

Irreversible thermodynamics of liquid crystal interfaces

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Abstract

A macroscopic theory for the dynamics of isothermal compressible interfaces between nematic liquid crystalline polymers and isotropic viscous fluids has been formulated using classical irreversible thermodynamics. The theory is based on the derivation of the interfacial rate of entropy production for ordered interfaces, that takes into account interfacial anisotropic viscous dissipation as well as interfacial anisotropic elastic storage. The symmetry breaking of the interface provides a natural decomposition of the forces and fluxes appearing in the entropy production, and singles out the symmetry properties and tensorial dimensionality of the forces and fluxes. Constitutive equations for the surface extra stress tensor and for surface molecular field are derived, and their use in interfacial balance equations for ordered interfaces is identified. It is found that the surface extra stress tensor is asymmetric, since the anisotropic viscoelasticity of the nematic phase is imprinted onto the surface. Consistency of the proposed surface extra stress tensor with the classical Boussinesq constitutive equation appropriate to Newtonian interfaces is demonstrated. The anisotropic viscoelastic nature of the interface between nematic polymers (NPs) and isotropic viscous fluids is demonstrated by deriving and characterizing the dynamic interfacial tension. The theory provides for the necessary theoretical tools needed to describe the interfacial dynamics of NP interfaces, such as capillary instabilities, Marangoni flows, wetting and spreading phenomena. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Interfacial viscoelasticity is a foundational aspect of interfacial dynamics and interfacial rheology [1–5]. For Newtonian interfaces, that is interfaces between viscous Newtonian fluids, it is well known that the fundamental interfacial material properties are the interfacial tension, the interfacial dilational viscosity, and the interfacial shear viscosity. These three 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]. For interfaces displaying nematic ordering, viscoelasticity plays a similar role, but now anisotropy must be taken into account.

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The physics of nematic liquid crystals interfaces and free surfaces is currently an active area of research [6–10] due to the important role that they play in the use and processing of liquid crystalline materials. The theoretical description of dynamical interfacial phenomena in nematic liquid crystalline materials requires, as in interfaces between Newtonian fluids, the formulation of viscoelastic models that describe material properties such as the dynamic interfacial tension and interfacial dilational and shear viscosities. Orientation phenomena at free surfaces and interfaces have been well characterized experimentally [7–9] and theoretically [7–9,11–14]. On the other hand, knowledge of interfacial dissipative phenomena is much 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 the magnetic reorientation of thin films of nematic polymers (NPs) 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 understand and characterize capillary phenomena involving nematic liquid crystal phases and will be presented in this paper.

The Boussinesq surface fluid model is a widely used constitutive equation for the surface stress tensor of Newtonian interfaces [1,5]. As is well known [1,5], the interfacial linear momentum balance equation involves the surface gradient of the surface 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]. Other generalizations, such as the generalized Boussinesq surface fluid, includes memory effects but lacks anisotropy. A study of the literature of interfacial constitutive equations indicates that there is a need to develop models that include orientational and positional ordering. In this paper, only orientational ordering is taken into account.

The bulk mechanical behavior of nematic liquid crystalline materials is characterized by their anisotropic viscoelasticity [21,22]. The degree of anisotropy is known to be a strong function of the molecular weight, and the tendency is in general increasing anisotropy with increasing molecular weight. Thus, it is expected that interfacial anisotropies will be more pronounced in interfaces involving NPs than low molar mass nematic liquid crystals [22]. The anisotropic Frank elasticity is now well established and is the driving force behind field-induced pattern formation phenomena [23]. The classical example is the splay-avoidance mechanism active in deformations of NPs [23]. Anisotropies in the viscous modes are also well-characterized experimentally [20,22] and theoretically [22,24]. One prominent classical example 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.

Another significant aspect of the behavior of NPs is the drastic effect of changes in the degree of molecular alignment on material properties such as the shear flow-aligning behavior [25–27]. Extensive reviews on the rheology of liquid crystal polymers have been presented [21,28–34]. In a simple shear flow

of an NP, a series of flow-induced regimes is expected to arise as the shear rate increases [34]. The regime transitions are only captured with a tensor order parameter model, that includes changes in orientation and in the degree of molecular alignment with respect to the average molecular orientation [33,34]. Director theories such as the Leslie–Ericksen theory are unable to capture many of the rheological features of NPs [33,34]. Similarly, we expect that the description of the interfacial rheology of NPs also requires models based on a tensor order parameter.

Although at present the anisotropic elastic nature of nematic interfaces is well understood [7–9,13,14], its complex consequences in the presence of deforming interfaces have not been systematically studied. Elastic models for deforming nematic–viscous fluid interfaces have already been proposed [36–41] and used to describe nematocapillarity phenomena such as bending stresses and Marangoni flows [39–41]. In these previous models, the nematic–isotropic viscous fluid interface was considered to be incompressible and purely elastic. More recently, a viscoelastic model [41] for such interfaces has been presented but only includes director modes, and thus, it is inappropriate to describe NP interfaces, where variations in the scalar order parameter are important. The presence of interfacial viscous modes and compressibility is now well established [1,5], and thus, more comprehensive models for NP interfaces including compressibility, variable degree of molecular alignment, and anisotropic viscous dissipation are needed. The present paper builds on previous work on incompressible elastic nematic interface models [36–41] and adds the required compressibility, variable degree of molecular alignment, and dissipative elements to build a general viscoelastic model appropriate for compressible NP–isotropic viscous fluid interfaces denoted below as NP/I.

The objectives of this paper are (1) to derive the interfacial rate of entropy production for deforming compressible isothermal interfaces between NPs and isotropic viscous fluids; (2) to derive a general expression for the interfacial anisotropic viscoelastic stress tensor for compressible interfaces between NPs and isotropic viscous fluids, and (3) to present a general theory based on classical irreversible thermodynamics that can be used to describe capillary nematodynamical phenomena.

The organization of this paper is as follows. Section 2 provides the necessary theoretical background, including the decomposition of the tensor order parameter, the definition of the kinematic fields, and the definition of the three nematic elasticities. Section 3 presents the basic equations for the interfacial elasticity of NP/I interfaces, including the surface elastic molecular field, and the surface elastic stress tensor. Section 4 presents the interfacial linear momentum and angular momentum balance equations. Section 5 presents a derivation of the rate of interfacial entropy production. Section 6 presents the application of classical irreversible thermodynamics to nematic interfaces, including derivations of the surface extra stress tensor and the surface molecular field. Section 7 presents a practical example of interfacial dissipation in nematic interfaces, by deriving the dynamic interfacial tension. Section 8 presents the conclusions.

2. Basic equations for order, kinematics, and elasticity of nematic polymer–isotropic fluid interfaces

2.1. Geometry and order in nematic polymer–isotropic fluid interfaces

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

$$X = -\frac{1}{2}\nabla_s \cdot \mathbf{k} = \frac{1}{2}\mathbf{I}_s : \mathcal{E} = -\frac{1}{2}\mathbf{I}_s : \nabla_s \mathbf{k} = \frac{1}{2}(v_1 + v_2); \quad (1a)$$

$$\mathcal{E} = -\nabla_s \mathbf{k} = v_1 \mathbf{e}_1 \mathbf{e}_1 + v_2 \mathbf{e}_2 \mathbf{e}_2, \quad (1b)$$

where $\nabla_s = \mathbf{I}_s \cdot \nabla$ is the surface gradient, $\mathbf{I}_s = \mathbf{I} - \mathbf{k}\mathbf{k}$ is the 2×2 unit surface dyadic, \mathbf{I} is the 3×3 unit dyadic, \mathcal{E} is the 2×2 symmetric surface curvature dyadic, and $\{v_i\}$ and $\{\mathbf{e}_i\}$, $i=1, 2$ are the eigenvalues and eigenvectors of \mathcal{E} . The divergence of \mathbf{I}_s is a normal vector: $\nabla_s \cdot \mathbf{I}_s = 2X\mathbf{k}$. The symmetric surface curvature dyadic \mathcal{E} is given in terms of a mutually perpendicular unit vector ($\mathbf{e}_1, \mathbf{e}_2$) in the respective directions of the principal axes of curvature. The principal curvatures (v_1, v_2) of the surface are defined by $\mathcal{E} \cdot \mathbf{e}_i = v_i \mathbf{e}_i$; $i=1, 2$. Finally, another common way to express the principal curvatures (v_1, v_2) is in terms of the principal radii of curvature (r_1, r_2), as follows: $v_i = -1/r_i$; $i=1, 2$.

At the NP/I interface, the nematic ordering is defined by the symmetric traceless tensor order parameter [20], $\mathbf{Q} = \mathbf{Q}(t, \mathbf{x}_s)$, where t is time and \mathbf{x}_s is the surface position vector. The tensor order parameter \mathbf{Q} can be expressed as

$$\mathbf{Q} = ann + bmm + c\mathbf{I}. \quad (2)$$

The orthogonal eigenvectors of \mathbf{Q} appearing in Eq. (2) are known as the director \mathbf{n} , and the biaxial director \mathbf{m} . The restrictions on \mathbf{Q} are: $\mathbf{Q} : \mathbf{I} = 0$ and $\mathbf{Q} = \mathbf{Q}^T$, where the superscript T denotes the transpose. The first restriction gives $a+b+3c=0$. Physically significant expressions for these coefficients are

$$a = S + \frac{P}{3}; \quad b = \frac{2P}{3}; \quad c = -\frac{S+P}{3}, \quad (3)$$

where S and P are the uniaxial scalar order parameter and biaxial scalar order parameter, respectively. For isotropic states $S=P=0$ ($a=b=c=0$), while for uniaxial states, $P=0$ ($a=-3c$).

A decomposition of the tensor order parameter \mathbf{Q} that reflects the symmetry breaking of the interface is

$$\mathbf{Q} = \mathbf{Q}_{//} + \mathbf{Q}_x + \mathbf{Q}_\perp, \quad (4)$$

where the 2×2 tangential tensor $\mathbf{Q}_{//}$, the 3×3 mixed tensor \mathbf{Q}_x , and the 3×3 normal tensor \mathbf{Q}_\perp are given by

$$\mathbf{Q}_{//} = \mathbf{I}_s \cdot \mathbf{Q} \cdot \mathbf{I}_s; \quad (5a)$$

$$\mathbf{Q}_x = \mathbf{k}\mathbf{k} \cdot \mathbf{Q} \cdot \mathbf{I}_s + \mathbf{I}_s \cdot \mathbf{Q} \cdot \mathbf{k}\mathbf{k}; \quad (5b)$$

$$\mathbf{Q}_\perp = \mathbf{k}\mathbf{k} \cdot \mathbf{Q} \cdot \mathbf{k}\mathbf{k}. \quad (5c)$$

The three tensor order parameters relevant to the present problem $\{\mathbf{Q}_j; j=//, x, \perp\}$ are symmetric: $\mathbf{Q}_j = \mathbf{Q}_j^T$, but only the mixed tensor \mathbf{Q}_x is traceless, $\mathbf{I} : \mathbf{Q}_x = 0$. Finally, since \mathbf{Q} is traceless, $\mathbf{I} : (\mathbf{Q}_{//} + \mathbf{Q}_\perp) = 0$.

The material time derivative of the tensor order parameter \mathbf{Q} in the frame of reference of the unit surface triad $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{k}\}$, which arises in the surface rate of entropy production (see Eq. (46)), can also be decomposed in terms of three components:

$$\dot{\mathbf{Q}} = \mathbf{I}_s \cdot \dot{\mathbf{Q}}_{//} \cdot \mathbf{I}_s + \mathbf{I}_s \cdot \dot{\mathbf{Q}}_x \cdot \mathbf{k}\mathbf{k} + \mathbf{k}\mathbf{k} \cdot \dot{\mathbf{Q}}_x \cdot \mathbf{I}_s + \mathbf{k}\mathbf{k} \cdot \dot{\mathbf{Q}}_\perp \cdot \mathbf{k}\mathbf{k}, \quad (6)$$

where the tangential $\mathbf{I}_s \cdot \dot{\mathbf{Q}}_{//} \cdot \mathbf{I}_s$ and normal $\mathbf{k}\mathbf{k} \cdot \dot{\mathbf{Q}}_\perp \cdot \mathbf{k}\mathbf{k}$ contributions are traceless.

2.2. Kinematics of deforming nematic polymer interfaces

The kinematic tensors that describe the NP/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]

$$\mathbf{A}^s = \frac{1}{2}(\nabla_s \mathbf{v}^o \cdot \mathbf{I}_s + \mathbf{I}_s \cdot [\nabla_s \mathbf{v}^o]^T); \quad (7a)$$

$$\mathbf{W}^s = \frac{1}{2}(\nabla_s \mathbf{v}^o \cdot \mathbf{I}_s - \mathbf{I}_s \cdot [\nabla_s \mathbf{v}^o]^T), \quad (7b)$$

where \mathbf{v}^o is the surface velocity field. The decomposition of the velocity surface gradient tensor $\nabla_s \mathbf{v}^o$ into its symmetric \mathbf{A}^s and antisymmetric parts \mathbf{W}^s is given by

$$\nabla_s \mathbf{v}^o \cdot \mathbf{I}_s = \mathbf{A}^s + \mathbf{W}^s. \quad (8)$$

The surface rate of deformation \mathbf{A}^s and the surface vorticity tensor obey the following relations:

$$\mathbf{A}^s = \mathbf{I}_s \cdot \mathbf{A}^s = \mathbf{A}^s \cdot \mathbf{I}_s = \mathbf{I}_s \cdot \mathbf{A}^s \cdot \mathbf{I}_s; \quad (9a)$$

$$\mathbf{A}^s \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{A}^s = 0, \quad (9b)$$

$$\mathbf{W}^s = \mathbf{I}_s \cdot \mathbf{W}^s = \mathbf{W}^s \cdot \mathbf{I}_s = \mathbf{I}_s \cdot \mathbf{W}^s \cdot \mathbf{I}_s; \quad (10a)$$

$$\mathbf{W}^s \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{W}^s = 0. \quad (10b)$$

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

$$\boldsymbol{\omega}^s = -\boldsymbol{\varepsilon} : \mathbf{W}^s, \quad (11)$$

where $\boldsymbol{\varepsilon}$ is the unit alternator tensor. The surface vorticity vector is orthogonal to the interface: $\boldsymbol{\omega}^s = \omega^s \mathbf{k}$.

One of the kinematic tensors needed to describe tensor order parameter dynamics is the surface Jaumann derivative of the tangential component of the tensor order parameter $\hat{\mathbf{Q}}_{//}$ [42]:

$$\hat{\mathbf{Q}}_{//} = \mathbf{I}_s \cdot \dot{\mathbf{Q}}_{//} \cdot \mathbf{I}_s + \mathbf{W}^s \cdot \mathbf{Q}_{//} - \mathbf{Q}_{//} \cdot \mathbf{W}^s, \quad (12a,b)$$

which is a 2×2 tangential symmetric tensor:

$$\hat{\mathbf{Q}}_{//} = \mathbf{I}_s \cdot \hat{\mathbf{Q}}_{//} = \hat{\mathbf{Q}}_{//} \cdot \mathbf{I}_s = \mathbf{I}_s \cdot \hat{\mathbf{Q}}_{//} \cdot \mathbf{I}_s; \quad (13a)$$

$$\hat{\mathbf{Q}}_{//} \cdot \mathbf{k} = \mathbf{k} \cdot \hat{\mathbf{Q}}_{//} = 0, \quad (13b)$$

but it is not traceless: $\hat{\mathbf{Q}}_{//} : \mathbf{I}_s \neq 0$. The second kinematic tensor that is involved in the surface dynamics of \mathbf{Q} is the Jaumann derivative of the mixed component \mathbf{Q}_x given by

$$\hat{\mathbf{Q}}_x = \dot{\mathbf{Q}}_x + \mathbf{W}^s \cdot \mathbf{Q}_x - \mathbf{Q}_x \cdot \mathbf{W}^s. \quad (14a,b)$$

In the surface frame, $\hat{\mathbf{Q}}_x$ becomes a 3×3 symmetric and traceless tensor:

$$\tilde{\mathbf{Q}}_x = \mathbf{k} \mathbf{k} \cdot \hat{\mathbf{Q}}_x \cdot \mathbf{I}_s + \mathbf{I}_s \cdot \hat{\mathbf{Q}}_x \cdot \mathbf{k} \mathbf{k}. \quad (15)$$

The objective rate $\tilde{\mathbf{Q}}_x$ is a ‘mixed’ tensor since

$$\tilde{\mathbf{Q}}_x = \mathbf{k} \mathbf{k} \cdot \tilde{\mathbf{Q}}_x \cdot \mathbf{I}_s + \mathbf{I}_s \cdot \tilde{\mathbf{Q}}_x \cdot \mathbf{k} \mathbf{k}. \quad (16)$$

As shown below, surface viscous flows are coupled to the tensor order parameter dynamics through $\hat{\mathbf{Q}}_{//}$ and $\tilde{\mathbf{Q}}_x$.

2.3. Bulk and surface nematic elasticity

In this section, the three free energies of NP are presented and discussed with reference to interfacial phenomena. Nematic ordering allows for anisotropic bulk and surface elasticity, not present in other isotropic polymer systems.

The total free energy in a volume V of the NP bounded by a surface according to the Landau–de Gennes (LG) theory is given by [10,11]

$$F = \int_V [f_G(\nabla \mathbf{Q}) + f_L(\mathbf{Q})] dV + \int_A \gamma(\mathbf{Q}, \mathbf{k}, \mathbf{N}) dA, \quad (17)$$

where the long-range Frank elastic free energy density f_G , the short-range free energy density f_L , and the interfacial free energy density γ are given by

$$f_G(\nabla \mathbf{Q}) = \frac{\ell_1}{2} \text{tr} \nabla \mathbf{Q}^2 + \frac{\ell_2}{2} (\nabla \cdot \mathbf{Q}) \cdot (\nabla \cdot \mathbf{Q})^T, \quad (18a)$$

$$f_L(\mathbf{Q}) = D_1 \text{tr} \mathbf{Q}^2 - D_2 \text{tr} \mathbf{Q}^3 + D_3 (\text{tr} \mathbf{Q}^2)^2, \quad (18b)$$

$$\gamma(\mathbf{Q}, \mathbf{k}, \mathbf{N}) = \gamma_{\text{is}} + \gamma_{\text{an}}; \quad \gamma_{\text{an}} = \beta_{11} \mathbf{k} \cdot \mathbf{N} + \beta_{20} \mathbf{Q} \cdot \mathbf{Q} + \beta_{21} \mathbf{N} \cdot \mathbf{N} + \beta_{22} (\mathbf{k} \cdot \mathbf{N})^2, \quad (18c)$$

$$\mathbf{N} = \mathbf{Q} \cdot \mathbf{k}, \quad (18d)$$

where ∇ is the gradient operator, $\{\ell_i\}$, $i=1, 2$ are the Frank elastic constants (energy/length), $\{D_i\}$; $i=1, 2, 3$ are the Landau coefficients (energy/volume), γ_{is} is the isotropic interfacial tension, γ_{an} is the anchoring energy, and $\{\beta_{ij}\}$, $ij=11, 20, 22, 22$ are the anchoring coefficients (energy/area). For a discussion of f_G , see [43].

The Frank elasticity is responsible for the long-range transmission of torques and forces and captures nematic textures and defects, while the short-range elasticity captures the nematic–isotropic phase transition. The interfacial free energy density is composed of the typical isotropic contribution γ_{is} and an anisotropic orientation dependent contribution γ_{an} . The anchoring energy γ_{an} is a function of \mathbf{Q} , and \mathbf{k} , which indicates that there are two mechanisms for storing surface elastic energy, one is through macroscopic orientation (\mathbf{n} , \mathbf{m}) and the other through molecular ordering (a , b , c). The preferred tensor order parameter \mathbf{Q}_p is the one that minimizes the interfacial free energy, which in turn selects the orientation of the eigenvectors and the eigenvalues of \mathbf{Q} at the interface, and satisfies $(d\gamma_{\text{an}}/d\mathbf{Q})^{[s]}=0$, $d\gamma_{\text{an}}/d\mathbf{k}=0$.

In a uniaxial nematic state ($P=0$), the easy axis of the interface is referred to the director (\mathbf{n}) orientation that minimizes the interfacial free energy. Fixed anchoring conditions exist when the director is always aligned along the easy axis. According to the signs and magnitudes of the anchoring coefficients $\{\beta_{ij}\}$, $ij=11, 20, 22, 22$, for uniaxial nematics, the following three cases occur [12,13]: (a) homeotropic anchoring, where the director is along the unit normal to the interface, (b) planar anchoring, where the director is in the tangent plane to the interface, and (c) oblique anchoring, where the director makes a constant angle to the unit normal. The conditions that lead to fixed anchoring

are given in terms of the dimensionless number F_A which is the ratio of Frank elasticity to anchoring energy:

$$F_A = \left| \frac{\ell_1}{\beta_{11}} \right| \frac{1}{h}, \quad (19)$$

where h is a characteristic length for spatial distortions of \mathbf{Q} . When $F_A \approx 1$, weak anchoring sets in and the surface orientation deviates from the easy axis because surface energy is comparable to Frank energy. On the other hand, when $F_A \ll 1$, strong anchoring prevails because surface energy is more costly than Frank energy.

3. Surface elastic molecular field and surface elastic stress tensor

In this section, we present expressions for the surface molecular field \mathbf{H}_s and the surface stress tensor \mathbf{t}_s for an interphase between an isotropic viscous fluid and an NP liquid crystal, since they are the two fundamental quantities of nematocapillarity [39,41]. As shown below, these two fundamental quantities appear, respectively, in the interfacial linear momentum balance equation and in the interfacial torque balance equation for such an interface. The existence of the surface molecular field \mathbf{H}_s and surface stress tensor \mathbf{t}_s reflects the specific nature of the nematic interface, whose definition requires the specification of interfacial nematic ordering as well as the interfacial shape. The surface stress tensor is involved in the interfacial shape selection process, and the surface elastic molecular field in the interfacial nematic ordering. Since \mathbf{t}_s and \mathbf{H}_s are two potentials of the same interfacial free energy γ , it follows that, for nematic interfaces, shape and ordering are coupled.

The bulk molecular field of nematics \mathbf{H}_b is the conjugate force of the time derivative of \mathbf{Q} , and accounts for the elastic torques acting on the eigenvectors $(\mathbf{n}, \mathbf{m}, \mathbf{l})$ and elastic forces acting on the eigenvalues of \mathbf{Q} , and is given by the following variational derivative of the total bulk free energy F_v [35]:

$$\mathbf{H}_b^{[s]} = - \left[\frac{\delta F_v}{\delta \mathbf{Q}} \right]^{[s]} = - \left[\frac{\partial f_v}{\partial \mathbf{Q}} - \nabla \cdot \frac{\partial f_v}{\partial \nabla \mathbf{Q}} \right]^{[s]}; \quad f_v = f_G + f_L, \quad (20a,b)$$

where F_v is the total bulk free energy, f_v is the bulk free energy density, and the superscript [s] denotes symmetric traceless. The molecular field \mathbf{H}_b tries to restore the equilibrium spatially homogeneous state. Likewise, the interfacial free energy γ gives rise to the elastic surface molecular field tensor \mathbf{H}_e , which is responsible for interfacial torques and forces. As we have seen above, since the interfacial free energy is anisotropic, deviations of \mathbf{Q} from the preferred value \mathbf{Q}_p give rise to the surface molecular field given by

$$\mathbf{H}_e^{[s]} = - \left[\frac{\delta \gamma}{\delta \mathbf{Q}} \right]^{[s]} = - \left[\frac{d\gamma_{an}}{d\mathbf{Q}} \right]^{[s]} = - \{ (\beta_{11} + 2\beta_{22}(\mathbf{k} \cdot \mathbf{N}))(\mathbf{k}\mathbf{k}) + 2\beta_{20}\mathbf{Q} + \beta_{21}(\mathbf{k}\mathbf{N}) \}^{[s]}. \quad (21)$$

In addition to the surface molecular field, surface anchoring energy gives rise to a new contribution to the surface elastic stress tensor \mathbf{t}_e . For an interface between an isotropic substrate and an NP, the surface elastic stress tensor is a 2×3 tensor given by the sum of the normal (tension) \mathbf{t}^n and bending \mathbf{t}^b stresses [39–41]:

$$\mathbf{t}_e = \mathbf{t}^n + \mathbf{t}^b; \quad (22a)$$

$$\mathbf{t}^n = \gamma \mathbf{I}_s; \quad (22b)$$

$$\mathbf{t}^b = -\mathbf{I}_s \cdot \left(\frac{d\gamma_{an}}{d\mathbf{k}} \mathbf{k} \right) = -\mathbf{I}_s \cdot \frac{\partial \gamma_{an}}{\partial \mathbf{N}} \cdot \mathbf{Q} \mathbf{k} - \mathbf{I}_s \cdot \frac{\partial \gamma_{an}}{\partial \mathbf{k}} \mathbf{k}, \quad (22c)$$

where we made use of the chain rule:

$$\frac{d\gamma_{an}}{d\mathbf{k}} = \frac{\partial \gamma_{an}}{\partial \mathbf{N}} \cdot \mathbf{Q} + \frac{\partial \gamma_{an}}{\partial \mathbf{k}}. \quad (23)$$

Bending stresses vanish at the local extrema of the anchoring energy, $d\gamma_{an}/d\mathbf{k}=0$, or when the vector $d\gamma_{an}/d\mathbf{k}$ is along the unit normal, since then $\mathbf{I}_s \cdot d\gamma_{an}/d\mathbf{k}=0$. In component form, the surface elastic stress tensor \mathbf{t}_e is given by the sum of the following normal stresses (t_{11}^n, t_{22}^n) and bending stresses (t_{13}^b, t_{23}^b):

$$\mathbf{t}_e = \mathbf{i}_1 \mathbf{i}_1 t_{11}^n + \mathbf{i}_2 \mathbf{i}_2 t_{22}^n + \mathbf{i}_1 \mathbf{k} t_{13}^b + \mathbf{i}_2 \mathbf{k} t_{23}^b, \quad (24)$$

where ($\mathbf{i}_1, \mathbf{i}_2$) are the orthonormal base vectors. The magnitudes of the normal stresses are given by

$$t_{11}^n = t_{22}^n = \gamma(\mathbf{k}, \mathbf{N}), \quad (25)$$

and of the bending stresses by

$$t_{13}^b = - \left[\mathbf{i}_1 \cdot \frac{\partial \gamma_{an}}{\partial \mathbf{N}} \cdot \mathbf{Q} + \mathbf{i}_1 \cdot \frac{\partial \gamma_{an}}{\partial \mathbf{k}} \right]; \quad (26a)$$

$$t_{23}^b = - \left[\mathbf{i}_2 \cdot \frac{\partial \gamma_{an}}{\partial \mathbf{N}} \cdot \mathbf{Q} + \mathbf{i}_2 \cdot \frac{\partial \gamma_{an}}{\partial \mathbf{k}} \right], \quad (26b)$$

$$\frac{\partial \gamma_{an}}{\partial \mathbf{N}} \cdot \mathbf{Q} = \beta_{11} \mathbf{k} \cdot \mathbf{Q} + 2\beta_{21} \mathbf{N} \cdot \mathbf{Q} + 2\beta_{22} (\mathbf{k} \cdot \mathbf{N}) \mathbf{N}, \quad (27)$$

$$\frac{\partial \gamma_{an}}{\partial \mathbf{k}} = \beta_{11} \mathbf{N} + 2\beta_{22} (\mathbf{k} \cdot \mathbf{N}) \mathbf{N}. \quad (28)$$

For interfaces between isotropic viscous fluids, the bending stresses are 0 [1]. The bending stresses are a direct consequence of the anisotropic anchoring energy of nematics. They vanish only when the tensor order parameter is equal to its equilibrium value \mathbf{Q}_p . The normal forces acting on an interface involving a nematic material can arise even in the absence of curvature. The presence of anchoring energy in nematic interfaces modifies the classical equations of momentum balance across interfaces (generalized Laplace equation) [1].

In partial summary, this section presents fundamental expressions needed to describe the anisotropic elasticity of nematic interfaces. The elastic surface stress tensor contains tension and bending components. The principal orientations of the surface stress tensor are identified with respect to the preferred anchoring conditions. In addition, an expression of the elastic surface molecular field has been obtained using the classical constitutive equation (18c) for the interfacial free energy.

4. Interfacial balance equations

4.1. Interfacial angular momentum balance equation

This section presents the tensorial angular momentum balance equation that governs the interfacial tensor order parameter. In the absence of strong anchoring, the interfacial value of \mathbf{Q} is unknown a priori, and it is coupled to the bulk tensor order parameter and to the orientation of the interface. As discussed in Section 2, the condition that leads to weak anchoring is that the ratio of characteristic Frank elastic energy to anchoring energy is close to unity. Thus, the conditions that lead to weak anchoring are relatively large bulk gradients and materials with relatively large Frank elastic moduli. Thus, if $F_A \approx 1$, the equations presented in this section apply.

The equation that governs the surface order parameter is the tensorial generalization of the interfacial angular momentum balance equation. From a variation of the free energy with respect to \mathbf{Q} , we find

$$[\mathbf{k} \cdot \mathbf{C}^N]^{[s]} = \mathbf{H}_e^{[s]} - \mathbf{H}_v^{[s]}; \quad (29a)$$

$$C_{ijk}^N = + \frac{\partial f_v}{\partial Q_{jk,i}}, \quad (29b)$$

where \mathbf{C}^N is the couple stress tensor in the nematic phase, and $\mathbf{H}_v^{[s]}$ is the surface viscous molecular field. Since in the isotropic phase the couple stress is 0, $\mathbf{C}^I = 0$, the couple stress jump is equal to $\mathbf{H}_e^{[s]} - \mathbf{H}_v^{[s]}$. To use the interfacial torque balance equation, a constitutive equation for $\mathbf{H}_v^{[s]}$ is needed.

4.2. Interfacial linear momentum balance equation

At the NP/I interface, the linear momentum balance equation, that generalizes the Laplace equation to non-equilibrium cases, is given by [1,5]

$$\frac{\partial}{\partial t}(\varrho^0 \mathbf{v}^0) + \nabla_s \cdot (\varrho^0 \mathbf{v}^0 \mathbf{v}^0 - \mathbf{t}) = \mathbf{k} \cdot (\mathbf{P}^I - \mathbf{P}^N); \quad \mathbf{t} = \mathbf{t}_e + \mathbf{t}_v, \quad (30)$$

where \mathbf{P}^N is the total stress tensor in the nematic phase at the NP/I interface, \mathbf{P}^I is the total stress tensor in the isotropic fluid phase at NP/I, \mathbf{t} is the total surface stress tensor, and \mathbf{t}_v is the surface extra stress tensor. The total stress tensor in the isotropic phase \mathbf{P}^I is given by

$$\mathbf{P}^I = -p^I \mathbf{I} + \mathbf{P}^{Iv}, \quad (31)$$

where p^I is the pressure and \mathbf{P}^{Iv} is the extra stress tensor. The total stress tensor in the nematic phase \mathbf{P}^N is given by [35]

$$\mathbf{P}^N = \mathbf{P}^E + \mathbf{P}^{Nv}; \quad (32a)$$

$$\mathbf{P}^E = -p^I \mathbf{I} - \frac{\partial f_G}{\partial \nabla \mathbf{Q}} : (\nabla \mathbf{Q})^T, \quad (32b)$$

where \mathbf{P}^E is the Ericksen stress tensor, and \mathbf{P}^{Nv} is the extra stress tensor.

The asymmetric surface extra stress tensor \mathbf{t}_v is a tangential tensor that can be decomposed into symmetric \mathbf{t}_v^s and antisymmetric \mathbf{t}_v^a components obeying

$$\mathbf{t}_v^s = \mathbf{I}_s \cdot \mathbf{t}_v^s = \mathbf{t}_v^s \cdot \mathbf{I}_s = \mathbf{I}_s \cdot \mathbf{t}_v^s \cdot \mathbf{I}_s; \quad (33a)$$

$$\mathbf{t}_v^s \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{t}_v^s = 0, \quad (33b)$$

$$\mathbf{t}_v^a = \mathbf{I}_s \cdot \mathbf{t}_v^a = \mathbf{t}_v^a \cdot \mathbf{I}_s = \mathbf{I}_s \cdot \mathbf{t}_v^a \cdot \mathbf{I}_s; \quad (34a)$$

$$\mathbf{t}_v^a \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{t}_v^a = 0. \quad (34b)$$

The 2×2 symmetric surface extra stress tensor \mathbf{t}_v^s is a function of the following tangential symmetric tensors:

$$\mathbf{t}_v^s = f(\mathbf{I}_s, \mathbf{Q}_{//}, \mathbf{A}^s, \hat{\mathbf{Q}}_{//}^s), \quad (35)$$

and in the absence of interfacial order ($\mathbf{Q}=0$), it should reduce to the Boussinesq stress tensor for Newtonian interfaces, that is, $\mathbf{t}_v^s = \mathbf{t}_v^s(\mathbf{I}_s, \mathbf{A}^s)$. The 2×2 antisymmetric surface extra stress tensor \mathbf{t}_v^a arises because interfacial elastic torques are non-zero. Since the interfacial elastic torques are balanced by the viscous surface molecular field $\mathbf{H}_v^{[s]}$, the asymmetric surface extra stress tensor \mathbf{t}_v^a has the following structure:

$$\mathbf{t}_v^a = f[\mathbf{I}_s \cdot (\mathbf{H}_v^{[s]} \cdot \mathbf{Q} - \mathbf{Q} \cdot \mathbf{H}_v^{[s]}) \cdot \mathbf{I}_s], \quad (36)$$

which shows that, if $\mathbf{H}_v^{[s]}=0$, then $\mathbf{t}_v^a=0$. In the following sections, we develop the constitutive equations for \mathbf{t}_v^s and \mathbf{t}_v^a needed to use the interfacial linear momentum balance equation (30).

In partial summary, this section presents the interfacial linear momentum balance equation, and identifies the nature of the contribution of nematic ordering to the surface stress tensor. In particular, it is shown that the surface stress tensor is anisotropic, asymmetric, and viscoelastic.

5. Rate of interfacial entropy production

In this section, we develop the expression for the interfacial rate of entropy production per unit volume for the NP/I interface. We assume that the system is isothermal, and that A is the interfacial area between an NP of volume ϖ^N and an isotropic viscous fluid of volume ϖ^I . As before, the unit normal \mathbf{k} is directed from the NP phase towards the I phase. The total free energy of the system F is

$$F = \int_{\varpi^N} \left[\frac{1}{2} \varrho^N |\mathbf{v}^N|^2 + f_L + f_G \right] d\varpi + \int_{\varpi^I} \frac{1}{2} \varrho^I |\mathbf{v}^I|^2 d\varpi + \int_A \left[\frac{1}{2} \varrho^o |\mathbf{v}^o|^2 + \gamma \right] dA, \quad (37)$$

where ρ is the density, \mathbf{v} is the velocity, and the superscript ‘o’ denotes an interfacial quantity. The total variation δF due to a displacement \mathbf{u} and distortion of \mathbf{Q} is

$$\delta F = \int_{\varpi^N} [\mathbf{P}^E : (\nabla \mathbf{u}^N)^T - \mathbf{H}_b^{[s]} : \delta \mathbf{Q}] d\varpi + \int_A [\mathbf{t}_s^e : (\nabla_s \mathbf{u}^o)^T - \mathbf{H}_v^{[s]} : \delta \mathbf{Q}] dA, \quad (38)$$

where we used integration by parts and Eqs. (20), (21), (22b) and (32b). The total rate of entropy production Σ times the temperature T is given by the total rate of decrease in free energy: $T\Sigma = \dot{\Phi} = -dF/dt$.

Using Eqs. (37) and (38), we find

$$\begin{aligned} \Phi = & -\frac{d}{dt} \left\{ \int_{\varpi^N} \left[\frac{1}{2} \varrho^N |\mathbf{v}^N|^2 \right] d\varpi + \int_{\varpi^I} \frac{1}{2} \varrho^I |\mathbf{v}^I|^2 d\varpi + \int_A \left[\frac{1}{2} \varrho^o |\mathbf{v}^o|^2 \right] dA \right\} \\ & - \int_{\varpi^N} [\mathbf{P}^E : (\nabla \mathbf{v}^N)^T - \mathbf{H}_b^{[s]} : \dot{\mathbf{Q}}] d\varpi + \int_A [\mathbf{t}_s^e : (\nabla_s \mathbf{v}^o)^T - \mathbf{H}_v^{[s]} : \dot{\mathbf{Q}}] dA. \end{aligned} \quad (39)$$

The linear momentum balances in the bulk phases are

$$\varrho^N \frac{d\mathbf{v}^N}{dt} = \nabla \cdot \mathbf{P}^N; \quad (40a)$$

$$\varrho^I \frac{d\mathbf{v}^I}{dt} = \nabla \cdot \mathbf{P}^I. \quad (40b)$$

Using these equations and the divergence theorem, the negative of the rate of decrease in kinetic energy in the bulk phases becomes

$$\begin{aligned} & -\frac{d}{dt} \left\{ \int_{\varpi^N} \left[\frac{1}{2} \varrho^N |\mathbf{v}^N|^2 \right] d\varpi + \int_{\varpi^I} \frac{1}{2} \varrho^I |\mathbf{v}^I|^2 d\varpi \right\} \\ & = \int_{\varpi^N} \mathbf{P}^N : (\nabla \mathbf{v}^N)^T d\varpi + \int_{\varpi^I} \mathbf{P}^I : (\nabla \mathbf{v}^I)^T d\varpi - \int_A \mathbf{k} \cdot (\mathbf{P}^N - \mathbf{P}^I) \cdot \mathbf{v}^o dA. \end{aligned} \quad (41)$$

To compute the total rate of change of kinetic energy associated with the interface, we dot the interfacial linear momentum balance equation with \mathbf{v}^o :

$$\frac{1}{2} \frac{\partial}{\partial t} (\varrho^o |\mathbf{v}^o|^2) + \frac{1}{2} \nabla_s \cdot (\mathbf{v}^o \varrho^o |\mathbf{v}^o|^2) = \nabla_s \cdot (\mathbf{t} \cdot \mathbf{v}^o) - \mathbf{t} : (\nabla_s \mathbf{v}^o)^T + \mathbf{k} \cdot (\mathbf{P}^I - \mathbf{P}^N) \cdot \mathbf{v}^o, \quad (42)$$

from which the time rate of decrease in the kinetic energy associated with the interface becomes

$$-\frac{d}{dt} \int_A \left[\frac{1}{2} \varrho^o |\mathbf{v}^o|^2 \right] dA = \int_A [\mathbf{t} : (\nabla_s \mathbf{v}^o)^T - \mathbf{k} \cdot (\mathbf{P}^I - \mathbf{P}^N) \cdot \mathbf{v}^o] dA - \int_{\varphi} d\varphi \cdot (\mathbf{t} \cdot \mathbf{v}^o), \quad (43)$$

where φ is the edge of A . Replacing Eqs. (41) and (43) into (39), we find that the product of the temperature and the total rate of entropy production Φ becomes

$$\begin{aligned} \Phi = & \int_{\varpi^N} [\mathbf{P}^{Nv} : (\nabla \mathbf{v}^N)^T - \mathbf{H}_b^{[s]} : \dot{\mathbf{Q}}] d\varpi + \int_{\varpi^I} \mathbf{P}^{Iv} : (\nabla \mathbf{v}^I)^T d\varpi \\ & + \int_A [\mathbf{t}_v : (\nabla_s \mathbf{v}^o)^T + \mathbf{H}_v^{[s]} : \dot{\mathbf{Q}}] dA - \int_{\varphi} d\varphi \cdot (\mathbf{t} \cdot \mathbf{v}^o). \end{aligned} \quad (44)$$

From the above equation, it follows that the interfacial rate of entropy production per unit volume times temperature, Φ , is given by

$$\Phi = \mathbf{t}_v : (\nabla_s \mathbf{v}^o)^T + \mathbf{H}_v^{[s]} : \dot{\mathbf{Q}}, \quad (45)$$

and using Eq. (6) to express $\dot{\mathbf{Q}}$ in a surface frame,

$$\Phi = \mathbf{t}_v : (\nabla_s \mathbf{v}^o)^T + \mathbf{H}_v^{[s]} \cdot [\mathbf{I}_s \cdot \dot{\mathbf{Q}}_{//} \cdot \mathbf{I}_s + \mathbf{I}_s \cdot \dot{\mathbf{Q}}_x \cdot \mathbf{k}\mathbf{k} + \mathbf{k}\mathbf{k} \cdot \dot{\mathbf{Q}}_x \cdot \mathbf{I}_s + \mathbf{k}\mathbf{k} \cdot \dot{\mathbf{Q}}_{\perp} \cdot \mathbf{k}\mathbf{k}]. \quad (46)$$

As usual, we find a dissipation term arising from deformations of the interface and an elastic storage term associated with time-dependent deviation of the surface tensor order parameter. The forces are the transpose of the surface gradient of the surface velocity $(\nabla_s \mathbf{v}^o)^T$ and the material derivative of the tensor order parameter $\dot{\mathbf{Q}}$, while the fluxes are the surface stress tensor \mathbf{t}_v and the surface viscous molecular field $\mathbf{H}_v^{[s]}$. In the next section, we derive constitutive equations for $(\mathbf{t}_v, \mathbf{H}_v^{[s]})$ by expanding the fluxes in terms of forces. Direct observation of Eq. (45) indicates that the surface stress tensor is in general not symmetric, as mentioned above.

In partial summary, this section presents the derivation of the interfacial entropy production using first principles. The entropy production consists of the usual dissipative term due to interfacial deformations, and a specific nematic contribution. The contribution of interfacial nematic ordering to the entropy production arises due to elastic storage through deviations of the tensor order parameter from the preferred value. Since anisotropic interfacial elasticity implies asymmetric stress, the surface stress tensor has a symmetric and an antisymmetric contribution.

6. Classical irreversible thermodynamics of nematic interfaces

In this section, we use classical irreversible thermodynamics [44] to develop constitutive equations for the surface extra stress tensor \mathbf{t}_v and the surface viscous molecular field $\mathbf{H}_v^{[s]}$, for isothermal, compressible NP/I interfaces. The classical theory of irreversible thermodynamics is based on the decomposition of the dissipation function, given in Eq. (46), into products of scalar, vector, and tensor forces and fluxes. In the present interfacial context, forces and fluxes are 2×2 or 3×3 tensors, since the tensor order parameter at the interface remains a 3×3 tensor, while the extra stress tensor is a tangential vector field. Having identified the nature (i.e. 2×2 or 3×3 tensor field) of the fluxes and forces, the next step is to expand the fluxes with the forces. The expansion coefficients are phenomenological tensors, and for liquid crystals, they are functions of the order parameter. In what follows, we give details of the application of irreversible thermodynamics to the interfacial dynamics of nematic liquid crystals in contact with isotropic materials. Extensions to other interfaces, such as nematic–nematic, nematic–cholesteric, and nematic–smectic A using the principles of irreversible thermodynamics are direct.

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 and the surface viscous molecular field $\mathbf{H}_v^{[s]}$, we decompose the forces and fluxes that contribute to the surface rate of entropy production Φ , as follows:

$$\begin{aligned} \Phi = & \underbrace{\mathbf{t}_v^s : \mathbf{A}^s}_{2 \times 2 \text{ symmetric tensors}} + \underbrace{\mathbf{t}_v^a : \mathbf{W}^s}_{2 \times 2 \text{ antisymmetric tensors}} + \underbrace{\mathbf{H}_{v//}^s : \mathbf{I}_s \cdot \dot{\mathbf{Q}}_{//} \cdot \mathbf{I}_s}_{2 \times 2 \text{ symmetric tensors}} \\ & + \underbrace{\mathbf{H}_{vx}^{[s]} : (\mathbf{I}_s \cdot \dot{\mathbf{Q}}_x \cdot \mathbf{k}\mathbf{k} + \mathbf{k}\mathbf{k} \cdot \dot{\mathbf{Q}}_x \cdot \mathbf{I}_s)}_{3 \times 3 \text{ symmetric traceless tensors}} + \underbrace{\mathbf{H}_{v\perp}^s : (\mathbf{k}\mathbf{k} \cdot \dot{\mathbf{Q}}_{\perp} \cdot \mathbf{k}\mathbf{k})}_{3 \times 3 \text{ symmetric tensors}}, \end{aligned} \quad (47)$$

where all quantities have been previously defined. As usual [20], the 2×2 antisymmetric extra stress tensor \mathbf{t}_v^a can be written in terms of the surface viscous molecular field $\mathbf{H}_v^{[s]}$:

$$\begin{aligned} \mathbf{t}_v^a &= \mathbf{I}_s \cdot (\mathbf{H}_v^{[s]} \cdot \mathbf{Q} - \mathbf{Q} \cdot \mathbf{H}_v^{[s]}) \cdot \mathbf{I}_s \\ &= \mathbf{H}_{v//}^s \cdot \mathbf{Q}_{//} - \mathbf{Q}_{//} \cdot \mathbf{H}_{v//}^s + \mathbf{I}_s \cdot (\mathbf{H}_{vx}^{[s]} \cdot \mathbf{Q}_x - \mathbf{Q}_x \cdot \mathbf{H}_{vx}^{[s]}) \cdot \mathbf{I}_s. \end{aligned} \quad (48)$$

Clearly, the proposed expression for \mathbf{t}_v^a is a 2×2 antisymmetric tangential tensor. Eliminating \mathbf{t}_v^a by use of Eq. (48), the surface entropy production Φ becomes

$$\Phi = \underbrace{\mathbf{t}_v^s : \mathbf{A}^s + \mathbf{H}_{v//}^s : \hat{\mathbf{Q}}_{//}}_{\text{tangential tensors}} + \underbrace{\mathbf{H}_{vx}^{[s]} : \tilde{\mathbf{Q}}_x}_{\text{mixed tensors}} + \underbrace{\mathbf{H}_{v\perp}^s : (\mathbf{k}\mathbf{k} \cdot \dot{\mathbf{Q}}_{\perp} \cdot \mathbf{k}\mathbf{k})}_{\text{normal tensors}}, \quad (49)$$

which shows that, due to the tensorial nature of the forces and fluxes (i.e. tangential, mixed, or normal), only the tangential fluxes ($\mathbf{t}_v^s, \mathbf{H}_{v//}^s$) are coupled. Eqs. (47)–(49) show how and why the objective surface Jaumann derivative [42] of the tangential and mixed components of the tensor order parameter arises in the interfacial dynamics of NPs. Expanding the tangential fluxes ($\mathbf{t}_v^s, \mathbf{H}_{v//}^s$) in terms of the tangential forces ($\mathbf{A}^s, \hat{\mathbf{Q}}_{v//}^s$), we find

$$t_{vij}^s = L_{ijkl}^s A_{lk}^s + G_{ijkl}^{s1} \hat{Q}_{//lk}^s, \quad (50a)$$

$$H_{v//ij}^s = G_{ijkl}^{s2} A_{lk}^s + M_{ijkl}^s \hat{Q}_{//lk}^s, \quad (50b)$$

where by Onsager reciprocal relations [44], the matrix coefficients satisfy $L_{ijkl}^s = L_{klij}^s$, $G_{ijkl}^{s1} = G_{klij}^{s2}$, and $M_{ijkl}^s = M_{klij}^s$. Imposing symmetry restrictions of forces and fluxes gives $L_{ijkl}^s = L_{jikl}^s = L_{ijlk}^s$, $G_{ijkl}^{s1} = G_{jikl}^{s1}$, $G_{ijkl}^{s2} = G_{ijlk}^{s2} = G_{jilk}^{s2}$. Expressing the tensorial coefficients $\{L^s, G^{s1}, G^{s2}, M^s\}$ in terms of $\mathbf{Q}_{//}$, and \mathbf{I}_s we find

$$\begin{aligned} \mathbf{t}_v^s = & 2\mu_1 \mathbf{A}^s + \mu_2 \mathbf{I}_s (\mathbf{I}_s : \mathbf{A}^s) + 2\mu_3 (\mathbf{A}^s \cdot \mathbf{Q}_{//} + \mathbf{Q}_{//} \cdot \mathbf{A}^s) + \mu_4 [\mathbf{Q}_{//} (\mathbf{I}_s : \mathbf{A}^s) + \mathbf{I}_s (\mathbf{Q}_{//} : \mathbf{A}^s)] \\ & + 2\mu_5 (\mathbf{Q}_{//} \cdot \mathbf{A}^s \cdot \mathbf{Q}_{//}) + \mu_6 \mathbf{Q}_{//} (\mathbf{A}^s : \mathbf{Q}_{//}) + 2\mu_7 [\mathbf{Q}_{//} \cdot \mathbf{Q}_{//} \cdot \mathbf{A}^s + \mathbf{A}^s \cdot \mathbf{Q}_{//} \cdot \mathbf{Q}_{//}] \\ & + \mu_8 [\mathbf{Q}_{//} \cdot \mathbf{Q}_{//} (\mathbf{I}_s : \mathbf{A}^s) + \mathbf{I}_s (\mathbf{Q}_{//} \cdot \mathbf{Q}_{//} : \mathbf{A}^s)] + 2\mu_9 \left[\hat{\mathbf{Q}}_{//} - \frac{(\mathbf{I}_s : \hat{\mathbf{Q}}_{//}) \mathbf{I}_s}{2} \right], \end{aligned} \quad (51a)$$

$$\mathbf{H}_{v//}^s = 2\mu_9 \left(\mathbf{A}^s - \frac{(\mathbf{I}_s : \mathbf{A}^s) \mathbf{I}_s}{2} \right) + 2\mu_{10} \hat{\mathbf{Q}}_{//}, \quad (51b)$$

where $\{\mu_i; i=1, \dots, 10\}$ are the surface viscosities. The expression for \mathbf{t}_v^s satisfies the above-mentioned restrictions on the symmetric component of the surface extra stress tensor, namely $\mathbf{t}_v^s = \mathbf{I}_s \cdot \mathbf{t}_v^s = \mathbf{t}_v^s \cdot \mathbf{I}_s = \mathbf{I}_s \cdot \mathbf{t}_v^s \cdot \mathbf{I}_s$. The expression for $\mathbf{H}_{v//}^s$ also satisfies the restrictions $\mathbf{H}_{v//}^s = \mathbf{I}_s \cdot \mathbf{H}_{v//}^s = \mathbf{H}_{v//}^s \cdot \mathbf{I}_s = \mathbf{I}_s \cdot \mathbf{H}_{v//}^s \cdot \mathbf{I}_s$.

The mixed $\mathbf{H}_{vx}^{[s]}$ and normal $\mathbf{H}_{v\perp}^s$ components of the molecular field are uncoupled to the tangential viscous flow process, and they can be written as

$$\mathbf{H}_{vx}^{[s]} = 2\mu_{11} \tilde{\mathbf{Q}}_x, \quad (52)$$

$$\mathbf{H}_{v\perp}^s = 2\mu_{10} \mathbf{k}\mathbf{k} \cdot \dot{\mathbf{Q}}_{\perp} \cdot \mathbf{k}\mathbf{k}, \quad (53)$$

where the expressions (52) and (53) for the mixed and normal components of \mathbf{H}_v properly obey the restrictions $\mathbf{H}_{vx}^{[s]} = \mathbf{I} \cdot \mathbf{H}_{vx}^{[s]} = \mathbf{H}_{vx}^{[s]} \cdot \mathbf{I} = \mathbf{I} \cdot \mathbf{H}_{vx}^{[s]} \cdot \mathbf{I}$; $\mathbf{H}_{v\perp}^s = \mathbf{k}\mathbf{k} \cdot \mathbf{H}_{v\perp}^s = \mathbf{H}_{v\perp}^s \cdot \mathbf{k}\mathbf{k} = \mathbf{k}\mathbf{k} \cdot \mathbf{H}_{v\perp}^s \cdot \mathbf{k}\mathbf{k}$. Hence, the total surface viscous molecular field $\mathbf{H}_v^{[s]}$ is given by

$$\mathbf{H}_v^{[s]} = 2\mu_9 \left(\mathbf{A}^s - \frac{(\mathbf{I}_s : \mathbf{A}^s) \mathbf{I}_s}{2} \right) + 2\mu_{10} (\hat{\mathbf{Q}}_{//} + \mathbf{k}\mathbf{k} \cdot \dot{\mathbf{Q}}_{\perp} \cdot \mathbf{k}\mathbf{k}) + 2\mu_{11} \tilde{\mathbf{Q}}_x, \quad (54)$$

where tracelessness and symmetry are satisfied.

Using Eq. (38), we obtain the following expression for the antisymmetric extra stress tensor:

$$\begin{aligned} \mathbf{t}_v^a = & 2\mu_9[\mathbf{A}^s \cdot \mathbf{Q}_{//} - \mathbf{Q}_{//} \cdot \mathbf{A}^s] \\ & + 2\mu_{10}(\hat{\mathbf{Q}}_{//} \cdot \mathbf{Q}_{//} - \mathbf{Q}_{//} \cdot \hat{\mathbf{Q}}_{//}) + 2\mu_{11}\mathbf{I}_s \cdot [\tilde{\mathbf{Q}}_x \cdot \mathbf{Q}_x - \mathbf{Q}_x \cdot \tilde{\mathbf{Q}}_x] \cdot \mathbf{I}_s. \end{aligned} \quad (55)$$

In the presence of surface isotropy, when the state is uniaxial and the director is aligned along the normal, the tensor order parameter reads $\mathbf{Q} = S(\mathbf{k}\mathbf{k} - \mathbf{I}/3)$. In this case, the asymmetric stress vanishes, and the predicted surface behavior is Newtonian, as it should be.

Adding Eqs. (50a) and (55), we find that the total surface extra stress tensor \mathbf{t}_v is given by

$$\begin{aligned} \mathbf{t}_v = & 2\mu_1\mathbf{A}^s + \mu_2\mathbf{I}_s(\mathbf{I}_s : \mathbf{A}^s) + 2\mu_3(\mathbf{A}^s \cdot \mathbf{Q}_{//} + \mathbf{Q}_{//} \cdot \mathbf{A}^s) + \mu_4[\mathbf{Q}_{//}(\mathbf{I}_s : \mathbf{A}^s) + \mathbf{I}_s(\mathbf{Q}_{//} : \mathbf{A}^s)] \\ & + 2\mu_5(\mathbf{Q}_{//} \cdot \mathbf{A}^s \cdot \mathbf{Q}_{//}) + \mu_6\mathbf{Q}_{//}(\mathbf{A}^s : \mathbf{Q}_{//}) + 2\mu_7[\mathbf{Q}_{//} \cdot \mathbf{Q}_{//} \cdot \mathbf{A}^s + \mathbf{A}^s \cdot \mathbf{Q}_{//} \cdot \mathbf{Q}_{//}] \\ & + \mu_8[\mathbf{Q}_{//} \cdot \mathbf{Q}_{//}(\mathbf{I}_s : \mathbf{A}^s) + \mathbf{I}_s(\mathbf{Q}_{//} \cdot \mathbf{Q}_{//} : \mathbf{A}^s)] + 2\mu_9 \left[\hat{\mathbf{Q}}_{//} - \frac{(\mathbf{I}_s : \hat{\mathbf{Q}}_{//})\mathbf{I}_s}{2} \right] \\ & + 2\mu_9[\mathbf{A}^s \cdot \mathbf{Q}_{//} \cdot \mathbf{Q}_{//} \cdot \mathbf{A}^s] \\ & + 2\mu_{10}(\hat{\mathbf{Q}}_{//} \cdot \mathbf{Q}_{//} - \mathbf{Q}_{//} \cdot \hat{\mathbf{Q}}_{//}) + 2\mu_{11}\mathbf{I}_s \cdot [\tilde{\mathbf{Q}}_x \cdot \mathbf{Q}_x - \mathbf{Q}_x \cdot \tilde{\mathbf{Q}}_x] \cdot \mathbf{I}_s. \end{aligned} \quad (56)$$

To check the consistency of the limiting behavior of \mathbf{t}_v with the symmetric Boussinesq stress tensor of compressible Newtonian interfaces [1,5], we set $\{\mu_i=0; i=3, \dots, 11\}$ and indeed find that the present model reduces to the classical Boussinesq constitutive equation:

$$\mathbf{t}_v^s|_{\text{Boussinesq}} = 2\mu_1\mathbf{A}^s + \mu_2\mathbf{I}_s(\mathbf{I}_s : \mathbf{A}^s), \quad (57)$$

where μ_1 is the interfacial shear viscosity and

$$\chi = \mu_1 + \mu_2 \quad (58)$$

is the interfacial dilational viscosity of Newtonian interfaces. 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 important in nematic interfaces. A second consistency check for \mathbf{t}_v is found in the isotropic phase ($a=b=c=0$), which again yields the Boussinesq constitutive equation.

Another prediction of the theory that should be consistent with the Boussinesq constitutive equation is the case of surface isotropy, that is, the uniaxial state with the director \mathbf{n} aligned along the unit normal. As mentioned above, in this case, $\mathbf{Q} = S(\mathbf{k}\mathbf{k} - \mathbf{I}/3)$ and $\mathbf{Q}_{//} = -S\mathbf{I}/3$. The Boussinesq constitutive equation (57) can be written in the following alternative form:

$$\mathbf{t}_v^s|_{\text{Boussinesq}} = 2\mu_{\text{shear}}\mathbf{A}^s + (\chi - \mu_{\text{shear}})\mathbf{I}_s(\mathbf{I}_s : \mathbf{A}^s). \quad (59)$$

In the presence of surface isotropy, the present model predicts the following Boussinesq constitutive equation:

$$\mathbf{t}_v = \left[2\mu_1 - \frac{4\mu_3 S}{3} + \frac{(2\mu_5 + 4\mu_7)S^2}{9} \right] \mathbf{A}^s + \left[\mu_2 - \frac{2\mu_4 S}{3} + \frac{(\mu_6 + 2\mu_8)S^2}{9} \right] \mathbf{I}_s(\mathbf{I}_s : \mathbf{A}^s). \quad (60)$$

Comparing Eqs. (59) and (60), we find that the interfacial and dilational viscosities in the case of surface

isotropy are

$$\mu_{\text{shear}} = \mu_1 - \frac{2\mu_3 S}{3} + \frac{(\mu_5 + 2\mu_7)S^2}{9}, \quad (61)$$

$$\chi = \mu_1 + \mu_2 - \frac{(2\mu_3 + 2\mu_4)S}{3} + \frac{(\mu_5 + 2\mu_7 + \mu_6 + 2\mu_8)S^2}{9}. \quad (62)$$

For normal nematic liquid crystals, the scalar order parameter is restricted as $0 \leq S \leq 1$. In the presence of surface isotropy, the effect of excess order (i.e. $S > 0$) on the interfacial viscosities is

$$\mu_{\text{shear}}(S) = \mu_{\text{shear}}(S = 0) + \frac{-6\mu_3 S + \mu_5 + 2\mu_7 S^2}{9}, \quad (63)$$

$$\chi(S) = \chi(S = 0) + \frac{(-6\mu_3 - 6\mu_4)S + (\mu_5 + 2\mu_7 + \mu_6 + 2\mu_8)S^2}{9}. \quad (64)$$

These expressions highlight the fact that, in the presence of surface isotropy, nematic interfaces may behave as Boussinesq and that their interfacial viscosities are apparent viscosities since they depend on the scalar order parameter, which in turn depends on deformation rates. Thus, we conclude that, for the simplest case of a nematic interface, the present model predicts the behavior of a generalized Boussinesq fluid.

In partial summary, this section presents the derivation of constitutive equations for the viscoelastic surface stress tensor and for the viscous surface molecular field. These two constitutive equations are needed to solve the interfacial momentum and interfacial angular momentum balance equations. Systematic checks on symmetry, dimensionality, and consistency with the classical Boussinesq surface fluid have been performed.

7. 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]:

$$\bar{\tau} = \frac{1}{2} \mathbf{I}_s : (\mathbf{t}_e + \mathbf{t}_v^s), \quad (65)$$

where we used the fact that $\mathbf{I}_s : \mathbf{t}_v^a = 0$. The dynamic interfacial tension $\bar{\tau}$ contains in addition to the thermodynamic interfacial tension γ , non-equilibrium contributions arising from compressible and director/flow coupling effects. For the present anisotropic viscoelastic stress tensor, the dynamic interfacial tension $\bar{\tau}$ is

$$\begin{aligned} \bar{\tau}(\mathbf{Q}, \mathbf{Q} \cdot \mathbf{k}, \mathbf{A}^s) = & \gamma(\mathbf{Q}, \mathbf{Q} \cdot \mathbf{k}, \mathbf{k}) + \left[\mu_1 + \mu_2 + \frac{\mu_4}{2} (\mathbf{I}_s : \mathbf{Q}_{//}) + \frac{\mu_8}{2} (\mathbf{Q}_{//} : \mathbf{Q}_{//}) \right] (\mathbf{I}_s : \mathbf{A}^s) \\ & + \left[2\mu_3 + \mu_4 + \frac{\mu_6}{2} (\mathbf{I}_s : \mathbf{Q}_{//}) \right] (\mathbf{Q}_{//} : \mathbf{A}^s) [\mu_5 + 2\mu_7 + \mu_8] (\mathbf{Q}_{//} \cdot \mathbf{Q}_{//} : \mathbf{A}^s) \\ & + [\mu_9] (\mathbf{I}_s : \hat{\mathbf{Q}}_{//}). \end{aligned} \quad (66)$$

A significant aspect of the expression for the dynamic surface tension $\bar{\tau}$ is that it is anisotropic since both the elastic and viscous contributions are functions of \mathbf{Q} . The elastic contribution is a function of the tensor

order parameter \mathbf{Q} , while the viscous contribution is only a function of the tangential component of \mathbf{Q} , $\mathbf{Q}_{//}$. In addition, the dynamic surface tension is a non-linear function of \mathbf{A}^s since $\mathbf{Q}_{//}$ is also a function of \mathbf{A}^s .

In the presence of surface isotropy (i.e. $\mathbf{Q} = S(\mathbf{k}\mathbf{k} - \mathbf{I}/3)$), the dynamic surface tension $\bar{\tau}$ simplifies to the following generalized Boussinesq expression:

$$\bar{\tau} = \gamma(S, \mathbf{n} \cdot \mathbf{k} = 1) + \left[\mu_1 + \mu_2 - \frac{(2\mu_3 + 2\mu_4)S}{3} + \frac{(\mu_5 + 2\mu_7 + \mu_6 + 2\mu_8)S^2}{9} \right] (\mathbf{I}_s : \mathbf{A}^s), \quad (67)$$

and since the scalar order parameter S is a function of the surface deformation rate \mathbf{A}^s , $\bar{\tau}$ is a non-linear function of the deformation rate. The presence of partial nematic ordering (i.e. $S > 0$) modifies the magnitude of the dynamic surface tension $\bar{\tau}$ by

$$\begin{aligned} \bar{\tau}(S, \mathbf{A}^s) = \bar{\tau}(S = 0, \mathbf{A}^s) + & \left\{ \beta_{11}S \left[\beta_{20} + \frac{2}{3}(\beta_{21} + \beta_{22}) \right] \frac{2S^2}{3} \right\} \\ & + \left[\frac{-(2\mu_3 + 2\mu_4)S}{3} + \frac{(\mu_5 + 2\mu_7 + \mu_6 + 2\mu_8)S^2}{9} \right] (\mathbf{I}_s : \mathbf{A}^s). \end{aligned} \quad (68)$$

The excess order contributes non-linearly to the elastic and viscous contributions. In principle, since external fields, such as electric or magnetic fields, influence the magnitude of S , the dynamic surface tension can be also tuned by these fields.

In partial summary, this section presents one of the most basic viscoelastic interfacial properties, known as the dynamic interfacial tension. For nematic interfaces, the dynamic interfacial tension is highly anisotropic, since it depends on the tensor order parameter through the elastic and viscous contributions. In the presence of surface isotropy, the model predicts an apparent Boussinesq interfacial tension that is a non-linear function of the scalar order parameter.

8. Conclusions

This paper derives the governing equations of compressible isothermal interfacial nematodynamics. The equations are derived by using first principles to construct the rate of entropy production for a deforming isothermal compressible interface between an NP liquid crystal and an isotropic viscous fluid. A useful decomposition, that takes into account the symmetry breaking of the interface, of the forces and fluxes that arise in the entropy production due to nematic ordering allows to identify the couplings between interfacial deformation and nematic ordering. In particular, it is found that, for nematic interfaces, the viscous stress tensor is asymmetric. The symmetric component of the stress tensor is a tangential (2×2) tensor that couples with the dynamics of the tangential component of the tensor order parameter ($\mathbf{Q}_{//}$). The objective rate that captures this coupling is the surface Jaumann derivative of $\mathbf{Q}_{//}$. Since the interface is anisotropic and viscoelastic, flow deformations contribute to internal angular momentum, and thus, the extra stress tensor has an antisymmetric component. It is shown that the antisymmetric surface extra stress tensor is in general non-zero except when the nematic ordering is isotropic with respect to the interface. In such case, the constitutive equation for the surface extra stress tensor is shown to be consistent with the generalized Boussinesq equation, and the interfacial shear and dilational viscosities are derived and characterized.

An example of interfacial anisotropic viscoelasticity due to nematic ordering is presented by evaluating and characterizing the dynamic interfacial tension. Explicit dependence, and hence anisotropy, of the interfacial tension on the tensor order parameter is discussed. It is found that, in the particular case of isotropy on the interface, the dynamic interfacial tension properly reduces to the generalized Boussinesq equation with a non-linear dependence of the shear and dilational viscosities on the nematic scalar order parameter.

The irreversible thermodynamic framework presented here gives a detailed treatment of interfacial nematodynamics by taking into account the intrinsic anisotropic viscoelastic nature of the interface between NPs and isotropic viscous fluids. The equations derived here will be required to describe interfacial transport phenomena in ordered fluid interfaces, including thin film hydrodynamics, liquid crystalline foams, freely suspended films, wetting and spreading of liquid crystalline films, interfacial wave propagation, Marangoni flows, to name a few. In addition, measuring interfacial material properties in ordered interfaces, such as interfacial tension, interfacial shear and dilational viscosities, must use model equations that take into account anisotropic viscoelasticity, as is done here.

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References

- [1] D.A. Edwards, H. Brenner, D.T. Wasan, *Interfacial Transport Processes and Rheology*, Butterworths, MA, 1991.
- [2] A.W. Adamson, *Physical Chemistry of Surfaces*, 4th Edition, Wiley, New York, 1982.
- [3] V.G. Levich, *Physicochemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, NJ, 1962.
- [4] R.F. Probstein, *Physicochemical Hydrodynamics*, Butterworths, MA, 1989.
- [5] J.C. Slattery, *Interfacial Transport Phenomena*, Springer, New York, 1990.
- [6] L.M. Blinov, V.G. Chigrinov, *Electrooptic Effects in Liquid Crystal Materials*, Springer, New York, 1994.
- [7] A.A. Sonin, *The Surface Physics of Liquid Crystals*, Gordon and Breach, Amsterdam, 1995.
- [8] B. Jerome, Surface alignment, in: D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds.), *Handbook of Liquid Crystals*, Vol. 1, Wiley-VCH, Weinheim, 1998.
- [9] H. Yokoyama, in: P.J. Collins, J.S. Patel (Eds.), *Handbook of Liquid Crystal Research*, Oxford University Press, New York, 1997, Chapter 6, p. 179.
- [10] M.A. Osipov, S. Hess, *J. Chem. Phys.* 99 (1993) 4181.
- [11] T.J. Sluckin, A. Poniewierski, in: C.A. Croxton (Ed.), *Fluid Interfacial Phenomena*, Wiley, Chichester, 1986 (Chapter 5).
- [12] A.K. Sen, D.E. Sullivan, *Phys. Rev. A* 35 (1987) 1391.
- [13] S. Faetti, in: I.-C. Khoo, F. Simoni (Eds.), *Physics of Liquid Crystalline Materials*, Gordon and Breach, Philadelphia, 1991, Chapter 12, p. 301.
- [14] G. Barbero, G. Durand, in: G.P. Crawford, S. Zumer (Eds.), *Liquid Crystals in Complex Geometries*, Taylor & Francis, London, 1996, pp. 21–52.
- [15] M. Kleman, S.A. Pikin, *Journal de Mecanique* 18(4) (1979).
- [16] A.D. Rey, *Macromolecules* 24 (1991) 177.
- [17] E.A. Oliveira, A.M. Figueiredo Neto, G. Durand, *Phys. Rev. A* 44 (1991) R825.
- [18] D. Langevin, M.A. Bouchiat, *Journal de Physique* 33 (1973) 101.
- [19] D. Bedeaux, A. Albano, P. Mazur, *Physica A* 82 (1976) 438–462.
- [20] P.G. de Gennes, J. Prost, *The Physics of Liquid Crystals*, 2nd Edition, Oxford University Press, London, 1993.

- [21] M. Srinivasarao, *Int. J. Mod. Phys. B* 9 (18/19) (1995) 2515.
- [22] S.-D. Lee, R.B. Meyer, in: A. Ciferri (Ed.), *Liquid Crystallinity in Polymers*, VCH, New York, 1991.
- [23] R.B. Meyer, in: A. Ciferri, W.R. Krigbaum, R.B. Meyer (Eds.), *Polymer Liquid Crystals*, Academic Press, New York, 1982.
- [24] H. Ehrentraut, S. Hess, *Phys. Rev. E* 51 (1995) 2203.
- [25] G. Marrucci, P.L. Maffettone, *J. Rheol.* 34 (1990) 1217–1230.
- [26] R.G. Larson, *Macromolecules* 23 (1990) 3983–3992.
- [27] B.J. Edwards, Ph.D. Dissertation, University of Delaware, 1991.
- [28] G. Marrucci, F. Greco, *Adv. Chem. Phys.* 86 (1993) 331.
- [29] R.G. Larson, *The Structure and Rheology of Complex Fluids*, Oxford University Press, New York, 1999.
- [30] J. Mewis, P. Moldenaers, *Curr. Opin. Colloid Interface Sci.* 1 (1996) 466.
- [31] B.J. Edwards, A.N. Beris, M. Grmela, *Mol. Cryst. Liq. Cryst.* 204 (1991) 54.
- [32] W.R. Burghardt, *Macromol. Chem. Phys.* 199 (1998) 471.
- [33] A.D. Rey, T. Tsuji, *Macromol. Theory Simul.* 7 (1998) 623.
- [34] T. Tsuji, A.D. Rey, *Phys. Rev. B* 57 (1998) 5609.
- [35] B.J. Edwards, A.N. Beris, M. Grmela, *J. Non-Newtonian Fluid Mech.* 35 (1990) 51–72.
- [36] J.T. Jenkins, P.J. Barrat, *Q. J. Mech. Appl. Math.* 27 (1974) 111.
- [37] J.L. Ericksen, in: G.H. Brown (Ed.), *Advances in Liquid Crystals*, Vol. 4, Academic Press, New York, 1979, p. 1.
- [38] E.G. Virga, *Variational Theories for Liquid Crystals*, Chapman & Hall, London, 1994.
- [39] A.D. Rey, *Phys. Rev. B* 60 (1999).
- [40] A.D. Rey, *J. Chem. Phys.* 110 (1999) 9769.
- [41] A.D. Rey, *Liq. Cryst.* 26 (1999) 913.
- [42] H. Stumpf, J. Badur, *Q. Appl. Math.* LI (1) (1993) 161.
- [43] B.J. Edwards, A.N. Beris, *J. Rheol.* 33 (1989) 1183–1193.
- [44] G.D.C. Kuiken, *Thermodynamics of Irreversible Processes*, Wiley, Chichester, West Sussex, England, 1994.