Tension gradients and Marangoni flows in nematic interfaces

Alejandro D. Rey*
Department of Chemical Engineering, McGill University, 3610 University Street, Montreal, Quebec, Canada H3A 2B2

(Received 10 February 1999)

This brief report (i) presents equations that govern the balance of tangential forces in interfaces between isotropic viscous fluids and nematic liquid crystals, and (ii) establishes the physical origin of nematic Marangoni flows. It is shown that surface gradients in the orientation dependent surface free energy gives rise to tangential nematic Marangoni forces. Tangential nematic Marangoni forces are caused by surface gradients of the nematic tensor order parameter, and the kinetic coefficient characterizing this interfacial phenomenon is proportional to nematic elastic storage. Expressions of the Marangoni forces using a classical constitutive equation for the surface free energy are given for general and uniaxial nematic ordering states. Nematic Marangoni flows or nematocapillarity augments the class of Marangoni flows present in electrocapillarity, diffusocapillarity, and thermocapillarity. [S1063-651X(99)12007-5]

PACS number(s): 61.30.−v

Capillary hydrodynamics in isotropic fluids is concerned with fluid flow phenomena in which interfacial tension is a significant effect [1–3]. An important case is flows with spatial gradients in the interfacial tension. For example, spatial gradients in the surface tension at the free surface of isotropic viscous fluids create a surface shear stress that can only be balanced by shear flow in the adjacent surface layers. The general phenomenon [1–3] is known as Marangoni flow, and the surface tension gradients driving the flow can be caused by temperature gradients (thermocapillarity flows), surface concentration gradients (diffusocapillary flows), and electric charges (electrocapillary flows). Applications of viscous flows driven by tangential stress caused by gradients in surface tensions are found in flow in porous media, damping of capillary waves, and cleavage of biological cells, to name a few.

Nematic liquid crystals [4] are known to have a component of the surface tension that is dependent on the nematic tensor order parameter [5]. Thus nematic liquid crystals will also exhibit surface-tension-driven flow caused by tangential stresses that appear to be due to tangential surface gradients of the tensor order parameter. The nematic tensor order parameter-driven Marangoni flow may thus appear only in the presence of weak anchoring, whenever the surface tensor order parameter deviates from the easy axis of the surface. As in other Marangoni flows [1–3], the effect is important when the gradients in surface tension are comparable to the characteristic kinetic energy density.

Consider the interfacial stress balance equation for an interphase between an isotropic viscous fluid and a uniaxial rodlike nematic liquid crystal [4]. The system is isothermal, and both phases are incompressible. The interphase is assumed to be elastic. Assume that a nematic liquid crystal (NLC) occupies region R^-, and that an isotropic viscous fluid region R^+. The NLC structure is given by the symmetric, traceless, 3×3 tensor order parameter $\mathbf{Q}$, usually [3] parametrized in terms of its eigenvectors as follows: $\mathbf{Q}=S(\mathbf{nn}-\delta/3)+P(\mathbf{mm}-\mathbf{ll})/3$, where $S(P)$ is the uniaxial (biaxial) scalar order parameter, and $(\mathbf{n},\mathbf{m},\mathbf{l})$ are the orthonormal eigenvectors; $\mathbf{n}$ is the director. The orientation of the interface between the $(\pm)$ regions is characterized by a unit normal $\mathbf{k}$, directed from R^- into R^+. The interfacial stress boundary condition at the NLC isotropic viscous fluid interface is expressed by [3]

$$-\mathbf{k}\cdot(\mathbf{t}^+-\mathbf{t}^-)=\boldsymbol{\nabla}_s\cdot\mathbf{t}^{\mathrm{se}}, \tag{1a}$$

$$\mathbf{t}^{\mathrm{se}}=F_s\mathbf{I}_s+\mathbf{t}^{\mathrm{sd}}, \tag{1b}$$

where $\mathbf{t}^{\pm}$ is the total stress tensor in the two $(\pm)$ bulk phases, $\boldsymbol{\nabla}_s=\mathbf{I}_s\cdot\boldsymbol{\nabla}$ is the surface gradient operator, $\mathbf{I}_s=\mathbf{I}-\mathbf{kk}$ is the surface idem factor, F_s is the interfacial free energy density, $\mathbf{t}^{\mathrm{se}}$ is the surface elastic stress tensor, and $\mathbf{t}^{\mathrm{sd}}$ is the surface distortion stress tensor.

A widely used expression for F_s is [5–7]

$$F_s(\mathbf{Q},\mathbf{k},\mathbf{N})=F_s(0)+\beta_{11}\mathbf{k}\cdot\mathbf{N}+\beta_{20}\mathbf{Q}\cdot\mathbf{Q}+\beta_{21}\mathbf{N}\cdot\mathbf{N}+\beta_{22}(\mathbf{k}\cdot\mathbf{N})^2, \tag{2a}$$

$$\mathbf{N}=\mathbf{Q}\cdot\mathbf{n}, \tag{2b}$$

where $F_s(0)$ is the usual isotropic part, $\{\beta_{ij}\}$, $ij=11$, 20, 21, and 22 are phenomenological parameters (energy and area); and where the $\mathbf{Q}$ dependent terms arise whenever the surface tensor order parameter deviates from the easy surface tensor order parameter $\mathbf{Q}^0$; where $\mathbf{Q}^0$ minimizes F_s. The constant β_{11} represents the effects due to the van de Waals interactions between the nematic and the isotropic phases. The easy axis for the director may be planar, homeotropic, or tilted, according to the signs and magnitudes of the $\{\beta_{ij}\}$; $ij=11$, 20, 21, and 22 [6].

Using the principle of virtual work, as done by de Gennes for the bulk Ericksen stresses [4], we find that the surface elastic stress tensor is given by

$$\mathbf{t}^{\mathrm{se}}=F_s\mathbf{I}_s+\mathbf{t}^{\mathrm{sd}}=F_s\mathbf{I}_s-\mathbf{I}_s\cdot\frac{\partial F_s}{\partial\mathbf{N}}\cdot\mathbf{Qk}-\mathbf{I}_s\cdot\frac{\partial F_s}{\partial\mathbf{k}}\mathbf{k}. \tag{3}$$

*FAX: (514) 398-6678.
Electronic address: inaf@musicb.mcgill.ca

In component form the surface elastic stress tensor $\mathbf{t}^{se}$ is given by the sum of the normal stresses (t_{11}^{se}, t_{22}^{se}) and bending stresses (t_{13}^{se}, t_{23}^{se}):

$$\mathbf{t}^{se} = \mathbf{i}_1\mathbf{i}_1 t_{11}^{se} + \mathbf{i}_2\mathbf{i}_2 t_{22}^{se} + \mathbf{i}_1\mathbf{k} t_{13}^{se} + \mathbf{i}_2\mathbf{k} t_{23}^{se}, \tag{4}$$

where $(\mathbf{i}_1, \mathbf{i}_2)$ are the surface orthonormal basis vectors. The surface elastic stress tensor $\mathbf{t}^{se}$ is a 2×3 tensor. The magnitudes of the normal stresses are given by

$$t_{11}^{se} = t_{22}^{se} = F_s(\mathbf{Q},\mathbf{k},\mathbf{N}), \tag{5}$$

and those of the bending stresses by

$$t_{13}^{se} = -\left[\mathbf{i}_1 \cdot \frac{\partial F_s}{\partial \mathbf{N}} \cdot \mathbf{Q} + \mathbf{i}_1 \cdot \frac{\partial F_s}{\partial \mathbf{k}}\right], \tag{6a}$$

$$t_{23}^{se} = -\left[\mathbf{i}_2 \cdot \frac{\partial F_s}{\partial \mathbf{N}} \cdot \mathbf{Q} + \mathbf{i}_2 \cdot \frac{\partial F_s}{\partial \mathbf{k}}\right]. \tag{6b}$$

As usual [3], surface gradients of normal stresses (t_{11}^{se}, t_{22}^{se}) generate tangential forces: $\mathbf{f}_\parallel = (\boldsymbol{\nabla}_s F_s)\cdot \mathbf{I}_s$. In nematic interfaces the surface gradients of the interfacial tension may arise due to surface gradients of the tensor order parameter. On the other hand, surface gradients in the bending stresses generate normal forces in addition to those arising from the usual curvature effects, i.e., $F_s \boldsymbol{\nabla}_s \cdot \mathbf{I}_s$. These additional normal forces $\mathbf{f}_\perp$ arise from surface gradients of the distortion stress tensor: $\mathbf{f}_\perp = \boldsymbol{\nabla}_s \cdot \mathbf{t}^{sd}$.

The tangential force balance equations involves gradients in the surface free energy density, and is obtained by projecting Eq. (1) along the tangent direction:

$$-\mathbf{k}\cdot(\mathbf{t}^+ - \mathbf{t}^-)\cdot \mathbf{I}_s = \boldsymbol{\nabla}_s \cdot \mathbf{t}^{se} \cdot \mathbf{I}_s = \mathbf{f}_\parallel, \tag{7}$$

where $\mathbf{f}_\parallel$ is the tangential Marangoni force due to surface gradients in the tensor order parameter. The Marangoni force is the driving force for surface flows [1–3]. Under isothermal conditions, in the absence of electromagnetic fields and concentration gradients, gradients the surface free energy may arise due to gradients in the nematic tensor order parameter, giving rise to the nematic Marangoni force

$$\mathbf{f}_\parallel = \left\{\left[\frac{dF_s(\mathbf{k},\mathbf{N},\mathbf{Q})}{d\mathbf{Q}}\right]^{[s]} : (\boldsymbol{\nabla}_s \mathbf{Q})^T\right\}\cdot \mathbf{I}_s = \left\{\left(\frac{\partial F_s}{\partial \mathbf{N}}\mathbf{k} + \frac{\partial F_s}{\partial \mathbf{Q}}\right)^{[s]} : (\boldsymbol{\nabla}_s \mathbf{Q})^T\right\}\cdot \mathbf{I}_s, \tag{8}$$

where the superscript $[s]$ denotes symmetric and traceless. The driving force for $\mathbf{f}_\parallel$ is $(\boldsymbol{\nabla}_s \mathbf{Q})$, and the kinetic coefficient is given by the gradient of the surface free energy with respect to $\mathbf{Q}$. Thus the nematic Marangoni force, like the other Marangoni forces such as in electrocapillarity, diffusocapillarity, and thermocapillarity, is directed from low energy regions toward high energy regions [1–3]. Using the constitutive equation (2), we obtain

$$\mathbf{f}_\parallel = \{[(\beta_{11} + 2\beta_{22}\mathbf{k}\cdot\mathbf{N})\mathbf{k}\mathbf{k} + 2\beta_{20}\mathbf{Q} + 2\beta_{21}\mathbf{N}\cdot\mathbf{k}]^{[s]} : (\boldsymbol{\nabla}_s \mathbf{Q})^T\}\cdot \mathbf{I}_s, \tag{9}$$

which gives the general phenomenological equation for the nematic Marangoni force.

Next we present the phenomenology predicted by Eq. (9) when $\mathbf{Q}$ is uniaxial: $\mathbf{Q} = S(\mathbf{nn} - \delta/3)$. In this case $\mathbf{f}_\parallel$ simplifies to

$$\mathbf{f}_\parallel = \left[\frac{\partial F_s}{\partial S}\boldsymbol{\nabla}_s S + \frac{\partial F_s}{\partial \mathbf{n}\cdot\mathbf{k}}\mathbf{k}\cdot(\boldsymbol{\nabla}_s \mathbf{n})^T\right]\cdot \mathbf{I}_s. \tag{10}$$

Consider a planar interface with unit normal $\mathbf{k} = \hat{\mathbf{z}}$, rectangular geometry (x,y,z), and a planar director field, $\mathbf{n}(x,y) = (\sin\theta, 0, \cos\theta)$, where $\mathbf{n}\cdot\mathbf{k} = \cos\theta$. For a planar director field $\mathbf{f}_\parallel$ is given by the general expression

$$\mathbf{f}_\parallel = \frac{\partial F_s}{\partial S}\boldsymbol{\nabla}_s S + \frac{\partial F_s}{\partial \theta}\boldsymbol{\nabla}_s \theta = \left[\beta_{11}(\cos^2\theta - 1/3) + \tfrac{4}{3}\beta_{20}S + \frac{2}{3}\beta_{21}S(\cos^2\theta + 1/3) + 2\beta_{22}(\cos^2\theta - 1/3)^2\right]\boldsymbol{\nabla}_s S \tag{11a}$$

$$-\left[2\beta_{11}S + \frac{2}{3}\beta_{21}S^2 + 4\beta_{22}S^2(\cos^2\theta - 1/3)\right]\cos\theta\sin\theta\boldsymbol{\nabla}_s\theta. \tag{11b}$$

Equation (11a) clearly shows that, as noted above, $\mathbf{f}_\parallel$ is directed away from low energy regions and toward high energy regions, as in gradient flows. Minimum energy regions are those corresponding to the three equilibrium points $\{\theta^i, S^i$, where i is planar, homeotropic, and tilted$\}$ of F_s in the uniaxial case, whose values were given in Ref. [3]. Thus the coefficient that governs the magnitude of the Marangoni force $\mathbf{f}_\parallel$ is a function of the deviation of $\{S,\theta\}$ from its equilibrium value or easy axis $\{\theta^i, S^i\}$.

As a representative case of interfacial conditions, let the director be fixed $(\boldsymbol{\nabla}_s \mathbf{n} = 0)$ and S variable $(\boldsymbol{\nabla}_s S \neq \mathbf{0})$. As mentioned above there are three possible stable preferred director orientations [6]: (i) planar (P) $\theta = \pi/2$; (ii) homeotropic (H) $\theta = 0$; and (iii) tilted (T) $0 < \theta < \pi/2$, according to the signs and magnitudes of the coefficients $\{\beta_{ij}\}$; $ij = 11$, 20, 21, and 22, appearing in Eq. (2). The three tangential forces $\mathbf{f}_\parallel^i$; $i = P$, H, and T are

$$\mathbf{f}_\parallel^P = \left[-\frac{\beta_{11}}{3} + \frac{4}{3}\beta_{20}S + \frac{2}{9}S(\beta_{21} + \beta_{22})\right]\boldsymbol{\nabla}_s S, \tag{12a}$$

$$\mathbf{f}_{\parallel}^{H}=\left[\frac{2}{3}\beta_{11}+\frac{4}{3}\beta_{20}S+\frac{8}{9}S(\beta_{21}+\beta_{22})\right]\nabla_s S, \tag{12b}$$

$$\mathbf{f}_{\parallel}^{T}=\left[\beta_{11}(\cos^2\theta-1/3)+\frac{4}{3}\beta_{20}S+\frac{2}{3}\beta_{21}S(\cos^2\theta+1/3)+2\beta_{22}(\cos^2\theta-1/3)^2\right]\nabla_s S, \tag{12c}$$

$$\cos^2\theta=-\left(1+4\frac{\beta_{20}}{\beta_{21}}\right). \tag{12d}$$

Given the nature of the nematic Marangoni force, a small fluctuation of S around its equilibrium value of wavelength λ gives rise to a fluctuation in $\mathbf{f}_{\parallel}$ of wavelength λ/2, and a symmetric pulse (singlet) in S gives rise to an antisymmetric doublet. Other, more complex, cases involving nonlinearities and $\mathbf{n}$-S couplings, as well considerations of the bulk stresses, can be analyzed with the framework presented in this Brief Report.

To give some more physical insights and suggest some experiments it is useful to compare the Marangoni force due to an interfacial temperature gradients in the nematic phase $\mathbf{f}_{\parallel}^{N}$ and in the isotropic phase $\mathbf{f}_{\parallel}^{\mathrm{is}}$:

$$\mathbf{f}_{\parallel}^{N}=\left[\frac{\partial F_s}{\partial T}\nabla_s T\right]\cdot\mathbf{I}_s, \tag{13a}$$

$$\mathbf{f}_{\parallel}^{\mathrm{is}}=\left[\frac{\partial F_s(0)}{\partial T}\nabla_s T\right]\cdot\mathbf{I}_s. \tag{13b}$$

The Marangoni force in the isotropic phase $\mathbf{f}_{\parallel}^{\mathrm{is}}$ is the well-characterized thermocapillarity force. $\partial F_s(0)/\partial T$ is always negative, almost linear, and typically of the order of -0.1 $\mathrm{mN\,m^{-1}\,K^{-1}}$ [2]. On the other hand, for well characterized low-molar-mass nematic liquid crystals, such as *PAA* and *p*-anisaldazine, $\partial F_s/\partial T$ shows the following features as a function of the temperature T [8]:

$$T<T_m,\quad \frac{\partial F_s}{\partial T}\equiv\left[\frac{\partial F_s}{\partial T}\right]<0,$$

$$T=T_m,\quad \frac{\partial F_s}{\partial T}\equiv\left[\frac{\partial F_s}{\partial T}\right]^0=0,$$

$$T>T_m,\quad \frac{\partial F_s}{\partial T}\equiv\left[\frac{\partial F_s}{\partial T}\right]^+>0.$$

The data show that the magnitude of $[\partial F_s/\partial T]^-$ is of the same order as $\partial F_s(0)/\partial T$, but smaller than $[\partial F_s/\partial T]^+$. Thus when $T<T_m$ the Marangoni force in the nematic phase is similar to the isotropic case, when $T=T_m$ it vanishes, and when $T>T_m$ it is larger and in the reverse direction than the isotropic case. We can spatially impress these three regimes onto a surface by introducing a temperature field that encompasses the three responses. The presence of a one-dimensional temperature field, $T=T(x)$ say, that includes T_m will give rise to a surface source line at $x=x_m$ at which the Marangoni force is zero because the surface tension is a minimum. To the left and right the flow is away from x_m. Finally we use the present model to estimate the magnitude of $\mathbf{f}_{\parallel}^{N}/\mathbf{f}_{\parallel}^{\mathrm{is}}$, or equivalently $(\partial F_s/\partial T)/(\partial F_s(0)/\partial T)$, for the planar case in the absence of orientation gradients, when S at the surface and at the bulk at equal. The temperature dependence is assumed as $S(T)=\Delta[(T_0-T)/T_0]^{1/2}$, where Δ is a constant and T_0 is few degrees above T^* [7]. Replacing for $S(T)$ in Eq. (12a), we find that

$$\frac{\partial F_s}{\partial T}\Bigg/\frac{\partial F_s(0)}{\partial T}=\frac{\beta_{11}S}{6(T_0-T)(\partial F_s(0)/\partial T)}+\cdots. \tag{14}$$

Using the $\beta_{11}=10^{-3}-1\ \mathrm{mN\,m^{-1}}$ [9], $\partial F_s(0)/\partial T=-0.1\ \mathrm{mN\,m^{-1}\,K^{-1}}$, we find that to first order the range of $(\partial F_s/\partial T)/(\partial F_s(0)/\partial T)$ is from $-1.66\times10^{-3}S/(T_0-T)$ to $-1.66S/(T_0-T)$, where the minus sign indicates that the Marangoni force from the anchoring energy acts in an opposite direction to the isotropic contribution, as observed experimentally.

In summary, as in all fluids, the interfacial stress balance equation involves the surface divergence of the surface stress tensor. The presence of anisotropic elastic storage due to weak anchoring conditions gives rise to bending stresses, in addition to the normal stresses. Surface gradients of the normal stresses generate tangential forces. The tangential forces are similar to those generated by surface tension gradients caused by thermal gradients, concentration gradients, and electric charge gradients. The nematic Marangoni forces that are the driving forces for surface flows are caused by surface gradients of the component of the interfacial free energy that depends on the nematic order parameter.

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

[1] V. G. Levich, *Physicochemical Hydrodynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1962).
[2] R. F. Probstein, *Physicochemical Hydrodynamics* (Butterworth, Stoneham, MA, 1989).
[3] D. A. Edwards, H. Brenner, and D. T. Wasan, *Interfacial Transport Processes and Rheology* (Butterworth, Stoneham, MA, 1991).
[4] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed (Oxford University Press, London, 1993).
[5] W. J. A. Goosens, Mol. Cryst. Liq. Cryst. **124**, 305 (1985).

[6] 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.

[7] A. L. Alexe-Ionescu, R. Barberi, G. Barbero, T. Beica, and R. Maldovan, Z. Naturforsch. A **47A**, 1235 (1992).

[8] S. Chandrasekhar, *Liquid Crystals*, 2nd ed. (Cambridge University Press, Cambridge, 1992), pp. 80–84.

[9] A. A. Sonin, *The Surface Physics of Liquid Crystals* (Gordon and Breach, Amsterdam, 1995), pp. 41–46.