = \beta_2^S = \alpha_7^S = 0$. Inequalities (49) and (50) are the dilational viscosities (see Sec. VII) of the N/I interface when the director is tangential and normal, respectively.

The Boussinesq surface fluid [1,5] is recovered in the present theory by setting all the interfacial viscosities in Eq. (47) except α_4^S and β_1^S equal to zero, and the surface extra stress tensor becomes

$$\mathbf{t}_{v\parallel}^{S1\text{Boussinesq}} = \alpha_4^S \mathbf{A}^S + \beta_1^S \mathbf{I}_S(\mathbf{I} : \mathbf{A}^S), \quad (56)$$

where $\alpha_4^S/2$ is the interfacial shear viscosity and

$$\eta^s = \frac{\mathbf{t}_v^S : \mathbf{I}_S}{2(\mathbf{I}_S : \mathbf{A}^S)} = \frac{\alpha_4^S}{2} + \beta_1^S, \quad (57)$$

is known as the dilational viscosity. For Newtonian interfaces it is found that the interfacial dilational viscosity is of the same order of magnitude as the interfacial shear viscosity [1]. Thus in contrast to bulk behavior, assuming compressible interfaces appears to be just as necessary for Newtonian and nematic interfaces.

Another check into the consistency of the present model can be obtained by considering homeotropic surface director

orientation. In this case the surface director orientation is along the unit normal: $\mathbf{n} = \mathbf{k}$, and therefore $\mathbf{n}_{\parallel} = 0$. Homeotropic surface director orientation results in surface isotropy because the plane of transverse isotropy is the interface itself. Thus for homeotropic alignment the present model should become equivalent to the classical Boussinesq surface fluid model. Indeed by setting $\mathbf{n}_{\parallel} = 0$ in Eq. (47) we find that resulting expression is identical to Eq. (56), and that Eq. (38) yields: $\mathbf{t}_{va}^S = 0$. Thus we can assert that for homeotropic surface orientation the interfacial viscous modes are identical to those describe by the classical Boussinesq Eq. (56).

In partial summary, Sec. V presents the surface rate of entropy production, and identifies the couplings between 2×2 tangential tensors and two component tangential vectors. Constitutive equations for the surface extra stress tensor and the surface viscous molecular field are found by expanding forces and fluxes and using irreversible thermodynamics principles. Inequalities of the surface viscosities are obtained and shown to be consistent with the Boussinesq surface fluid. The extra stress tensor is shown to be consistent with the Boussinesq constitutive equation appropriate for the Newtonian interface.

VI. DYNAMIC INTERFACIAL TENSION

Dynamic surface tension $\bar{\tau}$ is a measure of the local intensity of tension on a deforming surface and is given by the average normal surface stress [1]:

$$\bar{\tau} = \frac{1}{2} \mathbf{I}_S : \mathbf{t}^S. \quad (58)$$

According to previous results the total surface stress tensor for a N/I interface is

$$\begin{aligned} \mathbf{t}^S = & \alpha_1^S \mathbf{A}^S : \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} + \alpha_2^S \mathbf{n}_{\parallel} \mathbf{N}^S + \alpha_3^S \mathbf{N}^S \mathbf{n}_{\parallel} + \alpha_4^S \mathbf{A}^S + \alpha_5^S \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} \cdot \mathbf{A}^S + \alpha_6^S \mathbf{A}^S \cdot \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} + \alpha_7^S \mathbf{n}_{\parallel} \mathbf{n}_{\parallel} (\mathbf{n}_{\parallel} \cdot \mathbf{N}^S) + \beta_1^S \mathbf{I}_S (\mathbf{I}_S : \mathbf{A}^S) \\ & + \beta_2^S [\mathbf{n}_{\parallel} \mathbf{n}_{\parallel} (\mathbf{I}_S : \mathbf{A}^S) + \mathbf{I}_S (\mathbf{n}_{\parallel} \mathbf{n}_{\parallel} : \mathbf{A}^S)] - \mathbf{I}_S \cdot \left[\left(\frac{d\tau_{an}}{d(\mathbf{n} \cdot \mathbf{k})} \right) \mathbf{nk} \right] + F_S \mathbf{I}_S. \end{aligned} \quad (59)$$

The dynamic interfacial tension $\bar{\tau}$ contains in addition to the thermodynamic interfacial tension F_S , nonequilibrium contributions arising from compressible and director/flow coupling effects. For the present anisotropic viscoelastic stress tensor the dynamic interfacial tension $\bar{\tau}$ is

$$\begin{aligned} \bar{\tau} = & F_S + \frac{\alpha_1^S}{2} (\mathbf{A}^S : \mathbf{n}_{\parallel} \mathbf{n}_{\parallel}) (\mathbf{n}_{\parallel} \cdot \mathbf{n}_{\parallel}) + \frac{\alpha_4^S}{2} (\mathbf{I}_S : \mathbf{A}^S) + \frac{1}{2} (\alpha_5^S + \alpha_6^S) (\mathbf{A}^S : \mathbf{n}_{\parallel} \mathbf{n}_{\parallel}) + \frac{\alpha_7^S}{2} (\mathbf{n}_{\parallel} \cdot \mathbf{n}_{\parallel}) (\mathbf{n}_{\parallel} \cdot \mathbf{n}^S) + \gamma_2^S (\mathbf{N}^S \cdot \mathbf{n}_{\parallel}) + \beta_1^S (\mathbf{I}_S : \mathbf{A}^S) \\ & + \frac{\beta_2^S}{2} [(\mathbf{n}_{\parallel} \cdot \mathbf{n}_{\parallel}) (\mathbf{I}_S : \mathbf{A}^S) + 2(\mathbf{n}_{\parallel} \mathbf{n}_{\parallel} : \mathbf{A}^S)]. \end{aligned} \quad (60)$$

Thus the dynamic interfacial tension is anisotropic: $\bar{\tau} = \bar{\tau}(\mathbf{n}_{\parallel})$. Its two characteristic values are the tangential ($\bar{\tau}_{\parallel}$) and normal ($\bar{\tau}_{\perp}$) dynamic interfacial tensions:

$$\bar{\tau}_{\parallel} = \tau_0 + \frac{1}{2} (\alpha_1^S + \alpha_5^S + \alpha_6^S + 2\beta_2^S) (\mathbf{A}^S : \mathbf{n}_{\parallel} \mathbf{n}_{\parallel}) + \left(\frac{\alpha_4^S}{2} + \beta_1^S + \frac{\beta_2^S}{2} \right) (\mathbf{I}_S : \mathbf{A}^S), \quad (61)$$

$$\bar{\tau}_{\perp} = \tau_0 + \tau_2 + \tau_4 + \left[\frac{\alpha_4^S}{2} + \beta_1^S \right] (\mathbf{I}_S : \mathbf{A}^S). \quad (62)$$

The anisotropy in the dynamic interfacial tension $\Delta \bar{\tau}$ contains the following static and dynamic contributions,

$$\Delta \bar{\tau} = \bar{\tau}_{\parallel} - \bar{\tau}_{\perp} = \tau_2 + \tau_4 - \frac{1}{2}(\alpha_1^S + \alpha_5^S + \alpha_6^S + 2\beta_2^S)(\mathbf{A}^S : \mathbf{n}_{\parallel} \mathbf{n}_{\parallel}) - \left(\frac{\beta_2^S}{2}\right)(\mathbf{I}_S : \mathbf{A}^S). \quad (63)$$

Thus $\Delta \bar{\tau}$ is a representative measure of the anisotropic surface viscoelasticity of N/I interfaces since it is a function of $(\tau_{an}(1), \mathbf{A}^S, \mathbf{n}_{\parallel})$.

In partial summary, in Sec. VI the dynamic interfacial tension for a N/I interface has been defined, its expression has been derived and used to characterize the basic anisotropic viscoelasticity of the N/I interface.

VII. INTERFACIAL DILATIONAL VISCOSITIES

Dilational interfacial dissipation in the N/I interface arises during expansion or contraction flow, as it occurs for example during gas bubble growth or bubble shrinkage in a nematic liquid crystal. For example, injecting a gas at a rate Q into a nematic liquid crystal using a thin capillary tube creates an expanding gas bubble. As the nematic/gas interface grows, elasticity is stored and energy is dissipated by the growing interface. If gas flows into the bubble of radius a at a volumetric flow rate Q , the surface rate of deformation tensor and its trace are given by [1]

$$\mathbf{A}^S = \mathbf{I}_S \frac{Q}{4\pi a^3}, \quad (64)$$

$$\mathbf{A}^S : \mathbf{I}_S = \frac{Q}{2\pi a^3} = \Omega, \quad (65)$$

where Ω is the fractional rate of dilation of the bubble surface. To compute the dilational viscosity η^S we replace Eqs. (64) and (65) into Eq. (57). Not unexpectedly, for N/I interfaces the dilational viscosity is anisotropic and a function of the director orientation: $\eta^S = \eta^S(\mathbf{n})$. The orientation-dependent dilational viscosity is characterized by the tangential dilational viscosity η_{\parallel}^S , and the normal dilational viscosity η_{\perp}^S , given by

$$\eta_{\perp}^S(\mathbf{n} = \mathbf{n}_{\parallel}) = \frac{1}{4}(\alpha_1^S + 2\alpha_4^S + \alpha_5^S + \alpha_6^S) + \beta_1^S + \beta_2^S, \quad (66)$$

$$\eta_{\perp}^S(\mathbf{n} = \mathbf{k}) = \frac{\alpha_4^S}{2} + \beta_1^S, \quad (67)$$

where τ_{\perp}^S is, as expected, identical to the Newtonian result given in Eq. (57). The anisotropy in the dilational viscosity, or equivalently, its deviation from the Newtonian case is

$$\eta_{\parallel}^S - \eta_{\perp}^S = \frac{1}{4}(\alpha_1^S + \alpha_5^S + \alpha_6^S) + \beta_2^S. \quad (68)$$

Measurements of the dilational viscosities, including surface waves, droplet deformation, and maximum bubble pressure method are discussed in the literature [1]. The bubble pressure method is the most accurate and the theory behind the experiment is basically that given in this section.

In partial summary, in Sec. VII the dilational viscosity of the N/I interface has been defined, and its characteristic anisotropy has been derived. A method for its measurement has been suggested.

VIII. INTERFACIAL SHEAR VISCOSITIES

In bulk nematic shear flows the Miesowicz viscosities are measures of the viscous anisotropies [20,24]. For example for a simple shear flow defined by the velocity field \mathbf{v} :

$$\mathbf{v}(y) = (v_x, 0, 0), \quad v_x = \dot{\gamma}y \quad (69)$$

where $\dot{\gamma}$ is the constant shear rate, the following three Miesowicz viscosities $\eta_i, i=1,2,3$ arise

$$t_{yx} = \eta_i \dot{\gamma}, \quad i=1,2,3, \quad (70)$$

where t_{yx} is the nematic shear stress, and the value of i defines the director orientation along the x , y , and z axis, respectively. In this experiment the director is fixed by using a sufficiently strong magnetic field. For rodlike nematic liquid crystals the following viscosity orderings are predicted [24] and measured [20]

$$\eta_2 > \eta_3 > \eta_1. \quad (71)$$

As similar situation arises in interfacial planar shear flows on planar interfaces, and different shear viscosities are predicted according to whether the director is aligned along the velocity direction, the velocity gradient direction, or the unit normal. We consider a planar interface spanned by the x - y axes, with a unit normal \mathbf{k} along the z direction. As in the bulk case we define the following interfacial shear viscosities (i) $\eta_1^S : \mathbf{n}$ parallel to the surface velocity (x) direction; (ii) $\eta_2^S : \mathbf{n}$ parallel to the surface velocity gradient (y) direction; (iii) $\eta_3^S : \mathbf{n}$ parallel to the surface vorticity (z) direction.

The surface velocity field for an homogeneous simple shear flow in a planar interface is

$$\mathbf{v}^0 = \mathbf{v}_{\parallel}^0 = (\dot{\gamma}^S y, 0, 0). \quad (72)$$

The nonzero components of \mathbf{A}^S and \mathbf{N}^S are $A_{xy}^S = A_{yx}^S = \dot{\gamma}/2; N_i^S = -\dot{\gamma}^S n_j/2, i=x,y$. Substituting into the surface extra stress tensor we find the following three surface shear viscosities:

$$\eta_1^S = \frac{1}{2}(\alpha_3^S + \alpha_4^S + \alpha_6^S), \quad (73a)$$

$$\eta_2^S = \frac{1}{2}(-\alpha_2^S + \alpha_4^S + \alpha_5^S), \quad (73b)$$

$$\eta_3^S = \frac{\alpha_4^S}{2}. \quad (73c)$$

Predicting the ordering in terms of magnitudes of the surface viscosities requires a mesoscopic model of interfacial vis-

cosities, which has not yet been developed. Since the surface shear viscosities are functions of the nematic surface scalar order parameter [11,12] it is likely that a model based on excess viscosities will predict ordering reversals in the ordering of the magnitudes of the three shear viscosities when compared to the bulk case [(Eq. (71)].

In partial summary, Sec. VIII presents the interfacial shear viscosities, and in analogy to the bulk nematic shear flow case, it defines the three basic shear viscosities for a planar surface shear flow, when the director is aligned along the velocity direction, the velocity gradient direction, and the unit normal. It is noted that to determine the ordering of the magnitudes of the interfacial shear viscosities requires a mesoscopic model based on excess viscosities.

IX. CONCLUSIONS

A theory for anisotropic viscoelasticity of nematic-isotropic viscous fluid interface has been derived and used to identify the interfacial material properties and to characterize the principal elastic, viscous, and viscoelastic response modes. The anisotropic component of the surface tension is shown to generate tangential Marangoni elastic forces and as well as normal forces. Normal forces may exist even under planar interfaces, implying that pressure jumps may exist on flat interfaces. The viscoelastic nature of the nematic-isotropic viscous fluid interface is embodied by the dynamic surface tension, a material property that consists of the usual interfacial tension terms as well as interfacial dilational viscosities contributions. The dynamic surface tension is aniso-

tropic, and hence depends on the interfacial director orientation. The dilational viscosity of the nematic-isotropic viscous fluid interface is another anisotropic material property that describes dissipation modes during inflation or deflation, as in bubble growth or collapse. It is shown that the anisotropy arises because viscous resistance to interface growth or shrinkage depends on the director orientation; when the director is orthogonal the well-known Boussinesq surface fluid result is recovered. Finally, interfacial shear viscosity anisotropies are analogous to the Miesowicz shear bulk flow viscosities, and three basic material properties emerge according to whether the director is oriented along the interfacial velocity direction, its gradients, or the unit normal, respectively.

The theoretical framework of anisotropic viscoelasticity of nematic-viscous fluid interfaces presented here, including the interfacial tension, dynamical interfacial tension, interfacial shear viscosities, interfacial dilational viscosities, and tangential Marangoni forces provides the necessary tools to measure interfacial material properties and to analyze interfacial phenomena such as interfacial instabilities, thin liquid film hydrodynamics, and nematic freely suspended films and foams.

ACKNOWLEDGMENT

Financial support of the Natural Sciences and Engineering Research Council (NSERC) of Canada is gratefully acknowledged.

-
- [1] D. A. Edwards, H. Brenner, and D. T. Wasan, *Interfacial Transport Processes and Rheology* (Butterworth, MA, 1991).
 - [2] A. W. Adamson, *Physical Chemistry of Surfaces* (John Wiley, New York, 1982), 4th ed.
 - [3] V. G. Levich, *Physicochemical Hydrodynamics* (Prentice-Hall, Englewood Cliffs, N.J., 1962).
 - [4] R. F. Probstein, *Physicochemical Hydrodynamics* (Butterworths, MA, 1989).
 - [5] J. C. Slattery, *Interfacial Transport Phenomena* (Springer-Verlag, New York, 1990).
 - [6] L. M. Blinov and V. G. Chigrinov, *Electrooptic Effects in Liquid Crystal Materials* (Springer-Verlag, New York, 1994).
 - [7] A. A. Sonin, *The Surface Physics of Liquid Crystals* (Gordon and Breach, Amsterdam, 1995).
 - [8] B. Jerome, in *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Wiley-VCH, Weinheim, 1998), Vol. 1.
 - [9] H. Yokoyama, in *Handbook of Liquid Crystal Research*, edited by P. J. Collins and J. S. Patel (Oxford University Press, New York, 1997), Chap. 6, p. 179.
 - [10] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1992), 2nd ed.
 - [11] T. J. Sluckin and A. Poniewierski, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, Chichester, 1986), Chap. 5.
 - [12] A. K. Sen and D. E. Sullivan, *Phys. Rev. A* **35**, 1391 (1987).
 - [13] S. Faetti, in *Physics of Liquid Crystalline Materials*, edited by I.-C. Khoo and F. Simoni (Gordon and Breach, Philadelphia, 1991), Chap. XII, p. 301.
 - [14] G. Barbero and G. Durand, in *Liquid Crystals in Complex Geometries*, edited by G. P. Crawford and S. Zumer (Taylor and Francis, London, 1996), pp. 21–52.
 - [15] M. Kleman and S. A. Pikin, *J. Mecanique*, **18**, 661 (1979).
 - [16] A. D. Rey, *Macromolecules* **24**, 177 (1991).
 - [17] E. A. Oliveira, A. M. Figueiredo Neto, and G. Durand, *Phys. Rev. A* **44**, R825 (1991).
 - [18] D. Langevin and M. A. Bouchiat, *J. Phys.* **33**, 101 (1973).
 - [19] D. Bedeaux, A. Albano, and P. Mazur, *Physica A* **82**, 438 (1976).
 - [20] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, London, 1993), 2nd ed.
 - [21] M. Srinivasarao, *Int. J. Mod. Phys. B* **9**, 2515 (1995).
 - [22] S.-D. Lee and R. B. Meyer, in *Liquid Crystallinity in Polymers*, edited by A. Ciferri (VCH Publishers, New York, 1991).
 - [23] R. B. Meyer, in *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum, and R. B. Meyer (Academic, New York, 1982).
 - [24] H. Ehrentraut and S. Hess, *Phys. Rev. E* **51**, 2203 (1995).
 - [25] J. T. Jenkins and P. J. Barrat, *Q. J. Mech. Appl. Math.* **27**, 111 (1974).
 - [26] J. L. Ericksen, in *Advances in Liquid Crystals*, edited by G. H. Brown (Academic, New York, 1979), Vol. 4, p. 1.
 - [27] E. G. Virga, *Variational Theories for Liquid Crystals* (Chapman Hall, London, 1994).
 - [28] A. D. Rey, *Liq. Cryst.* **26**, 913 (1999).

- [29] A. D. Rey, *J. Chem. Phys.* **110**, 9769 (1999).
- [30] C. Papenfuss and W. Muschik, *Mol. Cryst. Liq. Cryst.* **262**, 473 (1995).
- [31] C. Papenfuss and W. Muschik, *Phys. Rev. E* **56**, 4275 (1997).
- [32] H. Stumpf and J. Badur, *Q. J. Mech. Appl. Math.* **LI**, 161 (1993).
- [33] D. Langevin and M. A. Bouchiat, *Mol. Cryst. Liq. Cryst.* **22**, 317 (1973).
- [34] H. Yokoyama, S. Kobayashi, and H. Kamei, *Mol. Cryst. Liq. Cryst.* **129**, 109 (1985).
- [35] C. Papenfuss and W. Muschik, *Thin Solid Films* **284–285**, 484 (1996).
- [36] B. J. Edwards, A. N. Beris, and M. Grmela, *Mol. Cryst. Liq. Cryst.* **204**, 54 (1991).