Mechanical theory of structural disjoining pressure in liquid crystal films

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A mechanical theory of structural disjoining pressure in nematic liquid crystal films is developed based on Laplace's interfacial stress balance equation. Identification of the interfacial stresses in nematic liquid crystal interfaces leads to two contributions to the structural disjoining pressure. It is shown that tensor order parameter gradients across the film give rise to bulk Ericksen stresses, whose normal component results in a disjoining pressure that tends to stabilize the film. In addition, tangential gradients in the tensor order parameter give rise to gradients in interfacial bending stresses whose normal component results in a film pressure that may be disjoining or conjoining. Phenomenological expressions for the two structural disjoining pressures are obtained using the classical equations of liquid crystal bulk and surface elasticity.

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Disjoining pressure is a term used to designate an excess pressure acting normal to a thin film interface [1,2]. When the excess pressure is positive (negative) it promotes film stability (instability) and is termed disjoining (conjoining) pressure. Classical excess film pressures due to van der Waals interactions are usually conjoining, while those due to electrostatic repulsion are disjoining. Disjoining pressure models are important to understand and characterize thin film hydrodynamics and thin film stability, and to model phenomena such as foam and emulsion coalescence, and wetting and dewetting [1,2].

For liquid crystalline (LC) films, such as freely standing films, additional structural disjoining pressures have been experimentally identified [2,3,4]. For nematic liquid crystal (NLC) films, orientation gradients across the film due to asymmetric interfacial conditions were shown to give rise to a structural disjoining pressure. A thermodynamic approach was used to formulate this structural disjoining pressure in asymmetric NLC films [4]. Experiments with symmetric NLC films lead to the identification of another source of structural disjoining pressure in NLC films. The additional source of disjoining pressure was identified as gradients in the scalar order parameter between the film and the meniscus in contact with the film. A general formulation of structural disjoining pressures that takes into account transverse and longitudinal nematic ordering gradients has not been formulated. Such a formulation will be necessary to study thin NLC film hydrodynamics and thin NLC film stability, and to model processes such as formation and stability of carbonaceous mesophase foams using discotic NLC precursors [5].

NLC's are anisotropic materials whose hydrostatics [6] and capillarity [7,8] involves short range elasticity, anisotropic long range bulk (Frank) elasticity, and anisotropic interfacial tension. It will be shown below that structural film pressures arise as a consequence of different gradients of these elasticities. The objectives of this paper are (1) to formulate a general mechanical model of all structural disjoining and conjoining pressures in NLC thin films using Laplace's equation; (2) to derive phenomenological expressions for the structural disjoining pressure in NLC thin films, surrounded by an isotropic fluid phase, using the classical elasticity theory of NLC; and (3) to provide representative examples of disjoining and conjoining film pressures in symmetric films. Extensions to other thin film cases [1], such as thin NLC films between a solid and air, or between a fluid droplet and a solid can be performed using the equations given here. The use of Laplace's equation to model disjoining pressures is common practice in Boussinesq interfaces [1].

The system considered in this paper is a planar thin NLC film in contact with an isotropic fluid phase. A classical example is a NLC film between two large fluid droplets [1]. The film is assumed to be isothermal, and both phases are incompressible. The NLC occupies region R^N and the isotropic fluid regions R^I. The orientation of the interface between the R^N/R^I regions, denoted by *NI*, is characterized by a unit normal $\mathbf{k}$, directed from R^N into R^I. The NLC structure is given by the symmetric, traceless, 3×3 tensor order parameter $\mathbf{Q}$, usually parametrized as follows [6]:

$$\mathbf{Q}=S(\mathbf{nn}-I/3)+P(\mathbf{mm}-\mathbf{ll})/3, \tag{1}$$

where $S(P)$ is the uniaxial (biaxial) scalar order parameter, and $(\mathbf{n,m,l})$ are the orthonormal eigenvectors; $\mathbf{n}$ is the director. The total free energy in a volume V of the nematic polymer bounded by a surface A according to the Landau–de Gennes theory is given by [9–12]

$$F=\int_V [f_G(\nabla\mathbf{Q})+f_L(\mathbf{Q})]dV+\int_A \gamma(\mathbf{Q,k,N})dA, \tag{2}$$

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

$$f_G(\nabla\mathbf{Q})=\frac{L_1}{2}\mathrm{tr}\nabla\mathbf{Q}^2+\frac{L_2}{2}(\nabla\cdot\mathbf{Q})\cdot(\nabla\cdot\mathbf{Q})^T, \tag{3}$$

$$f_L(\mathbf{Q})=a\,\mathrm{tr}\mathbf{Q}^2-b\,\mathrm{tr}\mathbf{Q}^3+c(\mathrm{tr}\mathbf{Q}^2)^2, \tag{4}$$

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$$\gamma(\mathbf{Q},\mathbf{k},\mathbf{N}) = \gamma_{\rm is} + \gamma_{\rm an}, \tag{5a}$$

$$\gamma_{\rm an} = \beta_{11}\mathbf{k}\cdot\mathbf{N} + \beta_{20}\mathbf{Q}\cdot\mathbf{Q} + \beta_{21}\mathbf{N}\cdot\mathbf{N} + \beta_{22}(\mathbf{k}\cdot\mathbf{N})^2; \quad \mathbf{N} = \mathbf{Q}\cdot\mathbf{n}, \tag{5b}$$

where ∇ is the gradient operator, $\{L_i\}, i=1,2$ are the Frank elastic constants (energy/length), $[i]; i=a,b,c$ are the Landau coefficients (energy/volume), $\gamma_{\rm is}$ is the isotropic interfacial tension, $\gamma_{\rm an}$ is the anchoring energy, and $\{\beta_{ij}\}, ij = 11,20,22,22$ are the anchoring coefficients (energy/area). For NLC the order of magnitude of the Frank elastic constants of 10^{-7} dynes [6], of the isotropic surface tension 10^2 ergs/cm^2 [2], and of the anchoring coefficients $10^{-3} - 1$ erg/cm^2 [2].

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 $\gamma_{\rm is}$ and an anisotropic orientation dependent contribution $\gamma_{\rm an}$. The anchoring energy $\gamma_{\rm an}$ is a function of $\mathbf{Q}$, and $\mathbf{k}$, which indicates that there are two mechanisms to store surface elastic energy, one is through macroscopic orientation (**n,m,l**) and the other through the molecular ordering (*S,P*). 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 $(d\gamma_{\rm an}/d\mathbf{Q})^{[s]} = 0, d\gamma/d\mathbf{k} = \mathbf{0}$, where $[s]$ denotes symmetric and traceless. Given space limitations we refer the reader to Refs. [12–15] for details on orientation anchoring conditions in interfaces involving nematic liquid crystals.

The interfacial stress balance equation accross the *NI* interface is given by [1]

$$-\mathbf{k}\cdot(\mathbf{t}^I - \mathbf{t}^N) = \nabla_s\cdot\mathbf{t}_s + \Pi_{cd}\mathbf{k} = \mathbf{f} + \Pi_{cd}\mathbf{k}, \tag{6}$$

where $\mathbf{t}^I$ is the total stress tensor in the isotropic fluid phase, $\mathbf{t}^N$ is the total stress tensor in the NLC film, $\mathbf{t}_s$ is the total elastic surface stress tensor acting on the *NI* interface, and Π_{cd} is the classical disjoining pressure, due to van der Waals and electrostatic interactions [2,14,15]. Of these three stress tensors only $\mathbf{t}^I$ is symmetric, while as seen below, $\mathbf{t}^N$ and $\mathbf{t}_s$ are asymmetric. Equation (6) is a generally valid interfacial stress balance equation, independent of the specific nature of the bulk phases [1]. In the absence of flow, it is the static limit of the interfacial momentum balance equation, also known as the generalized Laplace equation [1]. The specific characteristic nature of the hydrostatics of the *NI* interfaces resides in the constitutive equations for $\mathbf{t}^N$ and $\mathbf{t}_s$. The total stress tensor in the isotropic phase $\mathbf{t}^I$ is just

$$\mathbf{t}^I = -p^I\mathbf{I}, \tag{7}$$

where p^I is the hydrostatic pressure. The total stress tensor in the NLC phase $\mathbf{t}^N$ is given by

$$\mathbf{t}^N = -p^N\mathbf{I} + \mathbf{t}^E, \tag{8}$$

where p^N is the hydrostatic pressure and $\mathbf{t}^E$ is the Ericksen stress given by

$$\mathbf{t}^E = -\frac{\partial f_G}{\partial\nabla\mathbf{Q}}:(\nabla\mathbf{Q})^T = -L_1\nabla\mathbf{Q}:(\nabla\mathbf{Q})^T - L_2(\nabla\mathbf{Q})^T\cdot(\nabla\cdot\mathbf{Q}). \tag{9}$$

Following Ref. [6] the hydrostatic pressure in the NLC phase is given by

$$p^N = -(f_G + f_L) + \Phi, \tag{10}$$

where Φ is a function of density and temperature $\Phi(\rho,T)$ and is space independent,

$$\nabla\Phi = 0 \tag{11}$$

Surface anchoring energy gives rise to a new contribution to the surface stress tensor $\mathbf{t}_s$ of isotropic materials [7,8]. For an interface between an isotropic substrate and a NLC 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:

$$\mathbf{t}_s = \mathbf{t}^n + \mathbf{t}^b; \quad \mathbf{t}^n = \gamma\mathbf{I}_s; \quad \mathbf{t}^b = -\mathbf{I}_s\cdot\left(\frac{d\gamma_{an}}{d\mathbf{k}}\mathbf{k}\right). \tag{12}$$

For details on the physics of bending stresses in nematic interfaces the reader is referred to Refs. [7,8].

Using the expression for the surface stress tensor $\mathbf{t}_s$ we find the following expression for the interfacial force $\mathbf{f}$:

$$\mathbf{f} = \nabla_s.\mathbf{t}_s = \underbrace{\left\{\left[\frac{d\gamma_{\rm an}}{d\mathbf{Q}}\right] : (\nabla_s\mathbf{Q})^{\rm T}\right\}\cdot\mathbf{I}_s + \{2H\gamma\}\mathbf{k}}_{\text{normal stress contribution}} + \underbrace{\left\{-2H\left(\frac{d\gamma_{\rm an}}{d\mathbf{k}}.\mathbf{k}\right) - \nabla_s.\left(\frac{d\gamma_{\rm an}}{d\mathbf{k}}\right)\right\}\mathbf{k}}_{\text{bending stress contribution}} \tag{13}$$

where $H=-\nabla_s\cdot\mathbf{k}/2$ is the mean curvature. Equation (13) shows that surface gradients in the normal (tension) surface stress $\mathbf{t}^n$ give rise to tangential (perpendicular to $\mathbf{k}$) and normal forces (parallel to $\mathbf{k}$), while surface gradients of bending stress give rise only to normal forces. Tangential forces give rise to Marangoni nematic flows [16]. Equation (13) shows that the latter persist even in the absence of curvature ($H=0$).

The normal component of Eq. (6) is known as the generalized Laplace equation:

$$-\mathbf{k}\cdot(\mathbf{t}^1-\mathbf{t}^N)\cdot\mathbf{k}=\boldsymbol{\nabla}_s\cdot\mathbf{t}_s\cdot\mathbf{k}+\Pi_{cd}=f_\perp+\Pi_{cd}, \tag{14}$$

where $f_\perp$ is the magnitude of the interfacial normal force originating from the surface gradients of the bending stresses, and according to Eq. (13) it is given by

$$f_\perp=2H\gamma-2H\left(\frac{d\gamma_{an}}{d\mathbf{k}}\cdot\mathbf{k}\right)-\nabla_s\cdot\left(\frac{d\gamma_{an}}{d\mathbf{k}}\right). \tag{15}$$

The normal force originating at a nematic interface may be nonzero even for planar interfaces ($H=0$). Replacing expressions (7)–(9), (15) into Eq. (14) we find that the generalized Laplace equation for NI interfaces is

$$p^1-p^N=\Pi_{cd}+\left\{\frac{\partial f_G}{\partial\boldsymbol{\nabla}\mathbf{Q}}:(\boldsymbol{\nabla}\mathbf{Q})^T\right\}:\mathbf{kk}+\left\{2H\gamma-2H\left(\frac{d\gamma_{an}}{d\mathbf{k}}\cdot\mathbf{k}\right)-\nabla_s\cdot\left(\frac{d\gamma_{an}}{d\mathbf{k}}\right)\right\}, \tag{16}$$

where $p^N=-(f_G+f_L)+\Phi$.

According to the mechanical model of disjoining pressure for planar thin films obtained, as done here, by applying the normal stress balance at an interface, the total disjoining pressure Π is

$$p^1-p^N=\Pi=\Pi_{cd}+\Pi_s, \tag{17}$$

where Π_s is the structural disjoining pressure. For flat planar films, the curvature vanishes ($H=0$), and the normal stress balance equation (16) for a NLC film simplifies to

$$p^1-p^N=\Pi_{cd}+\left\{\frac{\partial f_G}{\partial\boldsymbol{\nabla}\mathbf{Q}}:(\boldsymbol{\nabla}\mathbf{Q})^T\right\}:\mathbf{kk}-\left\{\boldsymbol{\nabla}_s\cdot\left(\frac{d\gamma_{an}}{d\mathbf{k}}\right)\right\}\Big|_{b=0}. \tag{18}$$

Comparing Eq. (17) with Eq. (18) we see that the structural disjoining pressure Π_s is given by

$$\Pi_s=\Pi_\perp+\Pi_\parallel, \tag{19}$$

$$\Pi_\perp=\left\{\frac{\partial f_G}{\partial\boldsymbol{\nabla}\mathbf{Q}}:(\boldsymbol{\nabla}\mathbf{Q})^T\right\}:\mathbf{kk}=L_1[\boldsymbol{\nabla}\mathbf{Q}:(\boldsymbol{\nabla}\mathbf{Q})^T]:\mathbf{kk}+L_2[(\boldsymbol{\nabla}\mathbf{Q})^T\cdot(\boldsymbol{\nabla}\mathbf{Q})]:\mathbf{kk}, \tag{20}$$

$$\Pi_\parallel=-\nabla_s\cdot\left(\frac{d\gamma_{an}}{d\mathbf{k}}\right)\Big|_{b=0}=-\{\nabla_s\cdot[2\beta_{11}\mathbf{Q}\cdot\mathbf{k}+2\beta_{21}\mathbf{Q}\cdot\mathbf{k}\cdot\mathbf{Q}+4\beta_{22}(\mathbf{Q}:\mathbf{kk})\mathbf{Q}\cdot\mathbf{k}]\}|_{b=0}, \tag{21}$$

where $\Pi_\perp$ is the film pressure due to transverse (i.e., along $\mathbf{k}$) bulk gradients of the tensor order parameter and $\Pi_\parallel$ is the film pressure due to tangential (i.e., orthogonal to $\mathbf{k}$) surface gradients of the tensor order parameter. Since $\Pi_\perp$ is always positive it is a disjoining pressure that tends to promote film stability. On the other hand, $\Pi_\parallel$ can be disjoining or conjoining, since the surface gradients can be of either sign. To make explicit the origin of the structural disjoining pressure we can identify them with the corresponding stress tensor components, as follows:

$$\Pi_\perp=-\mathbf{t}^E:\mathbf{kk}=-t^E_{zz}, \tag{22}$$

$$\Pi_\parallel=\nabla_s\cdot\mathbf{t}^b_s|_{b=0}, \tag{23}$$

showing that the transverse disjoining pressure is minus the *zz* component of the Ericksen stress tensor, while the tangential disjoining pressure is the surface gradient of the surface bending stress tensor.

The transverse disjoining pressure $\Pi_\perp$ is well known and has been measured experimentally, although the analysis has been mainly restricted to director gradients and not on gradients of the scalar order parameters. As it appears certain that for uniaxial materials the uniaxial scalar order parameter varies across the film thickness [2], the equation presented here is appropriate, since it takes into account all contributions arising from bulk gradients across the film thickness. The tangential disjoining pressure $\Pi_\parallel$ due to tangential gradients of the scalar order parameter is a structural disjoining pressure contribution that arises naturally when using the generalized Laplace equation of liquid crystals, and its existence is a direct consequence of anisotropic surface tension and bending stresses. A similar effect to $\Pi_\parallel$ has already been discussed in the literature [4] and used to explain disjoining pressure measurements in the absence of director gradients across the film thickness, that is, when $\Pi_\perp=0$. In that case the experimental data was explained by the difference of the order parameter in the film and in the reservoir that is in contact with the film. Since the order parameters differ, a net change in the short range energy f_L between the film and the reservoir exists that results in a net disjoining pressure. In the mechanical model presented here this effect is taken into account since the model is presented in terms of tangential gradients of the tensor order parameter.

The magnitudes of the film pressures $\Pi_\perp$ and $\Pi_\parallel$ depend on the Frank elastic moduli and the anchoring energy, respectively, and the geometry of the film. As measured experimentally [2,3], the disjoining pressure $\Pi_\perp$ is of the order of $10^{-2}-10^{-3}$ atm, a value that is consistent with an order of magnitude calculation with $L\approx=10^{-6}$ dynes/cm and a film thickness of 0.01 μm. Similar order of magnitudes for $\Pi_\parallel$ are consistent with an order of magnitude calculation using the present model, with an anchoring strength of 10^{-1} erg/cm^2 and a characteristic tangential distance of 0.01 μm, representing the coherence length.

As a representative illustration of the calculation of the transverse structural disjoining pressure $\Pi_\perp$ we assume a uniaxial planar NLC film, with a constant director field, but a space dependent scalar order parameter. This situation could arise in a thin NLC film between two large viscous droplets, or in a freely suspended film, where both interfaces are

chemically and mechanically equivalent. In rectangular coordinates (x,y,z), with $\mathbf{k}$ along z, let $\mathbf{n}=(n_x,0,n_z)$, and $S=S(z)$. Using Eq. (26) we find that the transverse structural disjoining pressure for planar and homeotropic director orientation are

$$\Pi_{\perp}=\frac{2}{3}\left(L_1+\frac{L_2}{6}\right)\left(\frac{dS}{dz}\right)^2; \quad \text{for } \mathbf{n}=(1,0,0), \tag{24}$$

$$\Pi_{\perp}=\frac{2}{3}\left(L_1+\frac{2L_2}{3}\right)\left(\frac{dS}{dz}\right)^2; \quad \text{for } \mathbf{n}=(0,0,1). \tag{25}$$

Since $L_1>0$ and $L_1+2L_2/3>0$, then in both cases $\Pi_{\perp}>0$, as expected. In freely standing thermotropic NLC films it is found experimentally that at the surface layer $S\approx 0.4-0.8$ and at the bulk $S\approx 0.3-0.5$; the surface layer thickness is several hundred Å [2]. Using Eqs. (30), (31), $(dS/dx)^2=1/(500\,\text{Å})^2$, and an effective Frank constant $L=10^{-6}$ dynes, we found $\Pi_{\perp}=10^{-2}$ atm. As a representative illustration of the calculation of the tangential structural disjoining pressure $\Pi_{\parallel}$ we assume a uniaxial planar NLC film, with a constant director field, but a space dependent scalar order parameter. In rectangular coordinates (x,y,z), with $\mathbf{k}$ along z, let $\mathbf{n}=(n_x,0,n_z)$, $\mathbf{n}\cdot\mathbf{k}=\cos\theta$, and $S=S(x)$. This situation could arise in a thin NLC bridge, under conditions that promote changes in the order parameter along the NLC bridge, as occurs in classical disjoining pressure measurements [4]. Using Eq. (27) we find that the tangential structural disjoining pressure for an arbitrary director orientation is

$$\Pi_{\parallel}=\left(\beta_{11}+\frac{2}{3}\beta_{21}S+4\beta_{22}S(\cos\theta^2-1/3)\right)\sin 2\theta\frac{dS}{dx}, \tag{26}$$

which shows that if the director orientation is not an extrema of the anchoring energy, scalar order parameter gradients create a structural film pressure that can be disjoining or conjoining, depending on the sign of dS/dx. Using an anchoring strength of 10^{-1} erg/cm^2 and a characteristic tangential distance of 0.01 μm, representing the coherence length, $\Pi_{\parallel}$ is of the order of 10^{-2} atm.

The present mechanical model is based on the proper incorporation of the asymmetric 2×3 surface and 3×3 bulk elastic stress tensors of nematic liquid crystals [16] into the static limit of the interfacial linear momentum balance equation [1]. On the other hand, rigorous and accurate thermodynamic models of nematic liquid crystals have been developed and successfully applied to the description of structural forces in confined systems [17,18].

In summary, this paper presents a mechanical model of structural disjoining pressures in nematic liquid crystal films. Using the generalized Laplace equation for nematics, two types of disjoining pressures are identified. The transverse component of the disjoining pressure arises due to tensor order parameter gradients across the film thickness. The transverse structural disjoining pressure is positive definite and stabilizes the film. The tangential component of the disjoining pressure arises due to gradients of the tensor order parameter along the film, and it can be disjoining or conjoining. An order of magnitude analysis of the two structural pressures is consistent with experimental results. The mechanical model is based on the generally valid Laplace pressure balance equation for an interface; the transverse structural disjoining pressures arise as a consequence of the bulk Ericksen stress tensor present in nematics, while the tangential structural disjoining pressure is a consequence of gradients of the surface stress tensor. The theoretical framework developed in this paper can be used to study the stability of thin films, fluctuations in thin films, and liquid crystal foam stability.

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