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Anchoring of a nematic liquid crystal on an anisotropic substrate†

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A nematic liquid crystal in contact with a flat solid substrate is studied by means of a mesoscopic Landau–de Gennes theory. It is assumed that the substrate is anisotropic, i.e. the directions $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ in the surface of the substrate are not equivalent, and the only symmetry is the mirror symmetry $\hat{\mathbf{y}} \mapsto -\hat{\mathbf{y}}$. Assuming the simplest form of the bare surface free energy, where only the linear terms in the nematic order parameter are taken into account, we study anchoring directions induced by the interaction of the liquid crystal with the substrate. A phase diagram in terms of the surface fields and the temperature is obtained. Depending on the values of the surface fields we find four types of anchoring: the symmetric planar anchoring, with the director along $\hat{\mathbf{x}}$, the symmetric tilted anchoring, with the director in the xz plane, the antisymmetric planar anchoring, with the director along $\hat{\mathbf{y}}$, and the asymmetric tilted anchoring, with the director tilted with respect to all three axes.

1. Introduction

Orientation of liquid crystal molecules by interfaces is known as anchoring [1, 2]. The presence of a surface breaks both the translational and the rotational symmetry of a system. In the interfacial region, the order parameters differ from the bulk values. When the distance from the surface is larger than the thickness of the interface, the order parameters assume their bulk values and the average orientation of molecules, the director, is fixed by the surface, provided there are no other competing surfaces or fields. The orientation of the director chosen by the surface depends on the details of both the liquid–substrate and the liquid–liquid interactions. Therefore, various types of anchoring can be obtained [2, 3]. The symmetry of the substrate is also an important factor in studies of anchoring. This tells us whether to expect a monostable, a multistable or a degenerate anchoring. These terms refer to the number of anchoring directions corresponding to the same liquid crystal–substrate surface free energy. For instance, in the case of an isotropic substrate only monostable or degenerate anchorings are possible, where the former is known as homeotropic anchoring, and the latter can be either planar or conical anchoring.

A multistable anchoring is possible when the substrate is anisotropic. This case is particularly interesting from the point of view of practical applications in electro-optical devices. An example of an anisotropic substrate is a SiO_x film evaporated under oblique incidence [4–6]. The symmetry group of this substrate contains two elements: the identity and the reflection in the plane of incidence. Anchoring induced by the SiO_x film depends on the angle of incidence ε measured with respect to the surface normal. In some region of the incidence angle, a bistable anchoring is possible. This case is known as asymmetric tilted anchoring, which means that the director is neither in the plane of incidence nor perpendicular to it. The domains corresponding to the two possible orientations of the director have been observed by Jérôme and Pierański [7] in nematic droplets on SiO films. They also observed symmetric tilted anchoring (in the plane of incidence), for $\varepsilon > 75°$, and antisymmetric planar anchoring (normal to the plane of incidence), for intermediate incidence angles. All configurations compatible with the symmetry of the substrate are shown schematically in figure 1. The possibility of twofold degeneracy in molecular orientation has been suggested for bistable switching [8, 9]. Jägemalm *et al.* [10] have studied the effect of a field-induced reorientation of nematic liquid crystals on SiO_x surfaces both experimentally and theoretically. Faetti *et al.* [11] have measured the azimuthal anchoring energy of a nematic liquid crystal on a SiO substrate close to the nematic–isotropic transition temperature.

Another example of an anisotropic substrate studied experimentally is the mica surface. It has been observed that adsorption of non-mesogenic molecules, such as water or ethylene glycol, on the mica surface can induce anchoring transitions in a nematic liquid crystal in contact with the substrate [12–15]. The effect of adsorption

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†This paper is dedicated to Professor Jan Stecki on the occasion of his retirement.

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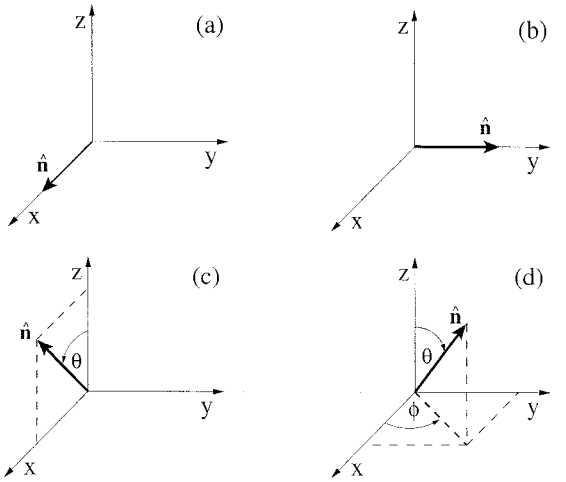

Figure 1. Schematic picture of all types of anchoring discussed in the text. The xz plane is the mirror symmetry plane. θ and ϕ are the polar and the azimuthal angles, respectively. (*a*) Symmetric planar anchoring, (*b*) antisymmetric planar anchoring (the orientations $\hat{\mathbf{n}}$ and $-\hat{\mathbf{n}}$ are equivalent), (*c*) symmetric tilted anchoring, and (*d*) asymmetric tilted anchoring (the mirror image of $\hat{\mathbf{n}}$ with respect to the xz plane corresponds to the same free energy).

of non-mesogenic molecules on anchoring transitions has also been studied theoretically by means of a microscopic theory [16]. Anchoring transitions can also occur as the result of a conformation change of the aligning agents, an effect which was demonstrated by Zhu *et al.* [17].

Microtextured substrates are also anisotropic, and they have been studied theoretically by Qian and Sheng [18, 19]. They considered an alternating stripe pattern of planar and homeotropic substrate potentials and showed that it leads to a first order transition between two states with bulk directors orthogonal to each other. These states are called by Qian and Sheng the 'yz state' and the 'x state', where z is normal to the substrate and y is parallel to the stripes. In the terminology used in our paper, they correspond to symmetric tilted anchoring and antisymmetric planar anchoring, respectively.

To study anchoring one usually considers the surface free energy γ of the nematic liquid crystal-substrate interface as a function of the bulk nematic director, the orientation of which is defined by the polar angle θ and the azimuthal angle ϕ. Then, $\gamma(\theta, \phi)$ can be expanded in spherical harmonics [2]

$$\gamma(\theta, \phi) = \sum_{l,m} A_l^m Y_l^m(\theta, \phi) \qquad (1)$$

where the coefficients $A_l^m \neq 0$ only if the corresponding spherical harmonics Y_l^m are compatible with the symmetry of the substrate. The anchoring direction corresponds to the global minimum of γ. Whether there is one minimum, a finite number or a continuous set of minima of the same depth, depends on the symmetry of the substrate and the values of the expansion coefficients. Thus, truncating expansion (1) at some low l one can obtain possible anchoring directions in terms of the coefficients A_l^m. For the SiO substrate this was done in [7]. However, this is a purely phenomenological approach as it does not relate the observed anchoring directions to the parameters characterizing the system.

In this paper, we study a nematic liquid crystal in contact with an anisotropic substrate of the same symmetry as an obliquely evaporated SiO film. To do this we use the Landau–de Gennes theory [1, 20, 21], which is also a phenomenological theory but formulated at a mesoscopic level, and the parameters appearing in the Landau–de Gennes free energy functional can, in principle, be derived from a microscopic model. Moreover, this approach does not require any assumptions concerning the expansion of γ in spherical harmonics and possibility of truncation of the expansion at low l. We note, however, a recent paper by Fournier and Galatola [22], in which Gaussian fluctuations of the director field in the interfacial region have been taken into account. The authors argue that the expansion of a renormalized surface potential can be truncated at low order. The expansion in question is not in spherical harmonics, but a double Fourier expansion in θ and ϕ.

In the Landau–de Gennes theory, the symmetry of the substrate is taken into account in the 'bare' surface free energy f_s, which mimics the interaction of the liquid crystal molecules with the substrate. We assume the simplest form of f_s compatible with the symmetry of the substrate, i.e. only linear couplings with the surface order parameter are considered. We calculate $\gamma(\theta, \phi)$ solving numerically the set of five non-linear Euler–Lagrange equations with the constraint of a fixed director in the bulk.

This paper is organized as follows. In § 2, we first recall the Landau–de Gennes theory of non-uniform nematic liquid crystals, and then study the phase diagram for a few specific cases. The conclusions are presented in § 3.

2. The model

We consider a nematic liquid crystal in contact with a flat solid substrate. The z axis of the coordinate system is oriented normal to the surface of the substrate. Both the liquid–liquid and the liquid–substrate interactions are described in terms of a continuum theory, in which the only relevant variable is the orientational order parameter $\mathbf{Q}(\mathbf{r})$, a second rank, symmetric and traceless tensor. Thus, in general, $\mathbf{Q}$ has five independent components. Here we neglect fluctuations and assume that $\mathbf{Q}$ depends only on z. The free energy density is given

by $f = f_G(d\mathbf{Q}/dz) + f_L(\mathbf{Q})$, where [20]

$$f_L(\mathbf{Q}) = \frac{2}{3}t \operatorname{Tr} \mathbf{Q}^2 - \frac{8}{3} \operatorname{Tr} \mathbf{Q}^3 + \frac{4}{9}(\operatorname{Tr} \mathbf{Q}^2)^2 \qquad (2)$$

is a Landau free energy of a homogeneous system, and

$$f_G = \frac{1}{2}L_1 \operatorname{Tr} \left(\frac{d\mathbf{Q}}{dz}\right)^2 + \frac{1}{2}L_2\hat{\mathbf{z}} \left(\frac{d\mathbf{Q}}{dz}\right)^2 \hat{\mathbf{z}} \qquad (3)$$

is the contribution to the free energy due to inhomogeneities ($\hat{\mathbf{z}}$ is a unit vector along the z axis). t is assumed to be a linear function of the temperature, whereas the elastic constants L_1 and L_2 are considered to be temperature independent. As independent variables, we choose q, p, Q_{xy}, Q_{xz}, and Q_{yz}, where $Q_{xx} = -1/2\, q + p$, $Q_{yy} = -1/2\, q - p$, and $Q_{zz} = q$. They satisfy the condition $\operatorname{Tr} \mathbf{Q} = 0$ and have a clear physical interpretation. The parameter $q \propto \langle P_2(\cos\theta_m)\rangle$ measures the alignment of molecules with respect to the z axis, and $p \propto \langle \sin^2\theta_m \cos 2\phi_m\rangle$ measures the biaxiality of the system in the xy plane, where the angles θ_m and ϕ_m define the orientation of the molecular long axis. If the director is tilted with respect to the z axis then some of the off-diagonal components, or all of them, do not vanish. If only $q \neq 0$ then the system is uniaxial with respect to the z axis. One finds that

$$\operatorname{Tr} \mathbf{Q}^2 = \frac{3}{2}q^2 + 2(p^2 + Q_{xy}^2 + Q_{xz}^2 + Q_{yz}^2) \qquad (4)$$

$$\operatorname{Tr} \mathbf{Q}^3 = 3\left[\frac{1}{4}q^3 - qp^2 - qQ_{xy}^2 + \left(\frac{1}{2}q + p\right)Q_{xz}^2 + \left(\frac{1}{2}q - p\right)Q_{yz}^2 + 2Q_{xy}Q_{xz}Q_{yz}\right]. \qquad (5)$$

For this choice of variables, the N–I transition is at $t = 1$, and at $t = 0$ the isotropic phase becomes unstable. It is also convenient to introduce a dimensionless z to have

$$f_G = \frac{1}{2}L_q\left(\frac{dq}{dz}\right)^2 + \frac{1}{2}L_p\left[\left(\frac{dp}{dz}\right)^2 + \left(\frac{dQ_{xy}}{dz}\right)^2\right] + \frac{1}{2}L_v\left[\left(\frac{dQ_{xz}}{dz}\right)^2 + \left(\frac{dQ_{yz}}{dz}\right)^2\right] \qquad (6)$$

where $L_q = 1$, $L_p = 2L_1/(3/2\, L_1 + L_2)$, and $L_v = (2L_1 + L_2)/(3/2\, L_1 + L_2)$.

The surface free energy functional for a semi-infinite system is given by

$$F[\mathbf{Q}] = \int_0^\infty [f(d\mathbf{Q}/dz, \mathbf{Q}) - f_b]\, dz + f_s[\mathbf{Q}(0)] \qquad (7)$$

where f_b is the free energy density in the bulk, and f_s is the surface contribution to the total free energy. It is assumed that f_s depends on $\mathbf{Q}(z = 0)$, the order parameter at the surface of the substrate. The form of f_s must be compatible with the symmetry of the substrate. Here, we restrict our considerations of f_s only to terms linear in $\mathbf{Q}$. Then, in the most general form, f_s is given by

$$f_s = -\operatorname{Tr}(\mathbf{h}\ \mathbf{Q}) \qquad (8)$$

where the surface field tensor $\mathbf{h}$ is also symmetric and traceless. The molecular origin of equation (8) is the term $\int dz d\omega V(z, \omega)\rho(z, \omega)$ in the free energy functional, where $V(z, \omega)$ denotes the potential energy of interaction between the liquid crystal molecules and the substrate, and $\rho(z, \omega)$ denotes the one-particle distribution function. Both V and ρ depend on z and the angular variable ω. For linear molecules, V can be expanded in spherical harmonics. Truncation of the expansion at the lowest order compatible with the symmetry of the molecules ($l = 2$) leads to equation (8). In the isotropic case, $h_{xx} = h_{yy} = -1/2\, h_{zz}$, and the remaining components of $\mathbf{h}$ vanish; then, $f_s = -3/2\, h_{zz}Q_{zz}$. Next, let us consider the case of broken rotational symmetry in the xy plane. That is, we assume that a particular direction in the xy plane has been chosen by some physical process, and the x axis is oriented along this direction; thus, $h_{xy} = 0$. In general, the remaining off-diagonal components do not vanish. Assuming that the substrate has the symmetry $y \mapsto -y$ we also have $h_{yz} = 0$. Then, we can express the tensor $\mathbf{h}$ as follows

$$\mathbf{h} = h_1\left(\frac{1}{3}\mathbf{I} - \hat{\mathbf{y}}\hat{\mathbf{y}}\right) + h_2(\hat{\mathbf{z}}\hat{\mathbf{z}} - \hat{\mathbf{x}}\hat{\mathbf{x}}) + h_3(\hat{\mathbf{x}}\hat{\mathbf{z}} + \hat{\mathbf{z}}\hat{\mathbf{x}}) \qquad (9)$$

where $\mathbf{I}$ denotes the unit tensor, which gives

$$f_s = h_1Q_{yy} + h_2(Q_{xx} - Q_{zz}) - 2h_3Q_{xz} = -\left(\frac{1}{2}h_1 + \frac{3}{2}h_2\right)q - (h_1 - h_2)p - 2h_3Q_{xz}. \qquad (10)$$

The case of an isotropic substrate corresponds to $h_1 - h_2 = h_3 = 0$. Alternatively, we can express $\mathbf{h}$ in the diagonal form

$$\mathbf{h} = h_1\left(\frac{1}{3}\mathbf{I} - \hat{\mathbf{y}}\hat{\mathbf{y}}\right) + h(\hat{\mathbf{k}}\hat{\mathbf{k}} - \hat{\mathbf{l}}\hat{\mathbf{l}}) \qquad (11)$$

where $\hat{\mathbf{k}} = \sin\alpha\hat{\mathbf{x}} + \cos\alpha\hat{\mathbf{z}}$ and $\hat{\mathbf{l}} = \cos\alpha\hat{\mathbf{x}} - \sin\alpha\hat{\mathbf{z}}$, hence $h_2 = h\cos 2\alpha$ and $h_3 = h\sin 2\alpha$.

It is instructive to find first the minima of the bare surface free energy f_s, for $\mathbf{Q}$ in the uniaxial approximation

$$\mathbf{Q} = Q_b\left(\frac{3}{2}\hat{\mathbf{n}}\hat{\mathbf{n}} - \frac{1}{2}\mathbf{I}\right) \qquad (12)$$

where Q_b denotes the bulk value of the main order parameter, and $\hat{\mathbf{n}} = \hat{\mathbf{n}}(\theta, \phi)$ is the bulk director. As usual, θ is measured from the z axis, and ϕ is measured from

the x axis. Then, f_s as a function of θ and ϕ is given by

$$f_s = \frac{3}{2}Q_b\{h_1 \sin^2\theta \sin^2\phi - h[\cos 2\alpha(\cos^2\theta - \sin^2\theta\cos^2\phi) + \sin 2\alpha \sin 2\theta \cos\phi]\} \quad (13)$$

where we have neglected the constant term. There are two possible minima of f_s: at $\theta = \phi = \pi/2$, corresponding to antisymmetric planar anchoring, and at $\phi = 0$, $\theta = \alpha$, for $h > 0$, or $\phi = 0$, $\theta = \alpha + \pi/2$, for $h < 0$, both corresponding to symmetric tilted anchoring. The transition between the two anchorings occurs when $|h| + h_1 = 0$. For $h_1 > 0$, only the symmetric tilted anchoring minimizes f_s. We shall see, however, that the true phase diagram obtained from minimization of $F[\mathbf{Q}]$ is much richer than that obtained on the basis of the bare surface free energy.

To find the equilibrium orientation of $\hat{\mathbf{n}}$ we proceed as follows [21]. First, we solve the Euler–Lagrange equations for the five independent components of $\mathbf{Q}$. The bulk director orientation, defined by θ and ϕ, is fixed at $z = l$ (this l should not be confused with the index of spherical harmonics) to provide the boundary condition for $\mathbf{Q}$ via equation (12). This is equivalent to placing a strongly anchoring wall a distance l from the substrate [23, 21]. The distance l should be large compared with the nematic correlation length, as only then can approximation (12) be used. The local director $\hat{\mathbf{n}}(z)$, for $0 \leqslant z \leqslant l$, can be deduced from $\mathbf{Q}(z)$; however, it is not relevant to our present studies. We define the surface free energy as follows: $\gamma(\theta, \phi) = F[\mathbf{Q}^{eq}]$, where $\mathbf{Q}^{eq}$ satisfies the Euler–Lagrange equations with the boundary conditions at $z = l$ specified above, and the integration in equation (7) is over $0 \leqslant z \leqslant l$. The anchoring direction is found by minimization of the function $\gamma(\theta, \phi)$. Note that γ depends also on l chosen to specify the boundary condition for $\mathbf{Q}$. In other words, it depends on the choice of the Gibbs dividing surface in the sense of Yokoyama [23]. Since in this work we are interested only in the anchoring directions, and not the anchoring energy [23, 24], this dependence is not so important, however, provided that l is placed outside the interfacial region. Then, θ_{min} and ϕ_{min} corresponding to the minimum of γ at the given l converge quickly to their limits at $l = \infty$. In practice, it is sufficient to take l of the order of a few correlation lengths. Since the orientations $\hat{\mathbf{n}}$ and $-\hat{\mathbf{n}}$ are physically equivalent, and because of the symmetry $\hat{\mathbf{y}} \mapsto -\hat{\mathbf{y}}$, we have

$$\gamma(\theta, \phi) = \gamma(\pi - \theta, \pi + \phi) = \gamma(\theta, -\phi) = \gamma(\pi - \theta, \pi - \phi). \quad (14)$$

From equation (14) one finds that both $\partial\gamma/\partial\theta$ and $\partial\gamma/\partial\phi$ vanish at $\theta = \phi = \pi/2$, and $\partial\gamma/\partial\phi = 0$ at $\phi = 0$.

In this paper, we do not explore the whole three-dimensional space of surface fields. Instead, we concentrate on the following three cases: (1) $h_2 = 0$, (2) $h_1 = -h_2$, and (3) $h_3 = 0$. In case (1), $f_s = h_1 Q_{yy} - 2h_3 Q_{xz}$, whereas in case (2), $f_s = -2h_1 Q_{xx} - 2h_3 Q_{xz}$.

Let us first consider case (1) with the additional assumption that $h_3 = 0$. For $h_1 > 0$, a negative Q_{yy} is favoured by f_s, which means $\hat{\mathbf{n}}$ in the xz plane. It is also clear from equation (13) that f_s does not favour any particular orientation of $\hat{\mathbf{n}}$ in the xz plane. However, γ does depend on $\hat{\mathbf{n}}$. To show this we compare γ for the homeotropic and for the planar director orientations, using the uniaxial approximation for $\mathbf{Q}$. Then, the equilibrium surface free energy is given by

$$\gamma = \sqrt{2M}\int_{Q_b}^{Q(0)} [f_L(Q) - f_b]^{1/2}\,dQ - \frac{1}{2}h_1 Q(0) \quad (15)$$

where $Q(0)$ is the surface value of the main order parameter satisfying the boundary condition: $\sqrt{2M}[f_L(Q(0)) - f_b]^{1/2} = 1/2\, h_1$. The constant $M = 1$ in the homeotropic case, and $M = (3/2\, L_1 + 1/4\, L_2)/(3/2\, L_1 + L_2)$ in the parallel case. Note that the ratio of the Frank elastic constants obtained from the Landau–de Gennes theory is $K_1/K_2 = K_3/K_2 = 1 + 1/2\, L_2/L_1$, thus $L_2 \sim 3L_1$ is in the experimental range. It is easy to show that γ is an increasing function of M, which means that for $L_2 > 0$ the parallel orientation is stable. However, this conclusion is valid only if a local biaxiality can be neglected. Therefore, we have solved numerically the set of Euler–Lagrange equations for the components of $\mathbf{Q}$, using a standard relaxation method [25], to find $\gamma(\theta, \phi = 0)$. In all cases considered in this paper, we assume $L_2/L_1 = 3$. It results from equation (10) that for $h_1 > 0$ and $h_2 = 0$, f_s favours positive values of $q(0)$ and $p(0)$. We have found that when h_1 is small then $\hat{\mathbf{n}}$ is along the x axis ($\theta = \pi/2$, $\phi = 0$). We call this case the symmetric planar anchoring. However, for h_1 larger than some critical value h_{1c}, which is a function of t, the director is tilted in the xz plane. This is the symmetric tilted anchoring. Because of the symmetry $\hat{\mathbf{x}} \mapsto -\hat{\mathbf{x}}$, for $h_3 = 0$, γ has two minima of equal depth: at $\theta = \theta_{min}$ and at $\theta = \pi - \theta_{min}$, where $0 < \theta_{min} < \pi/2$. This means that symmetric tilted anchoring is bistable for $h_1 > h_{1c}$ and $h_3 = 0$. The transition between symmetric planar anchoring and symmetric tilted anchoring is continuous and occurs at $h_1 = h_{1c}$ and $h_3 = 0$.

When $h_3 \neq 0$ the symmetry $\hat{\mathbf{x}} \mapsto -\hat{\mathbf{x}}$ is broken, and if $\hat{\mathbf{n}}$ is in the xz plane it is always tilted. For $0 < h_1 < h_{1c}$, the symmetric planar phase becomes symmetric tilted when h_3 is switched on. Therefore, there is no phase transition between the regions $h_1 < h_{1c}$ and $h_1 > h_{1c}$. The

transition occurs only when $h_3 = 0$. In the region $h_1 > h_{1c}$ and $h_3 \neq 0$, one of the two minima of γ becomes deeper than the other. The line $h_3 = 0$, $h_1 > h_{1c}$ is a line of a first order transition. Along this line the tilt angle jumps from θ^+_{min} to $\theta^-_{min} = \pi - \theta^+_{min}$, where $\theta^\pm_{min}$ correspond to the limits $h_3 \mapsto \pm 0$, respectively. In contrast, the tilt angle is a continuous function of h_3 in the region $0 < h_1 < h_{1c}$, and it tends to $\pi/2$ when $h_3 \to 0$. Thus, the first order transition is analogous to the transition between two states of opposite magnetization in ferromagnetic systems at zero magnetic field. Similarly, the symmetric planar–symmetric tilted continuous anchoring transition resembles the paramagnetic–ferromagnetic transition.

For $h_1 < 0$, $h_2 = 0$ and $h_3 \neq 0$, we find a first order transition between the symmetric tilted anchoring and the antisymmetric planar anchoring, where the latter corresponds to $\hat{\mathbf{n}}$ parallel or antiparallel to $\hat{\mathbf{y}}$. The transition occurs because of the competition between the first term in f_s (see equation (10)), which favours $q < 0$ and $p < 0$, i.e. the director along the y axis, and the third term, which favours the director in the xz plane. In figure 2, we present the phase diagram in the (h_1, h_3) plane, for $h_2 = 0$ and $t = 0$, and for the ratio of elastic constants $L_2/L_1 = 3$. The transition line between antisymmetric planar anchoring and symmetric tilted anchoring, found from the minimization of $F[\mathbf{Q}]$, differs only slightly from the line $|h_3| = -h_1$ obtained from the minimization of f_s given by equation (13). This means that the sample is only very weakly distorted. We note, however, that the analysis of $f_s(\theta, \phi)$ alone gives a rather peculiar result that although there is a jump in the director orientation, f_s does not have two minima of equal depth at the transition, as usually expected. Instead, one minimum is replaced by the other, as in a continuous transition. This also shows that expansion (1) may lead to non-physical results when it is truncated at low order. On the other hand, $\gamma(\theta, \phi)$ obtained from the minimization of $F[\mathbf{Q}]$ does not suffer from such a non-physical behaviour. Indeed, it exhibits two minima, although the region of metastability is rather narrow.

It is instructive to consider the anchoring transitions in terms of the tensor $\mathbf{Q}$. For both the symmetric tilted and the antisymmetric planar phases, $Q_{xy} = Q_{yz} = 0$, and $Q_{xz} \neq 0$. Indeed, $Q_{xz} = 0$ satisfies the Euler–Lagrange equations only if $h_3 = 0$. Thus, the transition between these two phases must be first order, since it is not a symmetry breaking transition. Above the critical point at $h_1 = h_{1c}$, $h_3 = 0$, there are two symmetric tilted phases: with $Q_{xz} > 0$, for $h_3 > 0$, and $Q_{xz} < 0$, for $h_3 < 0$, which coexists at $h_3 = 0$. At the critical point, the difference between the symmetric tilted phases disappears, and for $0 < h_1 < h_{1c}$, $Q_{xz} \to 0$ when $h_3 \to 0$.

For $t = 0$, h_{1c} is rather large. When the temperature decreases h_{1c} also decreases, and eventually it reaches $h_1 = 0$. This is shown in figure 3, where the phase diagram is presented in the (t, h_1) plane, for $h_2 = h_3 = 0$. The line of critical points (dashed line) divides the half plane $h_1 > 0$ into two regions. In the lower region, the symmetric planar phase is stable. In the upper region, there are two symmetric tilted phases with $Q_{xz} \neq 0$, corresponding to the limits $h_3 \to \pm 0$, respectively. Along the line $h_1 = 0$ there is a jump in the order parameter p, which changes sign from positive, for $h_1 > 0$ ($\hat{\mathbf{n}}$ in the xz plane) to negative, for $h_1 < 0$ ($\hat{\mathbf{n}}$ along the y axis).

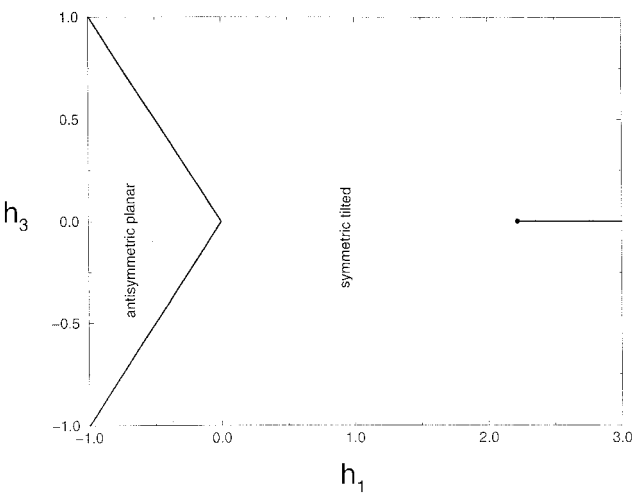

Figure 2. Phase diagram in the (h_1, h_3) plane, for $h_2 = 0$ and $t = 0$. The solid lines show first order phase transitions. The dot marks the critical point $(h_{1c}, 0)$, at which the difference between the two symmetric tilted phases disappears. The line $0 < h_1 < h_{1c}$, $h_3 = 0$ corresponds to symmetric planar anchoring ($\theta = \pi/2$, $\phi = 0$). The transition between the symmetric planar and symmetric tilted anchorings is continuous.

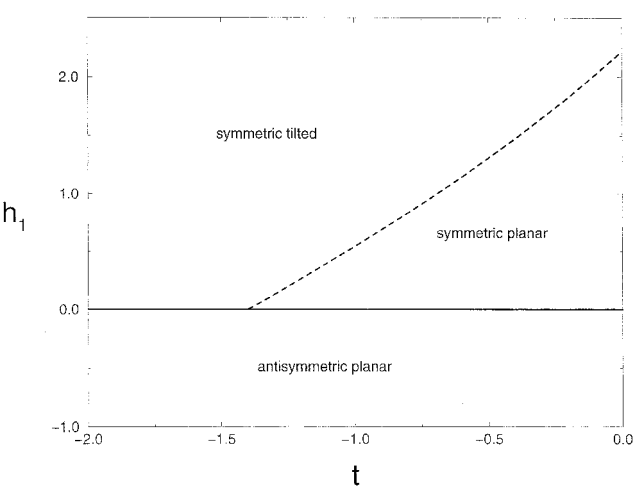

Figure 3. Phase diagram in the (t, h_1) plane, for $h_2 = h_3 = 0$. The symmetric planar–symmetric tilted anchoring transition is continuous (dashed line), whereas the transition to the antisymmetric planar anchoring is first order (solid line).

A richer phase diagram is obtained in case (2) ($h_2 = -h_1$). In figures 4 and 5 we show the phase diagram in the (h_1, h_3) plane, for the temperatures $t = 0$ and $t = -0.5$, respectively. For $h_1 > 0$ and $h_3 \neq 0$, f_s favours $Q_{xx} > 0$ and $Q_{xz} \neq 0$; thus, the only stable phase in this region is the symmetric tilted phase. For $h_1 < h_{1c} < 0$, there is a region of stability of the asymmetric tilted phases, in which none of the off-diagonal components of $\mathbf{Q}$ vanish. Because of the mirror symmetry $\hat{\mathbf{y}} \mapsto -\hat{\mathbf{y}}$, the anchoring in this region is bistable, i.e. $\gamma(\theta, \phi)$ has two minima of equal depth at $(\theta_{\min}, \pm\phi_{\min})$. Thus, the plane (h_1, h_3) is the plane of coexistence of the two asymmetric tilted phases. An additional surface or a bulk field, coupling with Q_{yz}, is required to remove this degeneracy. For $h_{1c} < h_1 < 0$ and h_3 around zero, the antisymmetric planar phase is stable. At some $|h_3| = |h_3(h_1)|$, a transition to the asymmetric tilted region occurs. This is a line of critical points, at which the difference between the asymmetric tilted phases disappears, i.e. Q_{xy} and Q_{yz} vanish at the transition. They also vanish at the asymmetric tilted-symmetric tilted transition, which is also continuous. When the temperature decreases from $t = 0$ (figure 4) to $t = -0.5$ (figure 5), the region of stability of the antisymmetric planar phase shrinks, and h_{1c} moves towards zero.

In figures 6–9, we present the polar angle θ and the azimuthal angle ϕ corresponding to the equilibrium orientation of $\hat{\mathbf{n}}$ as functions of h_3, for the temperature $t = 0$. $\theta(h_3)$ is shown in figures 6 and 7, for $h_1 = -1.25$

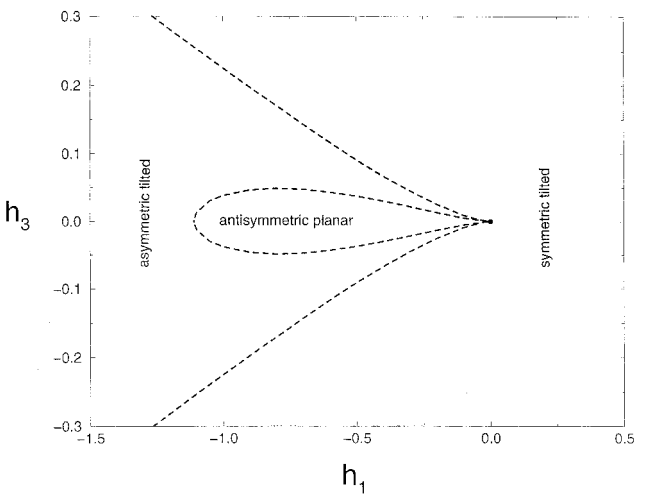

Figure 4. Phase diagram in the (h_1, h_3) plane, for $h_2 = -h_1$ and $t = 0$. The dashed lines show continuous transitions. In the asymmetric tilted region, two asymmetric tilted phases coexist. The difference between these two phases disappears along the lines of continuous transitions to the antisymmetric planar phase or the symmetric tilted phase.

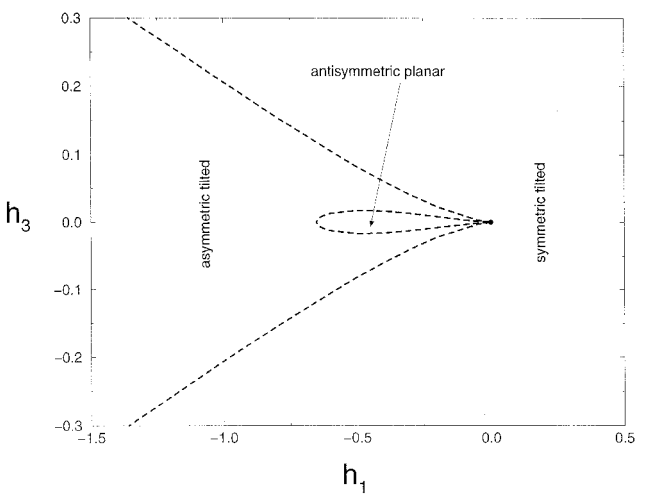

Figure 5. Phase diagram in the (h_1, h_3) plane, for $h_2 = -h_1$ and $t = -0.5$.

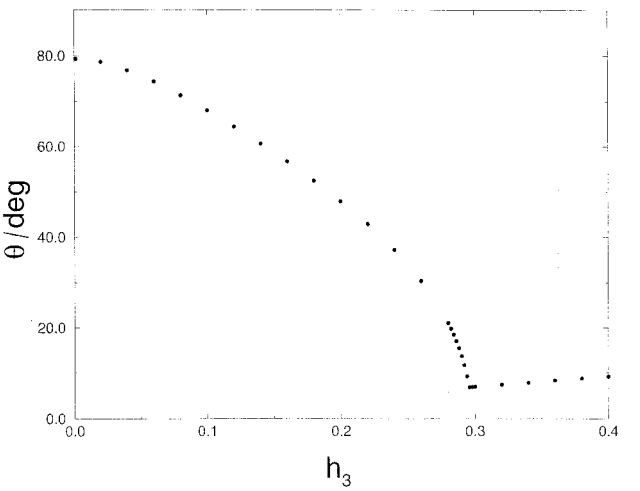

Figure 6. Polar angle θ as a function of h_3, for $h_1 = -h_2 = -1.25$ and $t = 0$.

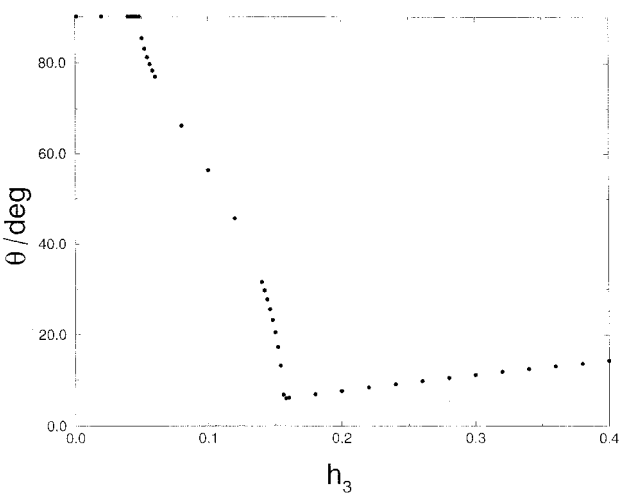

Figure 7. Polar angle θ as a function of h_3, for $h_1 = -h_2 = -0.75$ and $t = 0$.

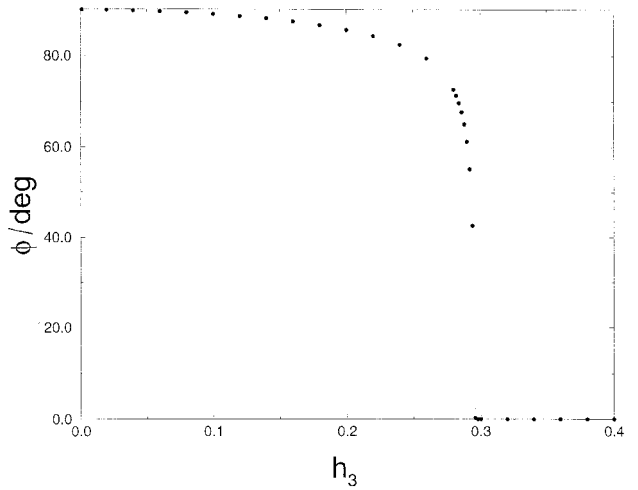

Figure 8. Azimuthal angle ϕ as a function of h_3, for $h_1 = -h_2 = -1.25$ and $t = 0$.

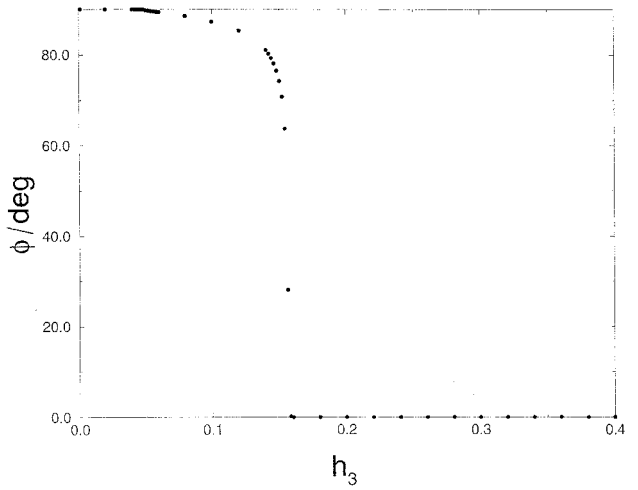

Figure 9. Azimuthal angle ϕ as a function of h_3, for $h_1 = -h_2 = -0.75$ and $t = 0$.

and $h_1 = -0.75$, respectively. In the first case (figure 6), $\theta(h_3)$ does not tend to $\pi/2$ when $h_3 \to 0$. Since $\phi(h_3) \to \pi/2$ when $h_3 \to 0$, the director is tilted in the yz plane at $h_3 = 0$, and there are two possible directions of the tilt. This situation is analogous with the symmetric tilted anchoring (in the xz plane) at $h_3 = 0$, obtained in case (1). The transition to the symmetric tilted phase occurs at a rather small value of θ. After the transition θ is a slowly increasing function of h_3. The angle ϕ decreases continuously from $\pi/2$ at $h_3 = 0$ to zero at the transition to the symmetric tilted phase (figure 8). For $h_1 = -0.75$, both θ and ϕ are equal to $\pi/2$ in the region of antisymmetric planar anchoring. In the region of asymmetric tilted anchoring, they are both decreasing functions of h_3. This is shown in figures 7 and 9, respectively.

Note that if we write the bare surface free energy in the form

$$f_s = -h_{xx}Q_{xx} - h_{yy}Q_{yy} - 2h_{xz}Q_{xz} \qquad (16)$$

where $h_{xx} = -2h_2$, $h_{yy} = -(h_1 + h_2)$ and $h_{xz} = h_3$, then cases (1) and (2) correspond to $h_{xx} = 0$ and $h_{yy} = 0$, respectively. Thus, in figure 2 we have presented the phase diagram in the (h_{yy}, h_{xz}) plane, whereas in figures 4 and 5, the phase diagram is in the (h_{xx}, h_{xz}) plane. For completeness, we have also studied case (3), i.e. $h_3 = 0$. The phase diagram in the (h_{xx}, h_{yy}) plane, for $t = 0$, is presented in figure 10. In this case, both mirror symmetries: $\hat{\mathbf{x}} \mapsto -\hat{\mathbf{x}}$ and $\hat{\mathbf{y}} \mapsto -\hat{\mathbf{y}}$ are present. Therefore, the phase diagram is symmetric with respect to the diagonal $h_{xx} = h_{yy}$. There are two anchoring transitions along the diagonal $h_{xx} = h_{yy}$. For $h_{xx} > 0$, the director jumps from the orientation along the x axis to the orientation along the y axis. For $h_{xx} < 0$, there is a continuous transition between $\hat{\mathbf{n}}$ in the xz plane and $\hat{\mathbf{n}}$ in the yz plane. Along the continuous transition line the orientation of $\hat{\mathbf{n}}$ is homeotropic. This is a phase transition, since in each region of the tilted anchoring either $Q_{yz} = 0$, $Q_{xz} \neq 0$ or $Q_{xz} = 0$, $Q_{yz} \neq 0$. The phase transitions between planar anchoring and tilted anchoring are also continuous. Although the lines of these transitions appear to be straight lines, in fact they are curves (see the inset in figure 10), and the crosses mark their intersections with the lines $h_{xx} = 0$ and $h_{yy} = 0$, respectively. In each region of tilted anchoring, there are two possible directions of the tilt. The application of an additional surface field h_{xz} chooses one of the tilt directions in the xz plane. Then, the region of tilted anchoring in the yz plane becomes

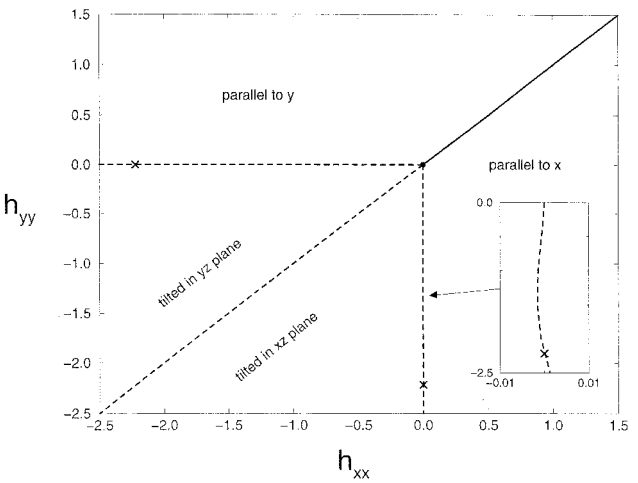

Figure 10. Phase diagram in the (h_{xx}, h_{yy}) plane ($h_3 = 0$), for $t = 0$. The solid line shows a first order transition, and the dashed lines show continuous transitions. The exact shape of the transition line between the planar and the tilted anchorings is shown in the inset. The crosses mark the intersection of the curves with the lines $h_{xx} = 0$ and $h_{yy} = 0$.

the region of asymmetric tilted anchoring, and the region of planar anchoring along the x axis disappears, since for $\hat{\mathbf{n}}$ in the xz plane only a tilted anchoring is possible when $h_{xz} \neq 0$.

3. Conclusions

We have applied the Landau–de Gennes model of the nematic liquid crystal–substrate interface to study anchoring at an anisotropic substrate. To mimic the nematic liquid crystal–substrate interactions we have used the simplest form of the bare surface free energy, in which only the terms linear in the order parameters at the surface are considered. Thus, f_s as a function of the surface director contains spherical harmonics only with $l = 2$. In general, the surface free energy $\gamma(\theta, \phi)$ can also be expanded in spherical harmonics, and the truncation of the expansion at $l = 2$, compatible with the mirror symmetry $\hat{\mathbf{y}} \mapsto -\hat{\mathbf{y}}$, leads to two possible anchorings: symmetric tilted anchoring and antisymmetric planar anchoring. A symmetry breaking transition to the asymmetric tilted anchoring is possible only when higher order terms ($l > 2$) are included in the expansion of $\gamma(\theta, \phi)$. In the framework of the Landau–de Gennes theory, higher order terms are effectively generated even if the expansion of f_s is truncated at $l = 2$. We have shown that in a special case, when the interactions of liquid crystal molecules with the substrate favour $\hat{\mathbf{n}}$ in the yz plane rather than in the xz plane, the transition from symmetric tilted anchoring to asymmetric tilted anchoring can occur. This shows that the description of liquid crystal interfaces in terms of the director field alone is insufficient in some cases, and a more refined analysis of the interfacial structure, which takes into account variations of the order parameters, is necessary.

We have presented phase diagrams in the space of surface fields, which means that for a fixed temperature, different values of these fields correspond to different substrates. This resembles the experimental situation with SiO films, where different types of anchoring are obtained by changing the incidence angle. Comparison of the experimental results with the results obtained in the framework of the Landau–de Gennes theory shows that an increase of the incidence angle has the same effect on the anchoring as an increase of the component $h_3 = h_{xz}$ of the surface field tensor. To find the relation between the surface fields and the experimentally measured angle of incidence, it would be necessary to derive the Landau–de Gennes free energy functional from a microscopic model. Although our results agree qualitatively with experiment in all cases that we have studied, the transition from symmetric tilted anchoring to asymmetric tilted anchoring occurs at a rather small value of the polar angle, whereas experimentally it is around 70° [7]. It is not clear at the moment whether this disagreement is because of the specific choice of the surface fields or because of neglecting higher order terms in f_s. Further exploration of the (h_{xx}, h_{yy}, h_{xz}) space should answer this question.

We note that Qian and Sheng [18, 19] have also studied the Landau–de Gennes model, with a different form of f_s, however. They assume that the substrate is inhomogeneous, and $f_s = GQ_{zz}$, where G is a step function, negative in the homeotropic regions and positive in the regions of planar alignment. Thus, the anisotropy of the substrate is due to an alternating stripe pattern of the homeotropic and planar alignment potentials. From the macroscopic point of view, anchoring on such an inhomogeneous substrate is similar to anchoring on a homogeneous anisotropic substrate considered by us. Thus, the case studied by Qian and Sheng corresponds to the case $h_{xz} = 0$ in equation (16), as far as the symmetry of the substrate is concerned. It is clear from figure 3 that in this case we also obtain a direct first order transition between the symmetric tilted and antisymmetric planar anchorings reported in [18, 19], although it occurs at rather low temperatures. For higher temperatures, the regions of symmetric tilted and antisymmetric planar anchorings are separated by the region of symmetric planar anchoring, not observed by Qian and Sheng.

In the next step, the terms quadratic in $\mathbf{Q}(z = 0)$ should be added to f_s. They take into account the effect of the reduction of interactions between liquid crystal molecules at the surface because of missing nearest neighbours. In the case of isotropic substrates, such an extension leads to the three second order terms: $\mathrm{Tr}\,\mathbf{Q}^2$, $(\hat{\mathbf{z}}\ \mathbf{Q}\ \hat{\mathbf{z}})^2$ and $\hat{\mathbf{z}}\ \mathbf{Q}^2\ \hat{\mathbf{z}}$. In general, there are 15 second order combinations of five independent components of $\mathbf{Q}$. In the case of the $\hat{\mathbf{y}} \mapsto -\hat{\mathbf{y}}$ symmetry, there are nine second order terms compatible with this symmetry. If we choose Q_{xx} and Q_{yy} as independent diagonal components then we have the following invariants: Q_{xx}^2, Q_{yy}^2, Q_{xz}^2, Q_{xy}^2, Q_{yz}^2, $Q_{xx}Q_{yy}$, $Q_{xx}Q_{xz}$, $Q_{yy}Q_{xz}$ and $Q_{xy}Q_{yz}$. Alternatively, we can express f_s in the following invariant form

$$
\begin{aligned}
f_s = &- h_{xx}(\hat{\mathbf{x}}\ \mathbf{Q}\ \hat{\mathbf{x}}) - h_{zz}(\hat{\mathbf{z}}\ \mathbf{Q}\ \hat{\mathbf{z}}) - 2h_{xz}(\hat{\mathbf{x}}\ \mathbf{Q}\ \hat{\mathbf{z}}) \\
&+ \frac{1}{2}\{g^{(0)}\,\mathrm{Tr}\,\mathbf{Q}^2 + g_{xx}^{(2)}(\hat{\mathbf{x}}\ \mathbf{Q}^2\ \hat{\mathbf{x}}) + g_{zz}^{(2)}(\hat{\mathbf{z}}\ \mathbf{Q}^2\ \hat{\mathbf{z}}) \\
&+ 2g_{xz}^{(2)}(\hat{\mathbf{x}}\ \mathbf{Q}^2\ \hat{\mathbf{z}}) + g_{xxxx}^{(4)}(\hat{\mathbf{x}}\ \mathbf{Q}\ \hat{\mathbf{x}})^2 \\
&+ g_{zzzz}^{(4)}(\hat{\mathbf{z}}\ \mathbf{Q}\ \hat{\mathbf{z}})^2 + 2g_{xxzz}^{(4)}(\hat{\mathbf{x}}\ \mathbf{Q}\ \hat{\mathbf{x}})(\hat{\mathbf{z}}\ \mathbf{Q}\ \hat{\mathbf{z}}) \\
&+ 4g_{xxxz}^{(4)}(\hat{\mathbf{x}}\ \mathbf{Q}\ \hat{\mathbf{x}})(\hat{\mathbf{x}}\ \mathbf{Q}\ \hat{\mathbf{z}}) \\
&+ 4g_{zzxz}^{(4)}(\hat{\mathbf{z}}\ \mathbf{Q}\ \hat{\mathbf{z}})(\hat{\mathbf{x}}\ \mathbf{Q}\ \hat{\mathbf{z}})\}. \qquad (17)
\end{aligned}
$$

When the order parameter is approximated by the uniaxial form $\mathbf{Q} = Q(3/2\,\hat{\mathbf{n}}\hat{\mathbf{n}} - 1/2\,\mathbf{I})$, then the $g^{(4)}$ terms

contribute to the spherical harmonics with $l = 4$, whereas the $g^{(2)}$ terms contribute only to the spherical harmonics with $l = 2$. Thus, if Q does not differ too much from Q_b in the interfacial region, then the $g^{(2)}$ terms and the linear terms should have similar effects on the equilibrium orientation of $\hat{\mathbf{n}}$. Stronger modifications of the phase diagram can be expected from the $g^{(4)}$ terms. This requires further studies, however. In future work, we also intend to apply the Landau–de Gennes formalism to the study of wetting on anisotropic substrates.

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