Dilution of nematic surface potentials: Statics

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The weak anchoring of a nematic liquid crystal is further illuminated by studying the consequences of finite-range surface torques. It is shown that the actual decay law of a diluted surface potential has little influence on either the equilibrium profile and the saturation field, provided that the range of the potential is small compared to the surface extrapolation length. This appears as a possible way to extend the conventional Rapini-Papoular model without altering its predictions away from the boundary. The net advantage of a dilution model is to better understand surface phenomena, which indeed pertain to a thin boundary layer.

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I. INTRODUCTION

Surface anchoring of nematic liquid crystals plays an important role in both the statics and dynamics in the bulk. Thus, it is no wonder that it was studied rather early [1], and both the strength of the surface potential and its dependence on the director orientation at a bounding surface have been determined experimentally. A phenomenological model for the dynamic evolution at the surface has also been proposed [2,3], which introduces a *surface viscosity* as the product of a typical bulk viscosity times a *surface length*. The interest in these topics has been renewed by some recent experiments. Measurements indeed yielded estimates for both the surface viscosity and the corresponding surface length [4]; however, they are inconsistent with the fast switching times that seem to be involved in a surface bistable device [5,6].

In an attempt to explain the experimental evidence and to justify the phenomenological surface viscosity, a hydrodynamic model has been put forward, based on the idea that surface actions are diluted in a thin boundary layer [7]. This allows one to treat surface effects within a continuum theory, where the surface viscosity results from a dissipation process of the bulk, though mainly localized near the bounding surfaces. According to this model, the phenomenological surface length is actually comparable to the thickness of the boundary layer.

Several specific aspects of finite-range surface potentials have already been studied in the past. For example, the result of combining a van der Waals interaction with a localized torque has been explored, both when these interactions favor the same orientation [8] and when they compete with one another [9]. Different specific long-range potentials have been considered, such as the one in [10], and a density functional approach has also shown that deviations from uniaxiality close to the surface can be of importance [11]. These contributions, however, all being special in some way, do not reveal any general aspect that different diluted surface potentials could have in common.

In this paper we aim at a general description of surface potentials, which may include both short- and long-range contributions. We are concerned with the consequences of introducing such potentials within the classical director theory, and less so with a specific microscopic motivation for the interactions behind them. As in [7], we disregard any degree of biaxiality, and we take the scalar order parameter as constant throughout the material. After describing the general form of surface potentials, we essentially focus attention on long-range interactions in the case of weak anchoring. This amounts to requiring the surface extrapolation length L to be much larger than the dilution length h defined in terms of the (arbitrary) decay law for the surface torques in the bulk. In this setting, a surface layer can be clearly identified, whose thickness is comparable with h. Thus, the *ad hoc* boundary layer introduced in [7] turns out to be fully justified.

The existence of this surface layer with its own dynamics is the main interest of this approach. The dilution model indeed deploys its full potential in dynamics, to which a future paper [12] will be entirely devoted, but it also raises a few central issues in statics, which need to be resolved to make this theory well grounded. We wonder, in particular, whether the effects of a surface potential are independent of the details of the decay law. To explore this, we consider a semi-infinite liquid crystal cell subject to different surface potentials in a broad class. We find that for weak anchoring, that is, when $h/L \ll 1$, the orientation at the surface and the saturation field strength are independent of the actual dilution law. In this case, our results coincide with those already found within the classical Rapini-Papoular model. The very novelty here is that a whole class of dilution laws are actually consistent with the old model, for which all surface effects are sharply localized. The differences between these models become significant only in the thin boundary layer: whenever this matters, the classical model is simply not applicable.

Here is the outline of this paper. In Sec. II, both the diluted potential and the dilution length are defined. In Sec. III, the Euler-Lagrange equation for a semi-infinite cell in an external field is derived along with the appropriate boundary condition on the supporting plate. In Sec. IV, we obtain an approximate expression for the boundary orientation, which is independent of the actual shape of the dilution function: in the case where the preferred surface direction and the external field are at right angles, this also allows us to estimate the *saturation* field, that is, the electric field required to completely *break* the surface anchoring. Numerical results obtained for both an exponential dilution law and a van der Waals surface potential show that this estimate is valid even

when h is comparable to L. In Sec. V, we show that the model of surface anchoring studied in this paper properly extends the classical model of Rapini and Papoular. To ease the comparison, we briefly recall both the equilibrium equation and the boundary condition used in that model to describe the same problem addressed here. We show that the saturation field remains unchanged, whereas the equilibrium configuration within the surface layer is simply inaccessible. In the last section we collect the main conclusions reached in this paper.

II. SURFACE ENERGY

We consider a nematic liquid crystal in the half space $z \geqslant 0$ with a single wall at $z=0$. The influence of the surface is thought of as being diluted in a thin layer adjacent to the boundary. The surface free energy per unit area is then given the form

$$\mathcal{F}_s = \tfrac{1}{2} \int_0^\infty D(z) F(\boldsymbol{n}(z) \cdot \boldsymbol{n}_s) dz, \tag{1}$$

where $\boldsymbol{n}$ denotes the nematic director, $\boldsymbol{n}_s$ is a given unit vector indicating a preferred direction of the surface, F is a scalar-valued function representing the dependence of the energy on the orientation, and $D(z)$ is the strength of the surface potential at the point with coordinate z relative to the anchoring wall. We assume that F is so normalized as to range in the interval $[0,1]$. In the following we restrict the director to a plane perpendicular to the anchoring plate so that the orientation can be described by a single angle ϑ (specifically, the angle that $\boldsymbol{n}$ makes with the plate), and we set $F(\boldsymbol{n} \cdot \boldsymbol{n}_s) =: f(\vartheta)$. For example, $f(\vartheta) = \sin^2(\vartheta - \vartheta_s)$, where ϑ_s is the preferred angle at the boundary.

Starting from Eq. (1), one can define a total strength A of the anchoring by letting $F \equiv 1$:

$$A := \int_0^\infty D(z) dz; \tag{2}$$

accordingly, a characteristic *dilution length* is given by

$$h := \frac{\int_0^\infty z D(z) dz}{\int_0^\infty D(z) dz}. \tag{3}$$

With these definitions the surface energy can be rewritten as

$$\mathcal{F}_s = \frac{A}{2h} \int_0^\infty d(z) f(\vartheta(z)) dz,$$

where

$$d(z) := \frac{h}{A} D(z) \tag{4}$$

is the dimensionless *dilution function* that satisfies

$$\int_0^\infty d(z) dz = h. \tag{5}$$

Furthermore, whenever d is a decreasing function, it also obeys

$$d(0) \geqslant \tfrac{1}{2}. \tag{6}$$

(See the Appendix for a formal proof.)

It should be noted that the usual localized potential is recovered in this setting by taking a Dirac delta distribution as dilution function: $D(z) = A\delta(z)$. The surface energy then becomes $\mathcal{F}_s = (A/2) f(\vartheta(0))$, and the dilution length h vanishes; accordingly, the common surface extrapolation length L is defined as

$$L := \frac{K}{A}. \tag{7}$$

We shall see below that this definition also makes sense for a diluted potential.

In general, we consider smooth distributions of surface torques in the volume: for a given total strength A, the corresponding dilution length h measures the thickness of the boundary layer where the surface torques are effectively confined. We regard h throughout as small compared to L. As shown below, under this assumption the main outcomes of our model are independent of the specific details of the dilution function.

As an example, we rephrase in this general setting one of the specific models already proposed in the literature. Dubois-Violette and De Gennes considered in [8] a nematic liquid crystal separated from the supporting substrate by a layer of a vitreous polymer of thickness a, which occupies the strip $-a \leqslant z \leqslant 0$. The substrate exerts on the nematic director a van der Waals torque with strength D that decays according to the law

$$D(z) = \frac{C\lambda}{(\lambda + a + z)(z + a)^3},$$

where C is a constant depending on the dielectric constants of the substrate, the liquid crystal, and the medium between them, while λ is a characteristic length that can be estimated from the ratio between the nonretarded and retarded van der Waals potentials. It is further assumed in [8] that the preferred orientation at the boundary is $\vartheta_s = 0$ and the angular dependence is given by $f = \sin^2 \vartheta$. According to definition (2), we compute the total strength A of this potential and determine the corresponding extrapolation length L as

$$\frac{LC}{K\lambda^2} = \frac{1}{\alpha^2/2 - \alpha + \ln(1+\alpha)},$$

where $\alpha := \lambda/a$. This formula coincides with (3.6) of [8], which was obtained there from a different definition of L, based on an estimate of the asymptotic behavior of the solution to the equilibrium equation for the director field. Likewise, we compute the dilution length

$$h = a \frac{\alpha^2/2 + \alpha - (1+\alpha)\ln(1+\alpha)}{\alpha^2/2 - \alpha + \ln(1+\alpha)}, \tag{8}$$

which is a strictly increasing function of α, ranging from $a/2$ to a. No counterpart of Eq. (8) is present in [8], because no boundary layer was properly defined there, though there were indirect indications of its existence. We remark that for the nonretarded potential considered in [8] the proper extrapolation length L can also be defined as in Eq. (7). However, the agreement between the two extrapolation lengths fails in the case of strong anchoring, where the length defined in [8] may even become negative. This corresponds to a virtual boundary plate *in* the bulk, a case which need not be treated here.

III. COMPETITION AGAINST A FIELD

To illustrate better the relevance to the Oseen-Frank equilibrium theory of a model where the surface torques are actually diluted in space, we study a simple problem with several possible applications, where an external electric field competes against the preferred anchoring at the wall. This problem is well understood within the Rapini-Papoular model, and we recall the classical results below in Sec. V to compare them to our findings.

The Oseen-Frank elastic free-energy density for the nematic director is given by [13,14]

$$W=\tfrac{1}{2}K_1(\boldsymbol{\nabla}\cdot\boldsymbol{n})^2+\tfrac{1}{2}K_2[\boldsymbol{n}\cdot(\boldsymbol{\nabla}\times\boldsymbol{n})]^2+\tfrac{1}{2}K_3[\boldsymbol{n}\times(\boldsymbol{\nabla}\times\boldsymbol{n})]^2,$$

where K_1, K_2, and K_3 are the elastic constants for splay, twist, and bend deformations, respectively. If the director is bound to a plane perpendicular to the plate, only splay and bend deformations are relevant. Since usually $K_1\approx K_3=:K$, we apply the one-constant approximation and reduce W to

$$W=\frac{K}{2}(\boldsymbol{\nabla}\boldsymbol{n})^2=\frac{K}{2}(\vartheta')^2 \tag{9}$$

with ϑ the in-plane angle as defined in Sec. II and the prime denoting differentiation with respect to z. The densities per unit volume of both the surface energy and the electric energy are given by

$$W_s=\frac{A}{2h}d(z)\sin^2(\vartheta-\vartheta_s) \tag{10a}$$

$$W_e=\frac{\varepsilon_a}{2}E^2\sin^2(\vartheta-\vartheta_e), \tag{10b}$$

respectively, where $\varepsilon_a>0$ is the dielectric anisotropy in SI units. The electric field is assumed to be uniform throughout the cell. Though this is strictly valid only when the director field is also uniform, it is an acceptable simplification for the comparison between the dilution and the classical models that we aim at establishing here for weak anchoring.

Equation (10a) shows how the usual Rapini-Papoular surface energy is being diluted. Here we treat in detail only the special case where $\vartheta_s=0$ and $\vartheta_e=\pi/2$, but the conclusions we reach are also valid in a more general setting. The electric torque would orient $\boldsymbol{n}$ along the normal $\boldsymbol{\nu}$ to the bounding plate, whereas the surface torque would orient $\boldsymbol{n}$ at right angles with $\boldsymbol{\nu}$. Away from the plate, the former torque prevails over the latter, whereas close to the plate it fails to do so, provided that the surface anchoring is not so weak as to *lose* the nematic director $\boldsymbol{n}$.

By Eqs. (9) and (10), the total free energy $\mathcal{F}$ of the system can be written as

$$\begin{aligned}\mathcal{F}[\vartheta]&=\tfrac{1}{2}\int_0^\infty\left(K(\vartheta')^2+\varepsilon_aE^2\cos^2\vartheta+\frac{A}{h}d(z)\sin^2\vartheta\right)dz\\&=\frac{K}{2}\int_0^\infty\left((\vartheta')^2+\frac{1}{\xi_e^2}\cos^2\vartheta+\frac{1}{\xi_s^2}d(z)\sin^2\vartheta\right)dz,\end{aligned} \tag{11}$$

where two distinct coherence lengths have been introduced,

$$\xi_s:=\sqrt{\frac{Kh}{A}} \tag{12}$$

and

$$\xi_e:=\frac{1}{E}\sqrt{\frac{K}{\varepsilon_a}}, \tag{13}$$

the former for the surface field and the latter for the electric field. The surface extrapolation length L is found to be related to ξ_s through

$$\xi_s^2=Lh.$$

Here we take $h\ll L$, which means that the anchoring on the plate is sufficiently *weak*. The three surface lengths h, ξ_s, and L are then ordered as follows: $h<\xi_s<L$.

Any conceivable dilution function has to decay to 0 at infinity so as to be integrable over the whole half line $z\geqslant 0$. Moreover, for the energy functional $\mathcal{F}$ in Eq. (11) to be finite, ϑ must obey both asymptotic conditions

$$\lim_{z\to\infty}\vartheta(z)=\frac{\pi}{2} \tag{14a}$$

$$\lim_{z\to\infty}\vartheta'(z)=0. \tag{14b}$$

On the other hand, since no anchoring is actually concentrated at $z=0$, no condition for ϑ can either be requested there.

Calculating the first variation of $\mathcal{F}$ only subject to Eqs. (14) yields both the Euler-Lagrange equation,

$$\vartheta''=\left(\frac{d(z)}{\xi_s^2}-\frac{1}{\xi_e^2}\right)\sin\vartheta\cos\vartheta, \tag{15}$$

and the natural boundary condition at the plate,

$$\vartheta'(0)=0. \tag{16}$$

This condition, which in a more general setting is to require the normal gradient of the director field to vanish on the bounding surface, is a direct consequence of the dilution: *no* localized torque is transmitted at the boundary.

Equation (15) subject to both Eqs. (14) and Eq. (16) always has the trivial solution $\vartheta\equiv\pi/2$, which corresponds to

the complete anchoring *breaking*. The problem then arises whether there is any other equilibrium solution for which the anchoring is not completely broken, as one would expect when the electric field is not too strong. For any diluted surface potential, ϑ' vanishes both on the plate and at infinity. Therefore, for a nontrivial equilibrium solution to exist, $\vartheta''(z)$ must possess an isolated zero, which results in an inflection point for the director profile. Letting z_0 be the coordinate of this point, we readily see from Eq. (15) that it satisfies

$$d(z_0)=\frac{\xi_s^2}{\xi_e^2}.$$

Thus, for a decreasing dilution function d there is only the trivial equilibrium solution whenever

$$d(0)\leqslant\frac{\xi_s^2}{\xi_e^2}. \tag{17}$$

We will discuss this condition in the following section, where we arrive at a more accurate value of the saturation field by estimating $\vartheta(0)$ for all possible solutions of Eq. (15).

IV. SURFACE ORIENTATION

The main objective of this section is to find a broad class of dilution functions within which the breaking of a weak anchoring could be expressed by one and the same general condition. We consider the class of functions that satisfy

$$\lim_{z\to\infty} d(z)=0, \tag{18a}$$

$$\lim_{z\to\infty} z\,d(z)=0, \tag{18b}$$

$$|d'(z)|\leqslant M \quad \forall \quad z\geqslant 0, \tag{18c}$$

and we show that it is indeed fit for this purpose. For these functions it is possible to estimate the director orientation at the boundary in the limit where $h/L=h^2/\xi_s^2\ll 1$ and $d(0)\gg\xi_s^2/\xi_e^2$. First, we multiply both sides of Eq. (15) by ϑ' and then integrate over the whole positive real line. By Eqs. (14b) and (16), we thus arrive at

$$\frac{\xi_s^2}{\xi_e^2}-d(0)=\int_0^\infty d'(z)\left(\frac{\cos\vartheta(z)}{\cos\vartheta_0}\right)^2 dz, \tag{19}$$

where we have set $\vartheta_0:=\vartheta(0)$.

We now make use again of Eq. (15) to compute all derivatives of ϑ at $z=0$, and so obtain a Taylor expansion for the function $z\mapsto\cos\vartheta(z)$; the sum of this series, with the aid of Eq. (18), can also be estimated as follows:

$$\frac{\cos\vartheta(z)}{\cos\vartheta_0}=1-\frac{h^2}{\xi_s^2}(\sin^2\vartheta_0)g(z)+o\left(\frac{h^2}{\xi_s^2}\right), \tag{20}$$

where g is the solution to the differential equation

$$g''=\frac{1}{h^2}d \tag{21}$$

with initial conditions $g(0)=0$ and $g'(0)=0$. By inserting the right-hand side of Eq. (20) into Eq. (19), and using Eqs. (18a) and (18c), we readily obtain

$$\frac{\xi_s^2}{\xi_e^2}+\frac{2h^2}{\xi_s^2}\sin^2\vartheta_0\int_0^\infty d'g\,dz=0. \tag{22}$$

Use of Eq. (21) and repeated integrations by parts give Eq. (22) the form

$$\sin^2\vartheta_0=\frac{\xi_s^4}{h^2\xi_e^2}=\left(\frac{L}{\xi_e}\right)^2 \tag{23}$$

because, by Eqs. (5) and (18b),

$$\lim_{z\to\infty} g'^2=\frac{1}{h^2} \quad \text{and} \quad \lim_{z\to\infty} dg=0.$$

Equation (23) is the desired estimate for the orientation of the nematic director at the bounding plate in terms of the applied field. Since Eq. (23) must hold for all nontrivial equilibrium solutions, whenever its right-hand side exceeds 1 there cannot be any. Thus, the anchoring is completely broken as soon as

$$\xi_e\leqslant\frac{\xi_s^2}{h}=L, \tag{24}$$

which, by Eq. (13), immediately leads to a critical value of the electric field. This being a sufficient condition, it is indeed a better estimate than the one given by Eq. (17). It is usually also much sharper, since a decreasing dilution function d obeys Eq. (6), and so the threshold for ξ_e by Eq. (17) would be only $\sqrt{2}\xi_s$. By contrast, Eq. (24) predicts that the anchoring is already broken by the weaker field with $\xi_e=L$.

In principle, this condition for the anchoring breaking is valid when $h/L\to 0$. We checked that it is also a reliable estimate for the critical electric field when h is comparable to L by computing numerically the nontrivial solutions of Eq. (15) subject to Eqs. (14) and (16) for the dilution functions $d_1(z)=\exp(-z/h)$ and $d_2(z)=2[h/(z+h)]^3$, the latter of which represents the nonretarded van der Waals potential. As can be seen from Fig. 1, the critical field is well predicted by Eq. (24) for both dilution functions.

When the applied field fails to be at right angles with the preferred orientation for the surface director, that is, when $\vartheta_e\neq\pi/2$ in Eq. (10b), all equilibrium solutions are not trivial. Moreover, precisely the same reasoning that led us to Eq. (23) now yields

$$\left(\frac{L}{\xi_e}\right)^2=\frac{\cos^2\vartheta_0\sin^2\vartheta_0}{\sin^2(\vartheta_0-\vartheta_e)}, \tag{25}$$

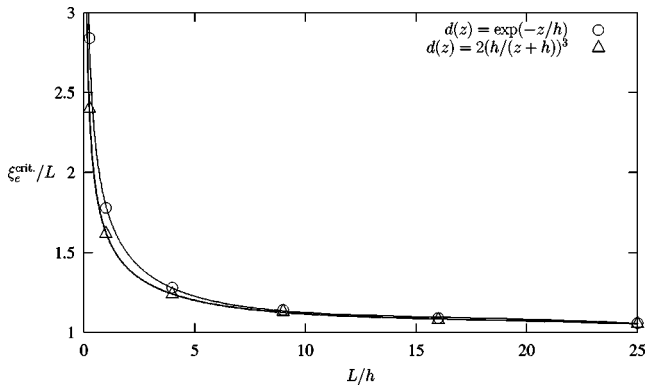

FIG. 1. Values of the electrical coherence length computed numerically at the saturation field for different dilution functions. By Eq. (24), the critical value of ξ_e is L. Though this estimate is valid only for large values of L/h, it also yields satisfactory results when this ratio is close to 1.

whence it follows that for every ξ_e there are two values of ϑ_0, one smaller and the other larger than ϑ_e, which eventually coalesce to ϑ_e as $\xi_e \to \infty$; for the energy minimizer $\vartheta_0 < \vartheta_e$.

V. CLASSICAL WEAK ANCHORING

We have seen that the details of the dilution law play no role in the anchoring breaking. We now compare the outcomes of the dilution model to those known for the classical model of Rapini and Papoular. We shall see that the two models predict the same saturation field, though the former is richer in details because it also describes the nematic orientation within the surface layer.

In the Rapini-Papoular model, for $\vartheta_e = \pi/2$ the energy functional is

$$\mathcal{F}[\vartheta] = \frac{K}{2}\left[\frac{1}{L}\sin^2\vartheta_0 + \int_0^\infty \left((\vartheta')^2 + \frac{1}{\xi_e^2}\cos^2\vartheta \right) dz \right], \tag{26}$$

where again $\vartheta_0 = \vartheta(0)$, so that the equilibrium equation reads like Eq. (15) without the first term on the right-hand side. Moreover, the boundary condition (16) at $z=0$ is replaced by the following:

$$L\,\vartheta'(0) = \sin\vartheta_0 \cos\vartheta_0, \tag{27}$$

whereas Eq. (14) still applies, so that neither ϑ_0 nor $\vartheta'(0)$ can vanish in a nontrivial equilibrium solution. As an immediate consequence, since here ϑ ranges in $[0,\pi/2]$ on the whole cell, ϑ'' is everywhere negative, and so the entire director profile is concave. A nontrivial solution of the equilibrium equation also satisfies

$$\vartheta' = \frac{1}{\xi_e}\cos\vartheta,$$

which combined with Eq. (27) leads again to Eq. (23), and so condition (24) for the anchoring breaking remains unchanged. Moreover, the nontrivial solution takes the following well-known explicit form:

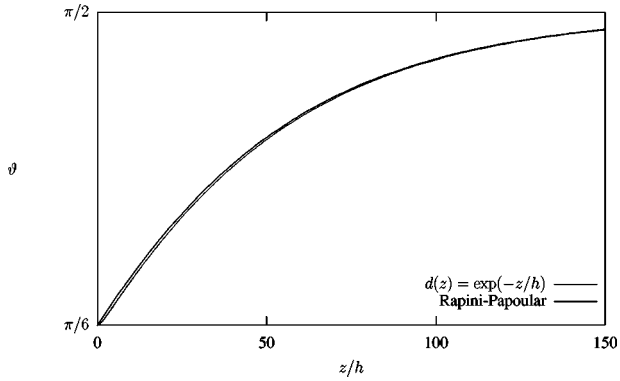

FIG. 2. Comparison between the localized Rapini-Papoular anchoring and an exponentially diluted surface potential with $\xi_e = 50h$ and $L = 25h$. The director profiles are quite similar on a large scale and differ only in the boundary layer where $z \leqslant h$.

$$\vartheta(z) = \sin^{-1}\left(\frac{L/\xi_e + \tanh z/\xi_e}{1 + (L/\xi_e)\tanh z/\xi_e} \right). \tag{28}$$

In Fig. 2 two director profiles are compared: one is obtained from an exponential dilution law $d(z)=\exp(-z/h)$ and the other is described by Eq. (28); both correspond to the same extrapolation length $L = 25h$ and the same electric coherence length $\xi_e = 50h$. If the profile obtained with the Rapini-Papoular boundary condition is shifted to the right by an amount of about h, it is seen nearly to coincide with the profile found with the diluted potential. In this sense, the sharp boundary is replaced by a thin boundary layer where the director, starting with $\vartheta'(0)=0$, is almost constant (see Fig. 3).

Likewise, when $0 < \vartheta_e < \pi/2$, Eq. (25) is still the condition for the anchoring breaking, and the equilibrium director profile has the representation

$$\vartheta(z) = \vartheta_e - 2\tan^{-1}[\exp(-z/\xi_e)\tan\tfrac{1}{2}(\vartheta_e - \vartheta_0)],$$

where ϑ_0 is the smallest root of Eq. (25).

VI. CONCLUSIONS

In [7] a diluted surface model was introduced to describe the dynamics of nematic liquid crystals close to a bounding plate. Here, to relate this model to the classical weak anchor-

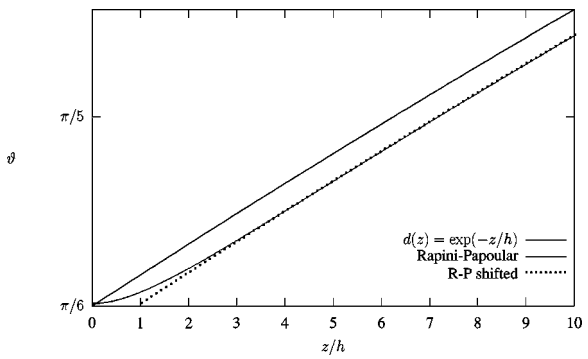

FIG. 3. Enlargement of the director profiles shown in Fig. 2. The dotted line represents the Rapini-Papoular profile shifted inward: it matches the dilution profile away from the boundary layer.

ing, we considered the effects of a diluted surface potential on static director fields. We found that the predictions of the dilution model are indeed similar to those obtained from the established Rapini-Papoular model, though this latter cannot access the details of the boundary layer introduced in [7].

A characteristic dilution length was defined in terms of the surface potential that describes how the action of the surface is extended into the bulk. It has been shown that the actual shape of the dilution potential has little influence on the key features of the director orientation: in the limit where the surface dilution length is small compared to the surface extrapolation length, the orientation at the boundary in the presence of an external field is independent of the dilution law: it is a function of the field coherence length and the surface extrapolation length alone. Moreover, the same surface orientation is also found within the Rapini-Papoular model. Indeed, the whole director profile predicted with a localized surface energy can be recovered from a profile computed with a diluted potential when the latter is shifted toward the boundary by an amount of roughly the dilution length h. In this way the rigid boundary plate is effectively replaced by a thin boundary layer where the director profile is almost uniform.

From a mathematical point of view, the boundary condition is reduced to the requirement that the normal gradient of the director vanishes at the boundary, while the action of the surface is born by a bulklike term in the equilibrium differential equation. This approach is easily extended to surface dynamics, while in statics it is compatible with the classical Rapini-Papoular model. In a forthcoming paper we address the dynamical aspects of this model and compare its outcomes to those expected within the model proposed in [3], where the Rapini-Papoular boundary coupling is the starting point for a surface balance equation bearing a phenomenological surface viscosity. We shall see that the agreement between nondilution and dilution models found in statics is soon to be spoiled in dynamics: the first signs of clash are already announced in [15].

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APPENDIX

Here we prove inequality (6). First, recall Jensen's inequality, which states that for a convex function Φ and a non-negative weight function $p \geqslant 0$

$$\Phi\left(\frac{\int_a^b f(z)p(z)dz}{\int_a^b p(z)dz} \right) \leqslant \frac{\int_a^b \Phi(f(z))p(z)dz}{\int_a^b p(z)dz}.$$

If the dilution function D is decreasing monotonically, we can set

$$p = -D',$$

and with

$$\Phi(u) = u^2 \quad \text{and} \quad f(z) = z$$

Jensen's inequality yields

$$\frac{-\int_0^\infty z^2 D'(z)dz}{-\int_0^\infty D'(z)dz} \geqslant \left(\frac{-\int_0^\infty zD'(z)dz}{-\int_0^\infty D'(z)dz} \right)^2,$$

whence we arrive via integrations by parts at

$$D(0)\int_0^\infty zD(z)dz \geqslant \frac{1}{2}\left(\int_0^\infty D(z)dz \right)^2.$$

This, by Eqs. (2)–(4), reads as $d(0) \geqslant 1/2$, which is the desired result.

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