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01 September 2025

Continuum description of the interfacial layer of nematic liquid crystals in contact with solid surfaces

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We investigate when it is possible to introduce surface physical parameters characterizing the nematic/substrate interface. The analysis is performed by solving the problem assuming that the presence of the surface introduces a spatial variation, mainly localized close to the limiting surfaces, of the bulk properties of the nematic (delocalized model). The results of the calculation are compared to the prediction of a model in which the presence of the surface is taken into account by means of new physical parameters, localized to the surface (localized model). We show that if the viscous dissipative effects or the surface alignment effects are considered, the two models predict the same relaxation times and the same threshold for the Freedericksz transition is obtained. From these results we deduce that the localized models are equivalent to the delocalized ones. A continuum description of the interfacial layer of nematic liquid crystals in contact with solid surface in terms of surface properties is then correct, which makes the solution of this kind of problems simpler. Also a softening of the elastic constants near the surfaces can be represented by a localized surface energy term. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3126657]

I. INTRODUCTION

Nematic liquid crystals are anisotropic liquids formed by molecules with anisotropic shapes such as rodlike or disklike molecules. The intermolecular forces responsible for the nematic order tend to orient the symmetry axes of the molecules along a common direction **n**. In the continuum description, a nematic liquid crystal is characterized by a volume (bulk) energy density connected to the elastic properties of the medium and to the anisotropic interaction of the medium with the external fields, commonly electric, and magnetic fields. The bulk contribution to the free energy density is well known, and it is characterized by the elastic constants, introduced by Oseen and Frank, and by the anisotropy of the bulk values of the dielectric and diamagnetic constants.[1] The actual nematic orientation, in the case in which the limiting surfaces imposes the nematic orientation, is obtained by means of a variational calculation.[2,3] This case corresponds to the strong anchoring situation. Very often, the interaction of the nematic liquid crystal with the aligning layer is comparable with the volume deformation energy of the nematic liquid crystal. This case, which is important for technological applications, is known as weak anchoring case. In this situation, the surface orientation of the nematic director depends on the bulk deformation imposed by means of external field. In the dynamical situation, dissipative effects related to the presence of the limiting surfaces are expected. To describe the aligning effect of the substrate on the nematic liquid crystal the concepts of anchoring energy strength and of easy axis have been introduced, by assuming that the surface potential due to the substrate is short range.[4] A simi-

lar procedure has been used for the surface viscosity, introduced to take into account the dissipative effects related to the presence of the limiting surfaces.[5] A simple inspection of the problem under consideration indicates that the surface properties are related to properties of the bulk, but confined to surface layers whose thicknesses are negligible compared to the thickness of the sample. The surface parameters assumed to describe the physics of the interface are, actually, integrals of the bulk properties in the surface layers. However, as it is well known, the use of localized properties usually simplifies the mathematics of the problem, but in some cases can give rise to absurd results. The aim of our paper is to investigate when it is possible to introduce surface parameters to describe interface effects, and when it gives rise to ill-posed problems.

In our analysis we consider the case in which the bulk viscosity changes close to the limiting surfaces. We will solve first the thin boundary layer case, which we denote the "delocalized model,"[6,7] and then the "localized" case in which the surface viscosity is considered as a property of the geometrical surface. The same type of analysis is performed for the surface potential, responsible for the anchoring energy, and for the spatial variation of the elastic constant. The introduction of surface viscosity means that system is allowed to spend a finite time to adjust to rapid changes of the surface torque. In that way we might avoid some mathematical difficulties that occur when the surface viscosity is assumed to be exactly zero, which would imply an infinitely fast adjustment of the surface conditions to a change in torque. The same mathematical difficulties might occur in problems related to the heat conduction with generalized boundary conditions, known as Robin's boundary

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conditions,[8] and also the introduction of the corresponding term might allow a soft relaxation in the case of rapidly changing conditions. We show, furthermore, that the introduction of the localized surface energy is a useful concept that does not give rise to any mathematical problem, and allows a simple description of the influence of a limiting surface on the nematic liquid crystals. Also a softening of the elastic constants near the surfaces might be represented by a localized surface energy term.

II. SURFACE VISCOSITY

A. Delocalized model for the surface viscosity

We consider a sample in the shape of a slab of thickness d. The Cartesian reference frame used for the description has the z-axis perpendicular to the limiting surfaces, located at $z = \pm d/2$. We indicate by k the elastic constant of the liquid crystal, in the one-constant approximation, and assume that the rotational viscosity of the nematic liquid crystal, η, is position dependent $\eta = \eta(z)$. The surface treatment of the limiting surfaces is assumed to be such to induce homeotropic alignment, with identical anchoring energies on the two limiting surfaces.[4] The angle formed by $\mathbf{n}$ with the z-axis is indicated by ϕ. In the bulk, $\eta(z)$ takes the value η_b, coinciding with the bulk rotational viscosity of the liquid crystal. Close to the border, the dissipation phenomenon could be associated to a different value of the viscosity, and $\eta(z)$ may differ from η_b.[6,7] We assume that the nematic orientation induced by the surface treatment is affected by an external field. We are interested in the relaxation of the initial deformation, described by the function $\Phi(z)$, when the external field is removed. In our framework $\phi = \phi(z,t)$, such that $\phi(z,0) = \Phi(z)$. The bulk differential equation stating that the elastic torque is balanced by the viscous torque is as follows:[9,10]

$$k\frac{\partial^2 \phi}{\partial z^2} = \eta(z)\frac{\partial \phi}{\partial t}, \tag{1}$$

that has to be solved with the boundary conditions

$$\pm k\left(\frac{\partial \phi}{\partial z}\right)_{z=\pm d/2} + w\phi(\pm d/2,t) = 0. \tag{2}$$

Equation (2) is valid in the case where the anchoring energy is sufficiently strong, in such a manner that the tilt angle at the surface is small, and $\sin[2\phi(-d/2)] \sim 2\phi(-d/2)$.[4] In the bulk $\phi(z)$ can be arbitrary large. We set $\eta(z) = \eta_b g(z)$, where $g(z)$ is a dimensionless function describing the z-variation of the viscosity, introduce the diffusion time defined by $\tau_{\text{diff}} = \eta_b d^2/(4k)$, and use the reduced coordinates $\zeta = 2z/d$ and $\tau = t/\tau_{\text{diff}}$, in terms of which Eq. (1) and the boundary condition (2) read

$$\frac{\partial^2 \phi}{\partial \zeta^2} = g(\zeta)\frac{\partial \phi}{\partial \tau}, \tag{3}$$

and

$$\pm\left(\frac{\partial \phi}{\partial \zeta}\right)_{\zeta=\pm 1} + u\phi(\pm 1) = 0, \tag{4}$$

where $u = d/(2L)$ and $L = k/w$ is the extrapolation length. In the following we consider the particular case where

$$g(z) = 1 + \frac{\eta_s - \eta_b}{\eta_b}\frac{\cosh(z/\lambda)}{\cosh[d/(2\lambda)]}. \tag{5}$$

In Eq. (5) λ is a mesoscopic length, indicating the penetration of the surface forces responsible for the surface viscosity. The function $g(z)$ defined by means of Eq. (5) represents the mathematical description of a typical property of the medium localized on the mesoscopic length scale λ. Similar choice will be used in the following to model the surface forces or the spatial variation of the elastic constant. The same type of analysis presented in our paper could be done by considering a piecewise continuous function. However, in this case, it should be necessary to impose the continuity of the torques at the interfaces separating the layers where the physical properties have different values, and to solve different bulk equations in the different layers. In order to avoid these type of problems we mimic the presence of the limiting surfaces by means of the continuous function $g(z)$ introduced in Eq. (5), describing the surface variation of a physical properties close to the geometrical surface.

In our analysis the function $g(z)$ will be written in terms of the reduced coordinate ζ as

$$g(\zeta) = 1 + h\cosh(p\zeta), \tag{6}$$

where $h = q/\cosh p$, $q = (\eta_s - \eta_b)/\eta_b$, and $p = d/(2\lambda)$. The parameter p is very large with respect to 1 since the penetration length λ of the surface forces is mesoscopic. To solve Eq. (3) with the boundary condition (4) we proceed in the standard manner.[11] We set $\phi(\zeta,\tau) = Z(\zeta)T(\tau)$ and rewrite Eq. (3) in the form

$$\frac{1}{Z}\frac{d^2 Z}{d\zeta^2} = g(\zeta)\frac{1}{T}\frac{dT}{d\tau}, \tag{7}$$

from which it follows that

$$\frac{1}{g(\zeta)}\left\{\frac{1}{Z}\frac{d^2 Z}{d\zeta^2}\right\} = \frac{1}{T}\frac{dT}{d\tau} = -a^2, \tag{8}$$

where a is a separation constant. Since we are analyzing a relaxation toward $\phi = 0$, we assume a real. From Eq. (8) it follows that

$$T(\tau) = A\exp(-a^2\tau), \tag{9}$$

and that $Z(\zeta)$ is solution of the ordinary differential equation

$$\frac{d^2 Z}{d\zeta^2} + a^2 g(\zeta)Z(\zeta) = 0, \tag{10}$$

where $g(\zeta)$ is defined in Eq. (6). Equation (10) has to be solved with the boundary condition related to Eq. (4) that are

$$\pm\left(\frac{dZ}{d\zeta}\right)_{\zeta=\pm 1} + uZ(\pm 1) = 0. \tag{11}$$

The solution set is spanned by functions of the type
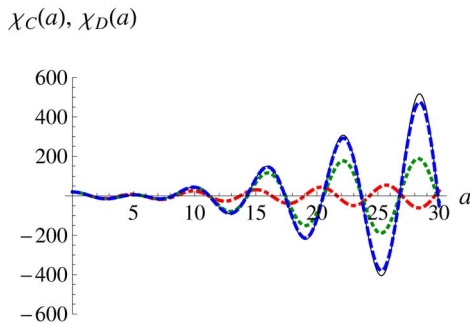
$\chi_C(a)$, $\chi_D(a)$

FIG. 1. (Color online) The eigenvalues defining the relaxation times for a nematic liquid crystal cell are the solutions of the characteristic equation $\chi(a)=0$. The continuous curve $\chi_C(a)$ corresponds to the case where the surface viscosity is localized to the surface, and across the sample the bulk rotational viscosity of the nematic is position independent, as proposed in Ref. 5. The dotted and dashed curves $\chi_D(a)$ correspond to the case in which the surface viscosity is taken into account by means of a spatial variation of the bulk viscosity near the limiting surface, as proposed in Ref. 7. The curves are drawn for $p=30$ (dotted-dashed), $p=300$ (dotted), and $p=3000$ (dashed) with $u=d/(2L)=20$, $p=d/(2\lambda)$, and $q=(\eta_s-\eta_b)/\eta_b=2p/3$, where L is the extrapolation length and λ is the penetration of the surface forces responsible for the new dissipation phenomenon close to the surface.

$$Z(\zeta;a) = \mathcal{M}\left(-4(a/p)^2, \quad 2h(a/p)^2, \quad i\frac{p\zeta}{2}\right). \tag{12}$$

In Eq. (12) $\mathcal{M}$ is an odd or even Mathieu function, in a notation where the arguments agree with those used in MATH-EMATICA. We are interested in obtaining numerical solutions to the differential equation, since that would make possible to compare with experimental data. MATHEMATICA (version 6) is, in principle, able to return numerical values for this function, but is unstable in the range of parameters that we have tested. With $p=3000$, $q=2000$, the parameter h becomes 5.23×10^{-1300}, representing the surface layer contribution to the viscosity in the middle of the sample. The solution is sensitive to the precise value of this parameter. However, the differential equation as such is quite robust and can be solved in a numerical stable way. Since the homogenous differential equation and the boundary conditions are symmetric under an inversion of the ζ axis, we should be able to write the solution as a sum of even and odd functions. By substituting the function $Z(\zeta;a)=C_a\Psi(\zeta,a)$ into the boundary conditions, we get that a solution different from the trivial one is possible only when a is a solution of the equation

$$\chi_D(a) = \frac{d\Psi}{d\zeta} + u\Psi(\zeta;a) = 0, \tag{13}$$

at $\zeta=1$. To obtain the even solutions we specify $\Psi=1$ and $d\Psi/d\zeta=0$ for $\zeta=0$, and to obtain the odd ones we might specify $\Psi=0$ and $d\Psi/d\zeta=1$ for $\zeta=0$. We have concentrated on looking at the even solutions, since the odd should behave similarly. We have then a "shooting problem" where the parameter a should be chosen in such a way that the boundary condition (11) is satisfied at $\zeta=1$. The boundary condition for $\zeta=-1$ will then be fulfilled automatically. In Fig. 1 we show the graphical solution of Eq. (13) for a few values of the parameters h, p, and u. Equation (13) has an infinite number of solutions, which we indicate by a_n. Since the equations of

the problem under consideration are linear, the solution we are looking for is

$$\phi(\zeta,\tau) = \sum_{n=0}^{\infty} C_n\Psi(\zeta;a_n)\exp(-a_n^2\tau). \tag{14}$$

The coefficients C_n are determined by imposing the initial condition $\phi(\zeta,\tau=0)=\Phi(\zeta)$.

There are some questions that remain to be answered. What happens if we have prepared the initial condition $\Phi(\zeta)$ in such a way that Eq. (4) does not seem to be fulfilled at $t=0$? That should be the most common case if we have not paid special attention to balance the initial function and its derivative, if we assume a continuous derivative in the whole closed interval $-1 \le \zeta \le 1$. We could also arrive at such a situation if there had been a rapid change in the boundary conditions. The most easy and common answer is that such an initial condition is not allowed, e.g., if we try to solve the differential equation Eq. (3) by the NDSOLVE command in MATHEMATICA, using Eq. (4) as boundary condition, we will obtain a warning: "Warning: Boundary and initial conditions are inconsistent," and the solution we obtain will be one where one of the conditions is ignored.[12] We will here pursue another approach. We observe that the conclusion here about inconsistency is based on the assumption of continuity of the derivative $d\Phi/d\zeta$ at the border, and note that we might interpret Eq. (4) in a different way. The equation is not a requirement to put on the initial condition, restricting the number set of allowed initial conditions. Equation (4) instead tells us that there is an infinitely fast decay mode, which forces the ζ derivative of $\phi(\zeta,\tau)$ at the border to take the value prescribed by Eq. (4) when we take the limit $\tau \to 0$ from the positive side. If we let this value be solely set by the boundary condition, we will remove the inconsistency. One way to achieve this is to subtract from the initial condition the sum of the functions $D_{-1}(\zeta+1)\exp[-(\zeta+1)/\lambda_0]$ and $D_1(\zeta-1)\exp[(\zeta-1)/\lambda_0]$, where λ_0 is a mesoscopic length, choosing the constants D_{-1} and D_1 in such a way that the boundary conditions Eq. (4) are fulfilled for a continuous derivative. In the limit of $\lambda_0 \to 0$, the function $\Phi(\zeta)$ is not changed, but the end point derivatives are modified. This is also a way to force NDSOLVE to return adequate solutions. We should thus modify Eq. (14) for $\tau=0$ to read

$$\Phi(\zeta) = \sum_{n=0}^{\infty} C_n\Psi(\zeta;a_n) + D_1 \lim_{\lambda_0 \to 0}\{(\zeta+1)\exp[-(\zeta+1)/\lambda_0]$$
$$+ (\zeta-1)\exp[(\zeta-1)/\lambda_0]\}. \tag{15}$$

B. Localized model for the surface viscosity

In the pioneering work of Derzhanskii and Petrov[5] the surface viscosity was assumed to be a surface property, not penetrating into the bulk, as discussed in Sec. II A. The same idea was used more recently to investigate the role of a surface dissipative layer on the dynamics relaxation of an imposed deformation in nematic cells by Refs. 13–19. According to the proposal of Ref. 5 the temporal evolution we are considering is described by the diffusion equation in the bulk, related to the bulk rotational viscosity η_b,

$$k \frac{\partial^2 \phi}{\partial z^2} = \eta_b \frac{\partial \phi}{\partial t}, \tag{16}$$

that has to be solved with the boundary conditions,

$$\pm k \left(\frac{\partial \phi}{\partial z} \right)_{z=\pm d/2} + w\phi(\pm d/2, t) + \gamma \left(\frac{\partial \phi}{\partial t} \right)_{z=\pm d/2} = 0, \tag{17}$$

where γ is a parameter describing the dissipation phenomena taking place at the surface. An equation of type (16) with the boundary conditions (17) was recently discussed by Favini et al.[8] Virga and co-workers[6,7] argued that this approach to the surface viscosity is not correct because the presence of the time derivative, of the same order, of the tilt angle at the surface and in the bulk can give rise to problems of compatibility. We argue below that there is no compatibility problem in this case since the relevant equation does not need to be valid for the initial condition. As it will be shown in this section, Eq. (16) with the boundary condition (17) gives rise to the similar relaxation times that it is possible to deduce by means of the approach described in Sec. II A. From this result we conclude that the use of the concept of localized surface viscosity allows a simple description of the dynamical relaxation of deformations in nematic cells when the distorting fields are modified. Furthermore, it can be successfully used to interpret experimental data, where only the relaxation times are experimentally accessible. Parameter γ can be related to η_s and η_b introduced above in the following manner. Let us assume that the sample is unbounded, and use, for the moment, a z-axis having the origin on the surface. The parameter γ has to take into account the spatial variation of the viscosity due to the presence of the surface. We set

$$\gamma = \int_0^\infty [\eta(z) - \eta_b] dz. \tag{18}$$

By assuming, in analogy with Eq. (6) for our half-space approximation, $\eta(z) = \eta_b + (\eta_s - \eta_b) \exp(-z/\lambda)$ and using Eq. (18) we obtain

$$\gamma = (\eta_s - \eta_b)\lambda. \tag{19}$$

This result shows that in the limit of $\lambda \to 0$, $\eta_s - \eta_b \to \infty$, as expected. To solve the problem in the present case of localized surface viscosity, we introduce again the reduced coordinates ζ and τ, and rewrite Eqs. (16) and (17) in the form

$$\frac{\partial^2 \phi}{\partial \zeta^2} = \frac{\partial \phi}{\partial \tau}, \tag{20}$$

and

$$\pm \left(\frac{\partial \phi}{\partial \zeta} \right)_{\zeta=\pm 1} + u\phi(\pm 1, \tau) + v \left(\frac{\partial \phi}{\partial \tau} \right)_{\zeta=\pm 1} = 0. \tag{21}$$

In the boundary conditions (21) we have introduced the parameter $v = 2\gamma/(\eta_b d) = q/p$, if the relation defining γ and the definitions of p and q introduced above are taken into account.

From Eqs. (20) and (21), and assuming that Eq. (20) also should be valid at the boundary, we get that the initial deformation $\Phi(z)$ has to satisfy the compatibility condition

$$\pm \left(\frac{d\Phi}{d\zeta} \right)_{\zeta=\pm 1} + u\Phi(\pm 1) + v \left(\frac{d^2\Phi}{d\zeta^2} \right)_{\zeta=\pm 1} = 0, \tag{22}$$

that, in general, cannot be satisfied for the presence of the last term.[20] This looks like a Wentzell boundary condition.[8] However, this boundary condition is not the primary one. It is just a derived condition, not valid under all circumstances, and we cannot in general assume that Eq. (20) is valid at the initial time $t=0$, e.g., in an applied field we will have an additional electric field term, and if the electric field vanishes in a discontinuous way at $t=0$, Eq. (20) and consequently also Eq. (22) will be invalid just at that moment. Further, to obtain incompatibility here we have to require continuity of the second order derivative of the initial function $\Phi(\zeta)$ at the boundary. Instead, we should expect this second order derivative to be discontinuous when there is a discontinuity in the applied field. The value of the second order derivative will not influence the time evolution and is not needed when solving the differential equation. In contrast to the delocalized case, we might thus in the localized case allow a continuous first order derivative of $\Phi(\zeta)$ in the closed interval $-1 \leq \zeta \leq 1$.

By proceeding as in the previous case we obtain for $\tau > 0$,

$$\phi(\zeta, \tau; a) = C_a \cos(a\zeta) \exp(-a^2\tau). \tag{23}$$

By substituting Eq. (23) into the boundary condition (21) we get that a solution different from the trivial one exists only if a is solution of the equation

$$\chi_C(a) = a \sin a - (u - a^2 v) \cos a = 0. \tag{24}$$

This equation has an infinite number of solutions, a_m. When these have been determined, the eigenfunctions of the problem are given by Eq. (23). The solution of the problem, for the linearity of the equations, is

$$\phi(\zeta, \tau) = \sum_{m=0}^{\infty} C_m \cos(a_m \zeta) \exp(-a_m^2 \tau). \tag{25}$$

As in the previous case the coefficients of the linear combination C_m are deduced by the initial boundary condition

$$\phi(\zeta, \tau = 0+) = \Phi(\zeta), \tag{26}$$

where the equality does not need to be valid for the second derivatives at the ends of the ζ interval.

Our aim is to show that the description of the dynamical evolution of the nematic profile given by means of the use of the concept of surface viscosity and in terms of the delocalized model for the viscosity, are in good agreement.

In Fig. 1 we show the graphical solution of Eq. (24) and we compare the solutions with the ones relevant to Eq. (13), concerning the case where the surface viscosity is delocalized. As it is evident from the quoted figure, the eigenvalues are practically coinciding in the case of large q and p, where the use of a localized surface viscosity γ is meaningful. As it is evident form the analysis reported above, the use of the localized surface viscosity γ simplifies the calculation by reducing the number of constants required, and allows
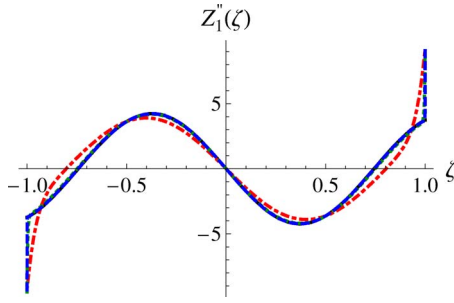
$$Z_1''(\zeta)$$

FIG. 2. (Color online) The eigenfunctions for the delocalized case for high values of p are very similar to those in the localized case, and to see visible difference one should look at the derivative. Here the derivative of the second eigenfunction is shown for the cases $p=30$ (dotted-dashed), 300 (dotted), 3000 (dashed), and ∞ (localized case, continuous curve) and $v=q/p=2/3$. The spike behavior in the boundary region with enhanced viscosity is typical for the derivatives of the eigenfunctions in the delocalized case, but the spikes vary in size.

capturing the most important points of the physical phenomenon, without introducing problems of compatibility. More detailed surface studies, such as for instance total internal reflection, might of course require a more detailed model.

We might compare the eigenfunctions $\Psi(\zeta;a_m)$ in the delocalized case to the eigenfunctions $\cos(a_m\zeta)$ in the localized case to understand how they differ. Let us keep $v=q/p$ constant, and check with different values of p. With $p=30$, 300, 3000, and ∞ and $v=2/3$ there is no visible difference in a graph of the first eigenfunction (corresponding to $m=0$). However, if we look at the derivative with respect to ζ, we see small spikes in the boundary regions near $\zeta=\pm 1$, sharper for higher values of p, but vanishing in the localized case $p=\infty$. The derivative in the spike varies from one finite value inside the boundary layer to another, somewhat higher, finite value at the border. The second eigenfunctions ($m=1$) behaves similarly, with the difference that the case $p=30$ deviates visibly from the rest. A graph of the derivative of the second eigenfunctions is illustrative for the spike behavior, see Fig. 2.

C. Orthogonality of the set of eigenfunctions for the problem of the surface viscosity

In the case where the surface viscosity is described by means of a delocalized model, the fundamental equation of the problem is Eq. (3), which has to be solved with the boundary condition (4). Using the separation of variables, we get that the spatial part of the solution we are looking for satisfies Eq. (10) with the boundary condition (11). This is the classical problem of Sturm–Liouville.[21] A standard calculation shows that the eigenfunctions of the problem are orthogonal with respect to the weight function $g(\zeta)$ in the interval $-1\le\zeta\le 1$. Let us now consider two eigenfunctions, Z_n and Z_m, associated to the eigenvalues a_n and a_m, respectively, which are solutions of the differential equations

$$\frac{d^2Z_n}{d\zeta^2}+a_n^2 g(\zeta)Z_n=0,$$

$$\frac{d^2Z_m}{d\zeta^2}+a_m^2 g(\zeta)Z_m=0. \tag{27}$$

Multiplying the first equation by Z_m and the second by Z_n and subtracting the second from the first we get

$$Z_m\frac{d^2Z_n}{d\zeta^2}-Z_n\frac{d^2Z_m}{d\zeta^2}+(a_n^2-a_m^2)g(\zeta)Z_nZ_m=0, \tag{28}$$

that can be rewritten as

$$\frac{d}{d\zeta}\left(Z_m\frac{dZ_n}{d\zeta}-Z_n\frac{dZ_m}{d\zeta}\right)+(a_n^2-a_m^2)g(\zeta)Z_nZ_m=0. \tag{29}$$

By integrating Eq. (29) over ζ on the interval $-1\le\zeta\le 1$, we obtain

$$\left[Z_m\frac{dZ_n}{d\zeta}-Z_n\frac{dZ_m}{d\zeta}\right]_{-1}^{1}+(a_n^2-a_m^2)\int_{-1}^{1}g(\zeta)Z_n(\zeta)Z_m(\zeta)d\zeta=0. \tag{30}$$

A simple calculation, taking into account the properties of symmetry of the eigenfunctions and the boundary condition (11), shows that

$$\left[Z_m\frac{dZ_n}{d\zeta}-Z_n\frac{dZ_m}{d\zeta}\right]_{-1}^{1}=0. \tag{31}$$

Consequently,

$$(a_n^2-a_m^2)\int_{-1}^{1}g(\zeta)Z_n(\zeta)Z_m(\zeta)d\zeta=0. \tag{32}$$

Since we assumed $n\ne m$, from Eq. (32) we get

$$\int_{-1}^{1}g(\zeta)Z_n(\zeta)Z_m(\zeta)d\zeta=0, \tag{33}$$

i.e., the eigenfunctions $Z_n(\zeta)$ form a set of orthogonal functions, with respect to the weight function $g(\zeta)$. In the special case where $\eta_s=\eta_b$, and hence $g(\zeta)=1$, that corresponds to the case in which the bulk viscosity is position independent, from Eq. (33) it follows that

$$\int_{-1}^{1}Z_n(\zeta)Z_m(\zeta)d\zeta=0. \tag{34}$$

In the general case, we might associate a scalar product to our delocalized model

$$(f_1,f_2)=\int_{-1}^{1}g(\zeta)f_1(\zeta)f_2(\zeta)d\zeta. \tag{35}$$

This can only be considered as a scalar product if we associate it with a linear space of equivalence classes, where two functions are equivalent when the corresponding norm of the difference in the two functions are zero. Thus the initial condition $\Phi(\zeta)$ and the modification where we have modified the end derivatives will be contained in the same equivalence class. In our even case we might add one dimension to our linear space and modify the scalar product to put these func-

tions in separate equivalence classes. If we want to do that, we could add the following term to the scalar product (35),

$$\left(\left(\frac{\partial f_1}{\partial \zeta}\right)_{\zeta=1} + u f_1(1)\right)$$
$$\cdot \left(\left(\frac{\partial f_2}{\partial \zeta}\right)_{\zeta=1} + u f_2(1)\right) + \left(-\left(\frac{\partial f_1}{\partial \zeta}\right)_{\zeta=-1} + u f_1(-1)\right)$$
$$\cdot \left(-\left(\frac{\partial f_2}{\partial \zeta}\right)_{\zeta=-1} + u f_2(-1)\right). \tag{36}$$

Let us consider now the case in which the surface viscosity is a localized surface quantity. In this framework the fundamental equation of the problem is Eq. (20) that has to be solved with the boundary conditions (21). By operating as in the previous case by means of the separation of the variables, we get for the bulk equation

$$\frac{d^2 Z}{d\zeta^2} + a^2 Z = 0, \tag{37}$$

and for the boundary condition

$$-\frac{dZ}{d\zeta} + (u - v a^2) Z = 0, \tag{38}$$

respectively. The present problem is a Sturm–Liouville problem with boundary conditions depending quadratically on the eigenvalue.[22,23] Let us consider, as in the previous case devoted to the delocalized surface viscosity, two eigenfunctions, Z_n and Z_m, associated to the eigenvalues a_n and a_m. Operating as before we get

$$\left[Z_m \frac{dZ_n}{d\zeta} - Z_n \frac{dZ_m}{d\zeta}\right]_{-1}^{1} + (a_n^2 - a_m^2) \int_{-1}^{1} Z_n(\zeta) Z_m(\zeta) d\zeta = 0, \tag{39}$$

where now, taking into account Eq. (38),

$$\left[Z_m \frac{dZ_n}{d\zeta} - Z_n \frac{dZ_m}{d\zeta}\right]_{-1}^{1} = 2v(a_n^2 - a_m^2) Z_n(1) Z_m(1). \tag{40}$$

It follows that in the present case instead of Eq. (32) we have

$$(a_n^2 - a_m^2)\left\{2v Z_n(1) Z_m(1) + \int_{-1}^{1} Z_n(\zeta) Z_m(\zeta) d\zeta\right\} = 0, \tag{41}$$

from which we have, in the considered case of $n \neq m$,

$$2v Z_n(1) Z_m(1) + \int_{-1}^{1} Z_n(\zeta) Z_m(\zeta) d\zeta = 0. \tag{42}$$

In this case the eigenfunctions are no longer orthogonal for $v \neq 0$ with respect to the weight function 1. However, they are orthogonal with respect to the weight function

$$G(\zeta) = 1 + v[\delta(\zeta+1) + \delta(\zeta-1)], \tag{43}$$

where δ is Dirac's function. We observe that the function g defined by Eq. (6) can be written as $g(\zeta) = 1 + vp[\cosh(p\zeta)/\cosh p]$ that in the limit of $\lambda \to 0$, which implies $p \to \infty$, reduces to Eq. (43).

By taking into account that $Z_n(\zeta) = \cos(a_n \zeta)$ and $Z_m(\zeta) = \cos(a_m \zeta)$ from Eq. (42) we obtain
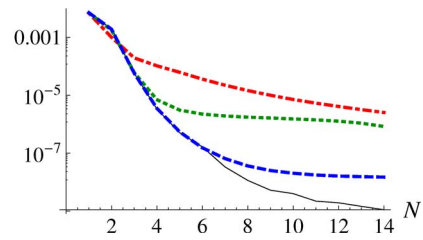

FIG. 3. (Color online) The quadratic deviation of the expansion of the initial condition as a function of the number of terms in the delocalized case for $p=30$ (dotted-dashed), 300 (dotted), 3000 (dashed) and in the localized case $p=\infty$ (continuous curve), measured by the relevant scalar product for each case.

$$v + \frac{a_n \tan a_n - a_m \tan a_m}{a_n^2 - a_m^2} = 0. \tag{44}$$

This relation is, obviously, verified by our eigenvalue Eq. (24). In fact, from Eq. (24) written for the eigenvalues relevant to the integers n and m we have

$$a_n \sin a_n - (u - a_n^2 v)\cos a_n = 0,$$
$$a_m \sin a_m - (u - a_m^2 v)\cos a_m = 0, \tag{45}$$

from which, with simple calculations, we reobtain Eq. (43).

To show that by means of the series expansion (25) we can satisfy the initial boundary condition $\phi(\zeta,0) = \Phi(\zeta)$, let us consider the particular case where the initial distortion is induced by an electric field, E, at an angle Φ_E with respect to the z-axis on a liquid crystal with positive dielectric anisotropy $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$, where $\parallel$ and $\perp$ refer to the nematic director. We assume, for simplicity, that Φ_E is small, in such a manner that $\sin \Phi_E \sim \Phi_E$. In this framework, the initial profile $\Phi(\zeta)$ is solution of the bulk differential equation

$$\frac{d^2\Phi}{d\zeta^2} + \mathcal{E}^2[\Phi(\zeta) - \Phi_E] = 0, \tag{46}$$

where $\mathcal{E} = (\pi/2)(E/E_0)$, and $E_0 = (\pi/d)\sqrt{k/\varepsilon_a}$ is the critical field for the Freedericksz transition.[1] For the static solution, independent of the viscosity distribution, the tilt angle $\Phi(\zeta)$ has to satisfy the boundary condition

$$-\frac{d\Phi}{d\zeta} + u\Phi = 0, \tag{47}$$

at $\zeta = -1$. The solution of Eq. (46) with the boundary condition (47) is

$$\Phi(\zeta) = \Phi_E\left\{1 - u \frac{\cosh(\mathcal{E}\zeta)}{\mathcal{E}\sinh\mathcal{E} + u\cosh\mathcal{E}}\right\}. \tag{48}$$

We might also compare the convergence rate of the delocalized and localized case by looking at the difference between the initial profile $\Phi(\zeta)$ and the approximation to order N. By taking the scalar product of this difference with itself, using the relevant scalar product with weight function $g(\zeta)$ or $G(\zeta)$, we see that in this case the expansion in terms of the eigenfunctions for the localized case gives much better convergence, see Fig. 3. The reason for this better convergence is the absence of spikes in the boundary layer in the localized

case, spikes do not have any correspondence in our initial condition that was chosen as the static solution in an applied field. Thus, if we have no special information about the thickness of the viscous surface layer, we might simplify the calculations by doing calculations along the localized scheme, and thereby we are reducing the experimental parameters connected to the surface viscosity layer from two (λ and η_s) to one (γ). The differential equations also become simpler to solve since we transform infinite fast decay modes at the boundary for the delocalized case into finite speed decay modes in the localized case, in practice allowing a wider range of initial-value and boundary condition combinations.

The problem discussed above relevant to the localized surface viscosity is known in the theory of differential equations as boundary problem with dynamic boundary conditions.[8,24–26] Our recipe for the solution of the problem related to the compatibility condition for the initial value can be used also for the analysis of evolution equations with boundary condition involving the spatial derivative in the boundary conditions.

III. ANCHORING ENERGY

A. Delocalized anchoring energy

Let us consider a nematic cell in the shape of a slab, as the one discussed in Sec. II A. We assume that the liquid crystal sample is oriented in the planar geometry by the substrate surfaces. The surface forces, responsible for the alignment are short range, with respect to the thickness of the sample. The relevant anisotropic energy is assumed to be of the type

$$f_s = -\frac{1}{2}U(z)\cos^2 \vartheta, \tag{49}$$

where ϑ is the angle formed by the nematic director with the x-axis, parallel to the limiting surface (the angle ϕ used in the previous sections is $\phi = \pi/2 - \vartheta$). The potential energy $U(z)$ is supposed to be localized close to the limiting surfaces, over a surface layer of thickness $\lambda \ll d$.[27] In analogy with the delocalized viscosity, the potential energy $U(z)$ is assumed to be of the form

$$U(z) = U_0 \frac{\cosh(z/\lambda)}{\cosh[d/(2\lambda)]}, \tag{50}$$

where U_0 and λ are related to the surface interaction, and hence depend on the substrate surface and on the liquid crystal.[28] Expression (49) is a generalization of the surface energy proposed by Rapini and Papoular.[4] Our aim now is to evaluate the threshold field for the transition of Freedericksz. In the one-constant approximation the bulk energy density for our sample, in the presence of an external field perpendicular to the limiting surfaces, is

$$f\left(\vartheta, \frac{d\vartheta}{dz}\right) = \frac{1}{2}k\left(\frac{d\vartheta}{dz}\right)^2 - \frac{1}{2}\varepsilon_a E^2 \sin^2 \vartheta - \frac{1}{2}U(z)\cos^2 \vartheta, \tag{51}$$

where ε_a is the dielectric anisotropy of the liquid crystal, assumed positive in the following. The total energy, per unit surface, is

$$F = \int_{-d/2}^{d/2} f\left(\vartheta, \frac{d\vartheta}{dz}\right)dz. \tag{52}$$

The actual ϑ profile is the one minimizing F given by Eq. (52). Simple calculations give[3] for the bulk equation

$$k\frac{d^2\vartheta}{dz^2} + \frac{1}{2}\varepsilon_a E^2 \left\{ 1 - \frac{U(z)}{\varepsilon_a E^2} \right\}\sin(2\vartheta) = 0, \tag{53}$$

and

$$\frac{d\vartheta}{dz} = 0, \tag{54}$$

at $z = \pm d/2$. The boundary condition (54) is the transversality condition for the functional (52). To evaluate the threshold field, we limit our analysis to the case of small ϑ, where Eq. (53) can be linearized. Using the reduced coordinated $\zeta = 2z/d$ we rewrite Eq. (53) in the form

$$\frac{d^2\vartheta}{d\zeta^2} + \mathcal{E}^2\{1 - \nu \cosh(p\zeta)\}\vartheta = 0, \tag{55}$$

where

$$p = \frac{d}{2\lambda}, \quad \mathcal{E} = \frac{\pi}{2}\frac{E}{E_0}, \quad \nu = \frac{c}{\mathcal{E}^2}, \quad c = \frac{U_0 d^2}{4k \cosh p}, \tag{56}$$

and $E_0 = (\pi/d)\sqrt{k/\varepsilon_a}$ is the critical field introduced in Sec. II C. As in the previous case of the surface viscosity γ and η_s, the localized anchoring energy, in the Rapini–Papoular's model, is related to $U(z)$ by the condition

$$w = \int_0^\infty U(z)dz, \tag{57}$$

in the half-space case. In the exponential approximation from Eq. (50) we get $w = U_0\lambda$. Taking into account this result, parameter c introduced in Eq. (56) can be rewritten as $c = up/\cosh p$, where $u = d/(2L)$, as before. The symmetric solution of Eq. (55) is the real part of Mathieu's function even in ζ, as discussed above. The eigenvalues are the solutions of

$$\omega_D(\mathcal{E}) = \left\{ \frac{d\Psi(\zeta;\mathcal{E})}{d\zeta} \right\}_{\zeta=-1} = 0, \tag{58}$$

obtained by the transversality condition (54). We are interested in the smallest solution of Eq. (58) since it is defining the threshold field.

B. Localized anchoring energy

In the case in which the surface potential is so localized that the concept of anchoring energy can be used, the bulk energy density of the sample is
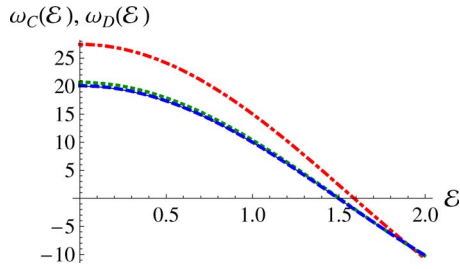
FIG. 4. (Color online) Threshold field for the Freedericksz instability on planar aligned nematic liquid crystal with positive dielectric anisotropy. The broken curves correspond to the case where the surface potential is assumed delocalized. The continuous curve corresponds to the case where the surface energy is considered localized to the surface. The curves are drawn for u $=20$ and $p=30$ (dotted-dashed), 300 (dotted), 3000 (dashed) and ∞ (localized case, continuous curve). As it is evident, the two models define the same threshold field for high p, coinciding with the first eigenvalue of the problem.

$$f_0\left(\vartheta, \frac{d\vartheta}{dz}\right) = \frac{1}{2}k\left(\frac{d\vartheta}{dz}\right)^2 - \frac{1}{2}\varepsilon_a E^2 \sin^2 \vartheta, \quad (59)$$

instead of the one given by Eq. (51), and the total energy per unit surface, is

$$F_0 = \int_{-d/2}^{d/2} f_0\left(\vartheta, \frac{d\vartheta}{dz}\right)dz + \frac{1}{2}w \cos^2 \vartheta(-d/2)$$

$$+ \frac{1}{2}w \cos^2 \vartheta(d/2), \quad (60)$$

where the last two terms are due to the localized surface energy, in the Rapini–Papoular approximation. By minimizing F_0 we get that in the present case ϑ is solution of the differential equation

$$\frac{d^2\vartheta}{d\zeta^2} + \mathcal{E}^2\vartheta = 0, \quad (61)$$

and has to satisfy the boundary condition

$$-\frac{d\vartheta}{d\zeta} + u\vartheta = 0, \quad (62)$$

at $\zeta=-1$. Equations (61) and (62) are valid in the limit of small deformations, where $\vartheta \ll 1$, and are written using the reduced coordinate $\zeta=2z/d$, and dimensionless quantities $u=d/(2L)$ and $\mathcal{E}=(\pi/2)(E/E_0)$, as before. Solution of Eq. (61), even in ζ, is $\vartheta(\zeta)=B \cos(\mathcal{E}\zeta)$. The threshold voltage is deduced by means of the boundary condition Eq. (62). Simple calculations give for the eigenvalues equation

$$\omega_C(\mathcal{E}) = -\mathcal{E} \sin \mathcal{E} + u \cos \mathcal{E} = 0, \quad (63)$$

which coincides with Rapini–Papoular's equation.

In Fig. 4 we show the graphical solution of Eq. (58) relevant to the delocalized surface potential (broken lines) and of Eq. (63) valid in the case of localized anchoring energy (continuous line). As it is evident from the quoted figure, the solutions defining the critical field coincide in the limit of large p. This indicate that the analysis of the problem can be performed by means of the concept of localized surface energy, or by means of the more realistic description in which the surface potential is described by means of a bulk

energy density, localized close to the limiting surfaces. With the two descriptions, the critical field is the same for reasonable value of the penetration length of the surface forces.

Note that the introduction of the localized anchoring energy is rather natural, and follows, in the half-space approximation, from the following calculation:

$$F_s = \int_0^\infty f_s dz = -\frac{1}{2}\int_0^\infty U(z)\cos^2 \vartheta dz$$

$$= -\frac{1}{2}\left\{\int_0^\infty U(z)dz\right\}\cos^2 \vartheta(z^*)$$

$$= -\frac{1}{2}w \cos^2 \vartheta(z^*), \quad (64)$$

where we have used the theorem of the average, and indicated by z^* a point in the range $0 \leq z^* \leq \lambda$. Since λ is very small with respect to d, we assume that $\theta(z^*) \sim \vartheta(0)$, and in this manner the localized anchoring energy follows directly.

IV. SURFACE ELASTIC CONSTANT

A. Localizing a delocalized elastic constant

The elastic properties of nematic liquid crystals are related to the intermolecular interaction responsible for the nematic phase. As it is well known, the presence of a limiting surface reduces the symmetry of the nematic phase, and elastic constants forbidden in the bulk can appear.[29] Furthermore, also the usual elastic constants of Frank have numerical values different from the bulk ones because the interaction volume of the nematic molecules in the surface layer is incomplete. In this section we want to investigate the effect of the position dependence of the usual elastic constant on the director profile. We consider again a cell in the shape of a slab, and use the same Cartesian reference frame used in Sec. II A. We assume that the surface interactions are short range, and very strong, in such a manner that the anchoring on the limiting surfaces can be considered strong. The easy axes are supposed forming an angle with the z axis $-\phi_0$ and ϕ_0 at the surfaces, i.e., at $z=-d/2$ and $z=d/2$, respectively. In this framework the bulk energy density is

$$f = \frac{1}{2}k(z)\left(\frac{d\phi}{dz}\right)^2, \quad (65)$$

where $k=k(z)$ describes the position dependence of the elastic constant of Frank, in the one-constant approximation. The spatial variation of k is localized to two surface layers of thickness λ, close to the limiting surfaces. The total energy per unit surface, F, is obtained by integrating f given by Eq. (65) over the thickness of the sample. By minimizing F, standard calculations give for the relevant Euler–Lagrange equation the expression

$$k(z)\frac{d\phi}{dz} = \beta, \quad (66)$$

where β is an integration constant. From Eq. (66) we get

$$\beta = 2\frac{\phi_0}{\mathcal{L}(-d/2, d/2)}, \tag{67}$$

where

$$\mathcal{L}(m,n) = \int_m^n \frac{dz}{k(z)} \tag{68}$$

depends on the spatial variation of the elastic constant. By integrating once more Eq. (66) we obtain for the tilt angle the expression

$$\phi(z) = -\phi_0\left\{1 - 2\frac{\mathcal{L}(-d/2, z)}{\mathcal{L}(-d/2, d/2)}\right\}. \tag{69}$$

Usually, the surface elastic constant is smaller than the one in the bulk, k_b, because the interaction volume, per surface molecule, is half of the one for a bulk molecule. This means that $k(z) \leq k_b$, and hence $\mathcal{L}(-d/2, d/2) > d/k_b$. From this observation it follows that the bulk derivative of the tilt angle, defined as $(d\phi/dz)_0$ is

$$\left(\frac{d\phi}{dz}\right)_0 = \frac{2\phi_0}{k_b\mathcal{L}(-d/2, d/2)} < 2\frac{\phi_0}{d} \tag{70}$$

that corresponds to the bulk derivative of the tilt angle in the case of strong anchoring and position independent elastic constant. This reduction of the spatial derivative of ϕ is equivalent to a finite anchoring energy, responsible for an extrapolation length L such that[3]

$$\left(\frac{d\phi}{dz}\right)_0 = 2\frac{\phi_0}{d + 2L}. \tag{71}$$

From this we obtain for the extrapolation length of the weak anchoring energy associated to the spatial variation of the elastic constant

$$L = \frac{k_b}{w_{eq}} = \frac{d}{2}\left\{\frac{1}{d}\int_{-d/2}^{d/2}\frac{k_b}{k(z)}dz - 1\right\}, \tag{72}$$

which is a well known result.[30] It is thus in the case $k(z) \leq k_b$ possible to replace a softness of the elastic constants near the surfaces with an elastic energy term, which at the upper surface will be

$$F_s = \frac{1}{2}w_{eq}[\phi(d/2, t) - \phi_0]^2, \tag{73}$$

with

$$w_{eq} = \frac{2}{\mathcal{L}(-d/2, d/2) - (d/k_b)}. \tag{74}$$

If the elastic constants increase instead of decrease near the surface, the extrapolation length approach can be used, also providing a reduction of the number of parameters.

Let us consider the case in which

$$k(\zeta) = k_b\left\{1 + b\frac{\cosh(p\zeta)}{\cosh p}\right\}, \tag{75}$$

where $\zeta = 2z/d$, $b = (k_s - k_b)/k_b$, and $p = d/(2\lambda)$, with λ a mesoscopic length defining the surface thickness in which the spatial variation of the elastic constant is localized. Simple calculations allow the evaluation of $\mathcal{L}(-d/2, d/2)$ and of
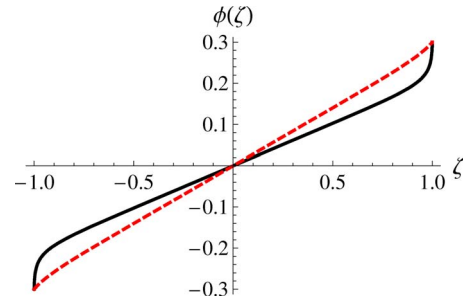

FIG. 5. (Color online) Profile of the tilt angle $\phi = \phi(\zeta)$ in a nematic cell with strong anchoring and easy axes forming the angles $-\phi_0$ and ϕ_0 on the limiting surfaces at $\zeta = -1$ and $\zeta = 1$, respectively. The curves are drawn for $\phi_0 = 0.3$, $p = d/(2\lambda) = 10$ for two values of $b = (k_s - k_b)/k_b$: dashed curve $b = -0.5$, continuous curve $b = -0.99$.

$\mathcal{L}(-d/2, z)$ in terms of elementary functions. The tilt angle $\phi(\zeta)$ is shown in Fig. 5 for two sets of the parameters p and b.

V. CONCLUSION

We have investigated when the introduction of surface properties of nematic liquid crystals, related to the presence of a limiting surface, is useful. We have considered the case in which the physical properties of the nematic liquid crystal are delocalized, and the delocalization is related to the change in physical properties close to the limiting surfaces. The case in which the bulk properties differ from the surface properties just at the surface has been also considered. We have shown that the relaxation times can be correctly calculated by assuming that the presence of the surface causes a surface viscosity. The utility of the anchoring energy, due to the presence of a surface potential describing the short range interaction of the liquid crystal with the substrate, has been discussed by considering the transition of Freedericksz. The effect of a spatial variation of the elastic constant on the anchoring energy has also been discussed, and the equivalent surface energy connected to it has been evaluated.

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