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Anchoring of nematic liquid crystals at a solid substrate

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A nematic liquid crystal in contact with a solid substrate is studied by means of the Landau–de Gennes formalism. The free-energy functional is expanded around the bulk nematic order parameter up to the second-order terms. This approximation is used to obtain an explicit condition for the anchoring direction in terms of the surface and bulk coupling constants, in a semi-infinite system. Then a finite system is studied and the equilibrium free energy is found as a function of the angular deviation from the anchoring direction and the sample thickness. A geometrical measure of the anchoring strength, resembling the de Gennes extrapolation length, is obtained from the asymptotic behavior of the free energy for large sample thicknesses.

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I. INTRODUCTION

Nematic liquid crystals are uniaxial media [1], and the orientation of the symmetry axis (nematic director) is arbitrary in the absence of external fields or limiting surfaces. Various limiting surfaces such as: the free nematic surface, the nematic-isotropic interface, or the solid substrate surface, fix the orientation of the nematic director. This phenomenon is called the anchoring of the nematic liquid crystal at the interface [2–7]. The anchoring of liquid crystals at solid substrates attracts particularly much attention. First, it is interesting as a fundamental problem in the statistical mechanics of nonuniform, ordered fluids. Second, it is important for the technology of liquid-crystal display devices. Three regions can be distinguished in the nematic liquid crystal in contact with the substrate [8]. Close to the surface, liquid-crystal molecules interact directly with the substrate, and this direct interaction determines the microscopic anchoring condition. Next, there is an interfacial region in which the order parameters and the nematic director change. Finally, far from the substrate, there is the bulk phase with the director orientation fixed by the surface. This bulk orientation is called the anchoring direction or the easy axis; it corresponds to the minimum of the interfacial tension γ between the nematic phase and the substrate. The structure of the interfacial region determines the macroscopic anchoring condition.

The energetic manifestation of the anchoring is referred to as the anchoring energy or the anchoring strength. In anchoring energy measurements, the director field in the nematic phase has to be distorted. Various experimental techniques are discussed in detail by Yokoyama [3], who also gives a thermodynamic definition of γ as a function of the director orientation. In order to define γ, a hypothetical dividing surface is introduced. Above the dividing surface the nematic phase is assumed to have a bulklike behavior, and distortions of the director field are described by the Frank elastic theory [9]. Then γ is defined as a function of the director orientation at the dividing surface. Yokoyama contrasts this thermodynamic definition with phenomenological formalisms, e.g., the Rapini-Papoular formalism [10], in which one simply postulates a particular form of γ. He also emphasizes a fundamental conceptual difference between the definitions of the anchoring direction and the anchoring energy. The anchoring direction has an unambiguous physical meaning, independent of a model of the interface. It refers to the director in the *bulk* nematic phase in the absence of deformations. The anchoring energy, on the other hand, is an interfacial parameter accessible only through an appropriate theoretical framework. It is defined as the second derivative of γ with respect to the director orientation calculated at the anchoring direction [2]. Therefore, it depends on the choice of the dividing surface. It is worth mentioning that some phenomenological formalisms assume that γ depends not only on the director orientation at the interface but also on its gradients. The surface elastic terms are usually referred to as the K_{24} and K_{13} terms, where K_{24} and K_{13} are the surface elastic constants [11–13]. Consequences of the presence of the surface elastic terms in γ have been studied by many authors [4,14–21]. As we do not discuss them in this paper, we only note that the K_{13} term leads to some mathematical problems, the solution of which has been proposed recently by Pergamenshchik [17].

A long time ago de Gennes [1] introduced a geometrical measure of the anchoring strength. He considered only the simplest case of the twist deformation. In that case, the director orientation is specified by the azimuthal angle φ, measured with respect to the easy axis parallel to the substrate. It results from the solution of the Euler-Lagrange equation that far from the substrate φ is a linear function of the distance z, $\varphi(z)=\text{const}\times(z+b)$, where b is called the extrapolation length. The anchoring strength can be characterized by the relation between b and the molecular dimensions. The anchoring is strong if they are comparable, and it is weak if b is much larger than the molecular dimensions. In the case of short-range forces, the anchoring energy is equal to K_2/b, where K_2 denotes the twist elastic constant. Dubois-Violette and de Gennes [22] also studied the case of

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long-range van der Waals forces, and found that b can be positive or negative. Yokoyama [3] has generalized the definition of the extrapolation length to other types of deformation.

In this paper, we use the Landau–de Gennes formalism to describe the nematic-substrate interface. It is assumed that the only relevant variable is the tensor nematic order parameter and density changes are neglected. The interaction of liquid-crystal molecules with the substrate and the modification of the liquid-liquid interactions by the substrate are taken into account in a similar way as in the case of simpler systems described by a scalar order parameter, i.e., the surface contribution to the free energy is approximated by a second-order polynomial of the surface order parameter. For instance, this form is suitable for studying wetting phenomena [23]. In the case of nematic liquid crystals, the only complication is due to the tensor nature of the order parameter [24,25].

We consider a nematic liquid crystal in contact with a solid substrate, sufficiently far from any bulk phase transitions. Although the Landau–de Gennes formalism has been applied by many authors in specific situations, a general method to predict the anchoring direction has not been formulated. Either the minimization of the surface part of the free-energy functional has been used to find the anchoring direction, or specific cases have been studied by means of numerical analysis. Although the first route may lead to reasonable results, in general, it oversimplifies the problem as it does not take into account any bulk properties of the nematic phase. In this paper, we go beyond this simple approximation and propose another approximate scheme to obtain an explicit condition for the anchoring direction. Our method is based upon the assumption that the modification of the nematic structure by the substrate, compared to the bulk, is relatively weak. Therefore, we can expand the Landau–de Gennes free energy around the bulk order parameter up to the second-order terms. This approximation will fail, however, when a disordered isotropic structure is preferred close to the substrate. Then, of course, it is necessary to consider the Landau–de Gennes free energy in the form capable of describing the nematic-isotropic interface.

Finally, we note that a more detailed characterization of the interfacial region would require a microscopic description of the system. The one-particle distribution function gives information both about the local density of the nematic phase and the local distribution of molecular orientations. For instance, microscopic theories have been used to study anchoring at the free nematic surface [26–28] and at surfaces of pure nematic liquid crystals and their mixtures [29]. In contrast with microscopic theories, the Landau–de Gennes formalism ignores density variations. It also neglects higher moments of the orientational distribution, which can be a good approximation only for weakly, orientationally ordered systems. Thus calculations based upon the Landau–de Gennes formalism may exhibit some variance from actual experiments. Nevertheless, we expect to gain some insight into the structure of the interfacial region and the mechanism of the anchoring transitions.

Our paper is arranged as follows. In Sec. II we study a semi-infinite sample and derive an explicit condition for the anchoring direction in terms of the surface coupling constants and the bulk elastic constants. We also derive an expression for the equilibrium free energy. Then, in Sec. III, we consider a finite nematic sample with an idealized, infinitely strong anchoring at the second limiting surface. The equilibrium free energy of the system is found as a function of the angular deviation from the anchoring direction and the distance between the limiting surfaces. An explicit expression for a geometrical measure of the anchoring strength, similar to the extrapolation length, is also found. Finally, Sec. IV is devoted to a discussion. Some mathematical details are presented in the Appendix.

II. ANCHORING DIRECTION

In this section, we consider a semi-infinite sample of a nematic liquid crystal in contact with a flat, structureless substrate (wall). The distance from the wall is measured along the z axis. Close to the wall, the nematic order may differ from the bulk one, and the local biaxiality may be important. Therefore, the description of the interfacial region in terms of the nematic director alone is, in general, insufficient. We apply the Landau–de Gennes formalism [1], in which the nematic phase is described in terms of the nematic order parameter $\mathbf{Q}$. $\mathbf{Q}$ is a traceless, symmetric tensor, and the director $\hat{\mathbf{n}}$ is the eigenvector corresponding to the largest eigenvalue of $\mathbf{Q}$, called the scalar order parameter Q. It is assumed that the free-energy density f is a local function of $\mathbf{Q}$ and its gradients. If the fluctuations are neglected $\mathbf{Q}$ depends only on z and $f=f_L(\mathbf{Q})+f_G(\dot{\mathbf{Q}})$, where $\dot{\mathbf{Q}}=d\mathbf{Q}/dz$. The following forms of f_L and f_G are usually assumed:

$$f_L(\mathbf{Q})=A\,\mathrm{Tr}\mathbf{Q}^2-B\,\mathrm{Tr}\mathbf{Q}^3+C(\mathrm{Tr}\mathbf{Q}^2)^2\ , \tag{1}$$

$$f_G(\dot{\mathbf{Q}})=\tfrac{1}{2}L_1\mathrm{Tr}\dot{\mathbf{Q}}^2+\tfrac{1}{2}L_2\hat{\mathbf{k}}\cdot\dot{\mathbf{Q}}^2\cdot\hat{\mathbf{k}}\ , \tag{2}$$

where $\hat{k}$ is normal to the wall. The parameter A is assumed to depend linearly on the temperature, whereas B,C and the elastic constants L_1,L_2 are considered temperature independent.

The free-energy functional has the following form [24,25]:

$$\mathcal{F}=\int_0^\infty dz[f_L(\mathbf{Q}(z))-f_L(\mathbf{Q}_b)+f_G(\dot{\mathbf{Q}}(z))]+f_s(\mathbf{Q}(0))\ , \tag{3}$$

where $\mathbf{Q}_b=\mathbf{Q}(z=+\infty)=Q_b(\hat{\mathbf{n}}_b\hat{\mathbf{n}}_b-\tfrac{1}{3}\mathbf{I})$, $\hat{\mathbf{n}}_b$ is the bulk director, and $\mathbf{I}$ denotes the unit tensor. The surface contribution to the total free energy, f_s, is assumed to depend only on the value of $\mathbf{Q}$ at the wall. In this paper, we consider only the isotropic substrates, for which f_s can be expanded in $\mathbf{Q}$ up to the second-order terms, as follows:

$$f_s(\mathbf{Q})=c_1\hat{\mathbf{k}}\cdot\mathbf{Q}\cdot\hat{\mathbf{k}}+c_2\mathrm{Tr}\mathbf{Q}^2+c_3(\hat{\mathbf{k}}\cdot\mathbf{Q}\cdot\hat{\mathbf{k}})^2+c_4\hat{\mathbf{k}}\cdot\mathbf{Q}^2\cdot\hat{\mathbf{k}}\ , \tag{4}$$

where $c_1, \dots, c_4$ are constants. The minimization of $\mathcal{F}$ with respect to $\mathbf{Q}$ leads to the set of Euler-Lagrange equations with the boundary conditions at $z=0$ and $z=+\infty$, and the latter is simply $\dot{\mathbf{Q}}(+\infty)=0$. The orientation of $\hat{\mathbf{n}}_b$ is a combined effect of the elastic properties of the nematic liquid crystal and the interaction of liquid-crystal molecules with the substrate. The aim of the theory is to determine $\hat{\mathbf{n}}_b$ as a function of the temperature and the phenomenological parameters appearing in $\mathcal{F}$. This is not an easy task if one considers f_L as a fourth-order polynomial of $\mathbf{Q}$, which leads to nonlinear Euler-Lagrange equations. Then only numerical analysis of the problem is possible. However, if $\mathbf{Q}(0)$ does not differ significantly from $\mathbf{Q}_b$ the expansion of $f_L(\mathbf{Q})$ around $\mathbf{Q}_b$ up to the second order in $(\mathbf{Q}-\mathbf{Q}_b)$ should be a reasonable approximation. This approximation leads to a set of linear second-order differential equations with linear boundary conditions, which can be solved analytically. Then an explicit condition for the anchoring direction is obtained. Below we present the general solution of the problem and derive some useful relations, which can be directly applied to study anchoring transitions.

We exclude the twist deformation from our considerations, and assume that the tensor $\mathbf{Q}(z)$ has only three independent components and the only nonvanishing off-diagonal components are $Q_{xz}=Q_{zx}$. For our present purpose, it is convenient to work in the coordinate frame $x'y'z'$ obtained from xyz by the rotation about the y axis by the angle ψ, where ψ is the tilt angle of $\hat{\mathbf{n}}_b$ with respect to $\hat{\mathbf{k}}$. In the $x'y'z'$ frame, $\mathbf{Q}$ is given by

$$\mathbf{Q}=\begin{bmatrix} -\frac{1}{3}q+p & 0 & v \\ 0 & -\frac{1}{3}q-p & 0 \\ v & 0 & \frac{2}{3}q \end{bmatrix}, \tag{5}$$

and

$$\begin{aligned} f_L(q,p,v)=&\,A[\tfrac{2}{3}q^2+2(p^2+v^2)] \\ &-B(q+3p)[\tfrac{2}{9}q(q-3p)+v^2] \\ &+C[\tfrac{2}{3}q^2+2(p^2+v^2)]^2 . \end{aligned} \tag{6}$$

Because the z' axis is along $\hat{\mathbf{n}}_b$, the boundary conditions at $z=+\infty$ are $q(+\infty)=Q_b$, $p(+\infty)=0$, and $v(+\infty)=0$. In the following we shall assume that q, p, and v do not deviate too much from their bulk values. Therefore, we can expand f_L around the minimum at $q=Q_b$ and $p=v=0$, and keep only the second-order terms, i.e.,

$$\begin{aligned} f_L(q,p,v)&\approx f_L(Q_b,0,0)+\tfrac{2}{3}(A-BQ_b+4CQ_b^2)(q-Q_b)^2+2(A+BQ_b+\tfrac{4}{3}CQ_b^2)p^2 \\ &=f_L(Q_b,0,0)+\tfrac{1}{2}a_{11}(q-Q_b)^2+\tfrac{1}{2}a_{22}p^2 , \end{aligned} \tag{7}$$

where Q_b satisfies the equation $2A-BQ_b+\frac{8}{3}CQ_b^2=0$. Note that in Eq. (7) v does not appear; however, it would appear in the third- and fourth-order terms. Then we express f_G in terms of $\dot{q}$, $\dot{p}$, and $\dot{v}$, taking into account that $\hat{\mathbf{k}}=(-\sin\psi,0,\cos\psi)$ in the $x'y'z'$ frame:

$$f_G(\dot{q},\dot{p},\dot{v})=\tfrac{1}{2}(L_{11}\dot{q}^2+L_{22}\dot{p}^2+L_{33}\dot{v}^2+2L_{12}\dot{q}\dot{p}+2L_{13}\dot{q}\dot{v}+2L_{23}\dot{p}\dot{v}) , \tag{8}$$

where the symmetric matrix $L=(L_{ij})$ has the following components:

$$\begin{aligned} L_{11}&=\tfrac{2}{3}L_1+\tfrac{1}{9}L_2+\tfrac{1}{3}L_2(\cos^2\psi) , \\ L_{22}&=2L_1+L_2(\sin^2\psi) , \\ L_{33}&=2L_1+L_2 , \\ L_{12}&=-\tfrac{1}{3}L_2(\sin^2\psi) , \\ L_{13}&=-\tfrac{1}{3}L_2(\sin\psi)(\cos\psi) , \\ L_{23}&=-L_2(\sin\psi)(\cos\psi) . \end{aligned} \tag{9}$$

It is also convenient to rewrite f_s in terms of $\mathbf{Q}_b$ and the difference $\Delta\mathbf{Q}=\mathbf{Q}-\mathbf{Q}_b$ as follows:

$$\begin{aligned} f_s(\mathbf{Q})=&\,f_s(\mathbf{Q}_b)+[c_1+2c_3Q_b(\cos^2\psi-\tfrac{1}{3})-\tfrac{2}{3}c_4Q_b](\hat{\mathbf{k}}\cdot\Delta\mathbf{Q}\cdot\hat{\mathbf{k}}) \\ &+2c_2Q_b(\hat{\mathbf{n}}_b\cdot\Delta\mathbf{Q}\cdot\hat{\mathbf{n}}_b)+2c_4Q_b(\cos\psi)(\hat{\mathbf{n}}_b\cdot\Delta\mathbf{Q}\cdot\hat{\mathbf{k}})+c_2\mathrm{Tr}(\Delta\mathbf{Q})^2+c_3(\hat{\mathbf{k}}\cdot\Delta\mathbf{Q}\cdot\hat{\mathbf{k}})^2+c_4\hat{\mathbf{k}}\cdot(\Delta\mathbf{Q})^2\cdot\hat{\mathbf{k}} , \end{aligned} \tag{10}$$

where

$$\begin{aligned} f_s(\mathbf{Q}_b)=&-\tfrac{1}{3}c_1Q_b+\tfrac{1}{9}Q_b^2(6c_2+c_3+c_4) \\ &+[c_1Q_b-\tfrac{1}{3}Q_b^2(2c_3-c_4)](\cos^2\psi) \\ &+c_3Q_b^2(\cos^4\psi) . \end{aligned} \tag{11}$$

For brevity we introduce matrix notation and define the (3×1) matrix ϕ', with its transposition $(\phi')^T=(q-Q_b,p,v)$. Now f can be written in a compact form as

$$f(\phi',\dot{\phi}')=f_L(Q_b,0,0)+\tfrac{1}{2}(\phi')^T a\phi'+\tfrac{1}{2}(\dot{\phi}')^T L\dot{\phi}' , \tag{12}$$

where a is a diagonal matrix defined in Eq. (7) ($a_{33}=0$). Similarly, we express f_s as

$$f_s(\phi')=f_s(\mathbf{Q}_b)-(h')^T\phi'-\tfrac{1}{2}(\phi')^T g'\phi' , \tag{13}$$

where h' and g' are (3×1) and (3×3) matrices, respectively. From Eq. (10) we find that

$$\begin{aligned} h'_1&=\tfrac{1}{3}c_1-\tfrac{2}{9}Q_b(6c_2+c_3+c_4)\\ &\quad-[c_1-\tfrac{2}{3}Q_b(2c_3-c_4)]\cos^2\psi-2c_3Q_b(\cos^4\psi) ,\\ h'_2&=-[c_1+\tfrac{2}{3}Q_b(2c_3-c_4)](\sin^2\psi)+2c_3Q_b(\sin^4\psi) ,\\ h'_3&=[c_1-\tfrac{1}{3}Q_b(2c_3-c_4)+2c_3Q_b(\cos^2\psi)](\sin 2\psi) , \end{aligned} \tag{14}$$

$$\begin{aligned} g'_{11}&=-\tfrac{2}{9}(6c_2+c_3+c_4)+\tfrac{2}{3}(2c_3-c_4)(\cos^2\psi)\\ &\quad-2c_3(\cos^4\psi) ,\\ g'_{22}&=-2[2c_2+c_4(\sin^2\psi)+c_3(\sin^4\psi)] ,\\ g'_{33}&=-2[2c_2+c_4+c_3(\sin^2 2\psi)] ,\\ g'_{12}&=-\tfrac{2}{3}(2c_3-c_4)(\sin^2\psi)+2c_3(\sin^4\psi) ,\\ g'_{13}&=[-\tfrac{1}{3}(2c_3-c_4)+2c_3(\cos^2\psi)](\sin 2\psi) ,\\ g'_{23}&=[c_4+2c_3(\sin^2\psi)](\sin 2\psi) , \end{aligned} \tag{15}$$

where g' is a symmetric matrix.

The next step involves simultaneous diagonalization of the quadratic forms in Eq. (12). This can be achieved by the following three transformations:

$$S=S_1S_2S_3=\begin{bmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ -\dfrac{L_{13}}{L_{33}} & -\dfrac{L_{23}}{L_{33}} & 1 \end{bmatrix}\begin{bmatrix} \dfrac{1}{\sqrt{a_{11}}} & 0 & 0\\ 0 & \dfrac{1}{\sqrt{a_{22}}} & 0\\ 0 & 0 & 1 \end{bmatrix}\times\begin{bmatrix} \cos\alpha & \sin\alpha & 0\\ -\sin\alpha & \cos\alpha & 0\\ 0 & 0 & 1 \end{bmatrix} , \tag{16}$$

where the last transformation is orthogonal. The free-energy density in the field variables, defined by the relation $\phi'=S\phi$, has the following simple form:

$$f(\phi,\dot{\phi})=f_L(Q_b,0,0)+\tfrac{1}{2}(\phi_1^2+\phi_2^2)+\tfrac{1}{2}\phi^T\Lambda\dot{\phi} , \tag{17}$$

where

$$\Lambda=S^TLS=\begin{bmatrix} \xi_1^2 & 0 & 0\\ 0 & \xi_2^2 & 0\\ 0 & 0 & L_{33} \end{bmatrix} .$$

For f_s, we obtain

$$f_s(\phi)=f_s(\mathbf{Q}_b)-h^T\phi-\tfrac{1}{2}\phi^T g\phi , \tag{18}$$

where $h=S^Th'$ and $g=S^Tg'S$. The Euler-Lagrange equations, obtained from the minimization of $\mathcal{F}$ with respect to ϕ, have the following solution satisfying the boundary condition $\dot{\phi}(+\infty)=0$:

$$\phi(z)=\begin{bmatrix} \phi_1(0)\exp(-z/\xi_1)\\ \phi_2(0)\exp(-z/\xi_2)\\ \phi_3(0) \end{bmatrix} . \tag{19}$$

Because of the relation $\phi_3(z)=\phi'_3(z)+[L_{13}\phi'_1(z)+L_{23}\phi'_2(z)]/L_{33}$ and the boundary condition $\phi'(+\infty)=0$, it must be $\phi_3(0)=\phi_3(+\infty)=0$. This must be compatible with the boundary condition at $z=0$: $\Lambda\dot{\phi}(0)=-h-g\phi(0)$, which can be expressed as

$$(g-\xi)\phi(0)+h=0 , \tag{20}$$

after the substitution of $\dot{\phi}(0)$, calculated from Eq. (19). ξ is a diagonal (3×3) matrix with the components $\xi_{11}=\xi_1$, $\xi_{22}=\xi_2$, and $\xi_{33}=0$. The solution of Eq. (20), together with the condition $\phi_3(0)=0$, leads to the following relation between g, ξ, and h:

$$\begin{vmatrix} g_{11}-\xi_1 & g_{12} & h_1\\ g_{12} & g_{22}-\xi_2 & h_2\\ g_{13} & g_{23} & h_3 \end{vmatrix}=0 . \tag{21}$$

Since g, ξ, and h depend on ψ, Eq. (21) must be satisfied by the equilibrium tilt angle. It will be shown below that Eq. (21) always has at least two solutions: $\psi=0$ and $\psi=\pi/2$. It is possible, however, that there are also other solutions if the parameters are suitably chosen. In such a case, the surface free energies corresponding to different solutions have to be compared.

The calculation of the equilibrium surface free energy is very simple and gives

$$\mathcal{F}_{\text{eq}}=-\tfrac{1}{2}[\phi(0)]^T\Lambda\dot{\phi}(0)+f_s(\phi(0))=f_s(\mathbf{Q}_b)-\tfrac{1}{2}h^T\phi(0) , \tag{22}$$

where $\phi(0)$ satisfies Eq. (20). Finally, we express $\mathcal{F}_{\text{eq}}$ in terms of g, ξ, and h as follows:

$$\mathcal{F}_{\text{eq}}=f_s(\mathbf{Q}_b)+\frac{h_1^2(g_{22}-\xi_2)-2h_1h_2g_{12}+h_2^2(g_{11}-\xi_1)}{2[(g_{11}-\xi_1)(g_{22}-\xi_2)-g_{12}^2]} . \tag{23}$$

To obtain the stability conditions, we assume that the Euler-Lagrange equations together with the boundary condition at $z=+\infty$ are satisfied, and consider $\mathcal{F}$ as a function of $\phi(0)$, which gives

$$\mathcal{F}=\tfrac{1}{2}[\xi_1\phi_1^2(0)+\xi_2\phi_2^2(0)]+f_s(\phi(0)) . \tag{24}$$

The minimization of $\mathcal{F}$ with respect to $\phi(0)$ gives Eq. (20) and $\partial^2\mathcal{F}/\partial[\phi(0)]^2=\xi-g$. Thus, $\xi-g$ must be a positive definite matrix for a stable system. Then the denominator in Eq. (23) is also positive.

It is convenient to express the condition for the equilibrium ψ in terms of the original prime variables. To do this, we first define the matrix ξ' as $S^T\xi'S=\xi$. The explicit expression for ξ' in terms of the matrices a and L is presented in the Appendix. The condition $\phi_3(0)=0$ transforms into

$$L_{13}\phi_1'(0)+L_{23}\phi_2'(0)+L_{33}\phi_3'(0)=0\ , \tag{25}$$

where $\phi'(0)$ satisfies

$$(g'-\xi')\phi'(0)+h'=0\ . \tag{26}$$

Finally, from Eqs. (25) and (26), we obtain the following condition for the equilibrium ψ:

$$R(\psi)=\begin{vmatrix} g_{11}'-\xi_{11}' & g_{12}'-\xi_{12}' & g_{13}' & h_1' \\ g_{12}'-\xi_{12}' & g_{22}'-\xi_{22}' & g_{23}' & h_2' \\ g_{13}' & g_{23}' & g_{33}' & h_3' \\ L_{13} & L_{23} & L_{33} & 0 \end{vmatrix}=0\ . \tag{27}$$

Because $(h')^T\phi'(0)=h^T\phi(0)$, we find from Eqs. (22) and (26) that

$$\mathcal{F}_{\text{eq}}=f_s(\mathbf{Q}_b)-\tfrac{1}{2}(h')^T(\xi'-g')^{-1}h' \tag{28}$$

where $(\xi'-g')$ is also positive definite. Using Eqs. (27) and (28) one can determine the anchoring direction and the equilibrium surface free energy in a semi-infinite nematic sample. One verifies that Eq. (27) is satisfied by $\psi=0$ and $\psi=\pi/2$. Indeed, components (13) and (23) of L and g', and also h_3', are odd functions of ψ or $\psi-\pi/2$, whereas the remaining components of L, g', and h', and also the components of ξ' (see the Appendix) are even functions of ψ or $\psi-\pi/2$; hence $R(-\psi)=-R(\psi)$ and $R(\pi/2-\psi)=-R(\psi-\pi/2)$.

III. GEOMETRICAL MEASURE OF THE ANCHORING STRENGTH

In this section, we consider a nematic sample of thickness l in contact with the substrate at $z=0$. At $z=l$ the orientation of the nematic director $\hat{\mathbf{n}}(l)$ is defined by the tilt angle θ_l, measured with respect to $\hat{\mathbf{k}}$. We want to calculate the free energy associated with the deviation of $\hat{\mathbf{n}}(l)$ from the anchoring direction $\hat{\mathbf{n}}_b$. We assume that $l\gg\xi_1,\xi_2$, and that $\mathbf{Q}(l)\approx Q_b[\hat{\mathbf{n}}(l)\hat{\mathbf{n}}(l)-\frac{1}{3}\mathbf{I}]$. Working as before in the $x'y'z'$ frame, we have

$$\begin{aligned} \phi_1'(l)&=q(l)-Q_b=-\tfrac{3}{2}Q_b\sin^2(\theta_l-\psi)\ , \\ \phi_2'(l)&=p(l)=\tfrac{1}{2}Q_b\sin^2(\theta_l-\psi)\ , \\ \phi_3'(l)&=v(l)=\tfrac{1}{2}Q_b\sin 2(\theta_l-\psi)\ . \end{aligned} \tag{29}$$

Again we express $\mathcal{F}$ in terms of ϕ, and solve the Euler-Lagrange equations, which gives

$$\begin{aligned} &\phi_i(z)=\{\phi_i(0)\sinh[(l-z)/\xi_i]+\phi_i(l)\sinh(z/\xi_i)\}/\sinh(l/\xi_i)\quad\text{for } i=1,2\ , \\ &\phi_3(z)=\phi_3(0)+[\phi_3(l)-\phi_3(0)]z/l\ . \end{aligned} \tag{30}$$

The equilibrium surface free energy is given by

$$\mathcal{F}_{\text{eq}}=f_s(\phi(0))+\tfrac{1}{2}[\phi(l)]^T\Lambda\dot{\phi}(l)-\tfrac{1}{2}[\phi(0)]^T\Lambda\dot{\phi}(0)\ . \tag{31}$$

If we neglect the exponential corrections then $\dot{\phi}_i(0)\approx-\phi_i(0)/\xi_i$, $\dot{\phi}_i(l)\approx\phi_i(l)/\xi_i$, for $i=1$ and 2, and $\dot{\phi}_3(0)=\dot{\phi}_3(l)=[\phi_3(l)-\phi_3(0)]/l$. This approximation, justified as long as l is large compared to the correlation lengths, leads to the following equation for $\phi(0)$:

$$[g-\Xi(l)]\phi(0)+h=\begin{bmatrix} 0 \\ 0 \\ -L_{33}\phi_3(l)/l \end{bmatrix}\ , \tag{32}$$

where $\Xi(l)$ is diagonal and $\Xi_{11}(l)=\xi_1$, $\Xi_{22}(l)=\xi_2$, and $\Xi_{33}(l)=L_{33}/l$. It follows from Eqs. (31) and (32) that

$$\mathcal{F}_{\text{eq}}=f_s(\mathbf{Q}_b)+\frac{1}{2}\left\{\xi_1[\phi_1(l)]^2+\xi_2[\phi_2(l)]^2-h^T\phi(0)-\phi_3(l)\left[h_3+\sum_{i=1}^{3}g_{i3}\phi_i(0)\right]\right\}\ . \tag{33}$$

The solution of Eq. (32) gives corrections $\sim 1/l$ to the solution $\phi^{\infty}(0)$ for a semi-infinite system:

$$\begin{aligned} \phi_1(0)&=[D(l)]^{-1}\left[D(\infty)\phi_1^{\infty}(0)-L_{33}l^{-1}\left\{\phi_3(l)\begin{vmatrix} g_{12} & g_{13} \\ g_{22}-\xi_2 & g_{23}\end{vmatrix}-\begin{vmatrix} h_1 & g_{12} \\ h_2 & g_{22}-\xi_2\end{vmatrix}\right\}\right]\ , \\ \phi_2(0)&=[D(l)]^{-1}\left[D(\infty)\phi_2^{\infty}(0)+L_{33}l^{-1}\left\{\phi_3(l)\begin{vmatrix} g_{11}-\xi_1 & g_{13} \\ g_{12} & g_{23}\end{vmatrix}+\begin{vmatrix} g_{11}-\xi_1 & h_1 \\ g_{12} & h_2\end{vmatrix}\right\}\right]\ , \\ \phi_3(0)&=-L_{33}\phi_3(l)[lD(l)]^{-1}\begin{vmatrix} g_{11}-\xi_1 & g_{12} \\ g_{12} & g_{22}-\xi_2\end{vmatrix}\ , \end{aligned} \tag{34}$$

where $D(l)=\det[g-\Xi(l)]$. Substitution of Eqs. (34) into Eq. (33) gives

$$\mathcal{F}_{\rm eq}=\mathcal{F}_{\rm eq}^{\infty}+\frac{1}{2}\left[\xi_1[\phi_1(l)]^2+\xi_2[\phi_2(l)]^2+\frac{D(\infty)L_{33}}{lD(l)}[\phi_3(l)]^2\right], \tag{35}$$

where $\mathcal{F}_{\rm eq}^{\infty}$ denotes the equilibrium surface free energy of a semi-infinite system, and is given by Eq. (28).

We assume that $(\theta_l-\psi)$ is small, and consider only the second-order contribution to $\mathcal{F}$, which is consistent with our approximation for f_L; note that $\phi_1(l)^2$ and $\phi_2(l)^2$ are $\sim(\theta_l-\psi)^4$. Then $\mathcal{F}_{\rm eq}\to\mathcal{F}_{\rm eq}^{\infty}$ when $l\to\infty$, for any θ_l, and we expect that this result will hold when higher-order terms are included in f_L. Indeed, rotations of the director infinitely far from the wall should not affect the free energy of the system, because the elastic forces vanish in the limit $l\to\infty$. Neglecting the fourth-order terms, we rewrite Eq. (35) in the following simple form:

$$\mathcal{F}_{\rm eq}=\mathcal{F}_{\rm eq}^{\infty}+\tfrac{1}{2}K\frac{(\theta_l-\psi)^2}{l+\bar{b}} \tag{36}$$

where $K=Q_b^2L_{33}$ is the splay/bend Frank elastic constant. The parameter $\bar{b}$ has the dimension of length and is given by

$$\bar{b}=\frac{L_{33}}{\det(\xi-g)}\begin{vmatrix} g_{11}-\xi_1 & g_{12} \\ g_{12} & g_{22}-\xi_2 \end{vmatrix}. \tag{37}$$

It is positive, because of the stability conditions derived in Sec. II.

Formally, the same expression as Eq. (36) is obtained when the free energy is considered as a functional of the director field alone. Neglecting the twist deformation and assuming $K_1=K_3=K$, we find [1]

$$\mathcal{F}=\text{const}+\tfrac{1}{2}\int_0^l K\left[\frac{d\theta}{dz}\right]^2 dz+\tfrac{1}{2}w(\theta_0-\psi)^2, \tag{38}$$

where θ_0 denotes the director orientation at the wall, and the coefficient w is the anchoring energy. The boundary condition $\theta(l)=\theta_l$ corresponds to the strong anchoring limit. $\mathcal{F}$ is minimal for $\theta(z)=\theta_0+(\theta_l-\theta_0)z/l$, where θ_0 is determined from the boundary condition at $z=0$: $Kd\theta/dz=w(\theta_0-\psi)$. The extrapolation length satisfies $\theta(z=-b)=\psi$ and is given by $b=K/w$, hence $\mathcal{F}=\text{const}+\frac{1}{2}K(\theta_l-\psi)^2/(l+b)$. The comparison of the above result with Eq. (36) shows that $\bar{b}$ plays a similar role to the extrapolation length, i.e., it can also be treated as a geometrical measure of the anchoring strength. We return to this point in Sec. IV.

Again, it is convenient to express $\bar{b}$ in terms of the prime variables, as it was done in Sec. II in the case of $\mathcal{F}_{\rm eq}^{\infty}$. First, using Eq. (23), we express the determinant appearing in Eq. (37) as follows:

$$\begin{vmatrix} g_{11}-\xi_1 & g_{12} \\ g_{12} & g_{22}-\xi_2 \end{vmatrix}=\frac{h_\perp^T(g-\xi)h_\perp}{2[\mathcal{F}_{\rm eq}^{\infty}-f_s(\mathbf{Q}_b)]}, \tag{39}$$

where $h_\perp^T=(h_2,-h_1,0)$. Substituting $(g-\xi)=S^T(g'-\xi')S$ into Eq. (39), we find from Eqs. (28) and (37) that

$$\bar{b}=\frac{L_{33}(h'_\perp)^T(\xi'-g')h'_\perp}{\det(\xi'-g')(h')^T(\xi'-g')^{-1}h'} \tag{40}$$

where $h'_\perp=Sh_\perp/\det S$. Then we express $h'_\perp$ in terms of $h'=(S^T)^{-1}h$ as follows:

$$h'_\perp=\begin{bmatrix} h'_2 \\ -h'_1 \\ 0 \end{bmatrix}+\frac{L_{13}}{L_{33}}\begin{bmatrix} 0 \\ h'_3 \\ -h'_2 \end{bmatrix}+\frac{L_{23}}{L_{33}}\begin{bmatrix} -h'_3 \\ 0 \\ h'_1 \end{bmatrix}. \tag{41}$$

IV. DISCUSSION

We have proposed an approximate scheme, which is based upon the Landau–de Gennes formalism, to derive an explicit condition for the anchoring direction. This condition involves not only the surface coupling constants, as in the case of the bare surface free-energy minimization, but also the bulk elastic constants and the temperature. We think that our method could be useful in studies of the temperature-driven anchoring transitions. It has the advantage that its self-consistency can always be checked *a posteriori*. To estimate how strongly $\mathbf{Q}(z)$ deviates from $\mathbf{Q}_b$, one simply determines $\mathbf{Q}(0)$ from Eq. (26). If the difference $\mathbf{Q}(0)-\mathbf{Q}_b$ is large compared to Q_b, one can suspect a disordering effect of the substrate on liquid-crystal molecules. In such a case, the expansion of the free energy around $\mathbf{Q}_b$ should not be truncated after the second-order terms. This means that some interesting phenomena involving the nematic-isotropic interface, such as wetting [29–32], are beyond the scope of our method. They can be studied, for instance, by solving the full Landau–de Gennes model or by using the interface Hamiltonian approach [33].

We note that our expression for the equilibrium free energy [see Eq. (36)] can be treated as a generalization of the result obtained in a simplified manner by Teixeira, Sluckin, and Sullivan [30] in the case of the homeotropic anchoring. It follows from Eq. (36) that information about the anchoring strength can be extracted from the asymptotic analysis of the free energy for $l\to\infty$. This approach has the advantage that to define the geometrical measure of the anchoring strength $\bar{b}$ it is not necessary to refer to any dividing surface. In principle, the definition of the anchoring strength, which is based upon the asymptotic form of the free energy for large l and for infinitesimal deviations from the anchoring direction, could be applied without a reference to any particular model of the interface. However, at present we are not certain whether the asymptotic form given by Eq. (36) is generic. Therefore, it would be interesting to study this problem using both the Landau–de Gennes formalism, without any additional approximations, and a microscopic description of the liquid crystal.

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APPENDIX

We want to find $\xi' = (S^{-1})^T \xi S^{-1} = S_2^{-1} S_3 \xi S_3^T S_2^{-1}$, where ξ is diagonal and $\xi_{33}=0$. Since ξ acts in a two-dimensional subspace, S_1 has the same effect on ξ as the identity transformation. Using the definitions of S and Λ [see Eqs. (16) and (17)], we find that

$$S_3^T \begin{bmatrix} M & 0 \\ 0 & 0 \end{bmatrix} S_3 = \xi^2 , \tag{A1}$$

where the (2×2) matrix M is given by

$$M = \begin{bmatrix} (L_{11} - L_{13}^2/L_{33})/a_{11} & (L_{12} - L_{13}L_{23}/L_{33})/\sqrt{a_{11}a_{22}} \\ (L_{12} - L_{13}L_{23}/L_{33})/\sqrt{a_{11}a_{22}} & (L_{22} - L_{23}^2/L_{33})/a_{22} \end{bmatrix} . \tag{A2}$$

To find $S_3 \xi S_3^T$, we calculate the square root of M, which is a symmetric and positive definite matrix, and find that

$$\sqrt{M} = (\mathrm{Tr}M + 2\sqrt{\det M}\,)^{-1/2} \begin{bmatrix} M_{11} + \sqrt{\det M} & M_{12} \\ M_{12} & M_{22} + \sqrt{\det M} \end{bmatrix} , \tag{A3}$$

where $\det M = (\det L)/(a_{11}a_{22}L_{33})$ and $\det L = \frac{4}{9} L_1 (2L_1 + L_2)(3L_1 + 2L_2)$. Finally,

$$\xi' = S_2^{-1} \begin{bmatrix} \sqrt{M} & 0 \\ 0 & 0 \end{bmatrix} S_2^{-1} , \tag{A4}$$

which gives

$$\xi'_{11} = \frac{1}{\sqrt{D_2}} \left[L_{11} - \frac{L_{13}^2}{L_{33}} + \left[\frac{a_{11}\det L}{a_{22}L_{33}} \right]^{1/2} \right] , \tag{A5}$$

$$\xi'_{22} = \frac{1}{\sqrt{D_2}} \left[L_{22} - \frac{L_{23}^2}{L_{33}} + \left[\frac{a_{22}\det L}{a_{11}L_{33}} \right]^{1/2} \right] , \tag{A6}$$

$$\xi'_{12} = \frac{1}{\sqrt{D_2}} \left[L_{12} - \frac{L_{13}L_{23}}{L_{33}} \right] , \tag{A7}$$

where

$$D_2 = \frac{L_{11} - L_{13}^2/L_{33}}{a_{11}} + \frac{L_{22} - L_{23}^2/L_{33}}{a_{22}} + 2 \left[\frac{\det L}{a_{11}a_{22}L_{33}} \right]^{1/2} , \tag{A8}$$

and the remaining components of ξ' are equal to zero.

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