Curvature induced quasi-melting from rough surfaces in nematic liquid crystals

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Curvature induced quasi-melting from rough surfaces in nematic liquid crystals

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Résumé. — Le modèle de Berreman-de Gennes, qui décrit l'ancrage azimuthal d'un nématique orienté par une surface ondulée est rediscuté Quand la période des ondulations est plus courte que la longueur de cohérence nématique-isotrope, le nématique préfère fondre que se courber Ce mécanisme explique la décroissance du paramètre d'ordre observée sur des surfaces rugueuses obtenues par évaporation oblique de SiO.

Abstract. — The Berreman-de Gennes model, describing the azimutal anchoring energy of a nematic material oriented by a grooved surface, is revisited When the groove wave-length is shorter than the nematic-isotropic coherence length, the nematic should decrease locally its order parameter to decrease the too large curvature energy induced by the boundaries. This curvature induced surface quasi-melting could explain recent observations on the order parameter decrease close to oblique SiO evaporated rough surfaces

1. Introduction.

The orientation of nematic liquid crystals (NLC) by solid interfaces is a problem of practical and conceptual interest Many kinds of interactions can be invoked to explain these orientating phenomena, including van der Waals and steric forces [1] Rubbed or grooved surfaces are known [1] to orientate NLC One of the most simple and popular model is the one proposed long time ago by Berreman [2] and de Gennes [3] to explain this quasi-geometrical orientation by a grooved surface In this model, (BG), the anisotropy of the surface interaction is directly related to the elastic energy of the curvature distortion geometrically induced by the surface on the NLC. This « valley » effect was invoked to explain the orientations induced by SiO obliquely evaporated glass surfaces [4-6]. An important feature of the BG model is that the order parameter modulus S of the NLC is assumed uniform , only the mean orientation $\mathbf{n}$ of the NLC (the « director » $\mathbf{n}^2 = 1$) varies in space, because of a purely geometrical constraint at the undulating solid boundary. Recently, this constraint was partially released [7], by the introduction of an additional local finite anchoring energy at the interface, but the uniformity of S was not really discussed. It has been shown, however, that the order parameter modulus S can be very weak [8-12] close to a rough solid interface like SiO evaporated glasses. It seems then not too realistic to use the BG model to describe the effect of very short wave-length undulations on the nematic orientation. In this paper we reconcile these points of view by showing that, when the wave-length of surface

undulations becomes comparable to the coherence length ξ of the nematic → isotropic transition, a simple extension of the BG model leads also to a decrease of the surface order parameter and eventually to a total isotropic melting.

2. The general model.

Assume a cylindrically undulated solid surface defined by

$$z = A \sin (qx) \tag{1}$$

where z is the normal to the averaged surface $z = 0$, and the NLC fills the $z > 0$ space. $q = 2\pi/\lambda$ is the wave vector of the undulation, of angular amplitude $Aq \leq 1$, as in the BG model. We also keep from BG the geometrical constraint to maintain the NLC director $\mathbf{n}$ in the (x, z) plane and locally parallel to the interface Calling $\mathbf{N}$ the local normal to the surface, this means

$$\mathbf{N} \cdot \mathbf{n} = 0\,, \quad \text{on the solid surface}\,. \tag{2}$$

The NLC volume free energy density is written as [13]:

$$F = f(S) + (3/4)\, L_1 (\nabla S)^2 + (9/4)\, L_1\, S^2 (\nabla\theta)^2\,, \tag{3}$$

where θ is the $(\mathbf{n}, \mathbf{x})$ angle F is written for simplicity in the one curvature elastic constant approximation In this isotropic situation ($L_2 = 0$, see Ref [13]) there is no direct coupling term between ∇S and $\nabla\theta$. The $f(S)$ uniform part of F has a minimum at $S = S_b$. The $S(x, z)$ and $\theta(x, z)$ must minimize the total free energy G defined as $G = \iiint F\, \mathrm{d}v$, in which the surface energy is assumed to be independent of S and θ.

By taking into account that $F = F(S, \nabla S, \nabla\theta)$, trivial calculations give for the first variation of G

$$\delta G = \delta \iiint_v F\, \mathrm{d}V = \iiint_v \left\{ \frac{\partial F}{\partial S}\, \delta S + \frac{\partial F}{\partial (\nabla S)} \cdot \delta (\nabla S) + \frac{\partial F}{\partial (\nabla\theta)} \cdot \delta (\nabla\theta) \right\} \mathrm{d}V$$

where V is the volume of the nematic sample bounded by the surface Σ. By taking into account that in a reorientational problem the δ operator commute with the ∇-operator, δG can be classically rewritten as

$$\delta G = \iiint_v \left\{ \left[\frac{\partial F}{\partial S} - \nabla \cdot \frac{\partial F}{\partial (\nabla S)} \right] \delta S + \left[- \nabla \cdot \frac{\partial F}{\partial (\nabla\theta)} \right] \delta\theta \right\} \mathrm{d}V + \\ + \oint_\Sigma \mathbf{N} \cdot \left\{ \frac{\partial F}{\partial (\nabla S)}\, \delta S + \frac{\partial F}{\partial (\nabla\theta)}\, \delta\theta \right\} \mathrm{d}\Sigma$$

In the event in which $\mathbf{n}$ is fixed on the surface, $\delta\theta(\Sigma) = 0$, and the surface contribution to δG reduces to

$$\oint_\Sigma \frac{3}{2} L_1 (\mathbf{N} \cdot \nabla S)\, \delta S\, \mathrm{d}\Sigma$$

where equation (3) has been taken into account

In our case in which S is not fixed by the surface, $\delta S(\Sigma)$ is an arbitrary quantity. By imposing $\delta G = 0$ for every continuous functions δS and $\delta\theta$, one deduces

$$\frac{\partial F}{\partial S} - \nabla \cdot \frac{\partial F}{\partial(\nabla S)} = 0$$

$$- \nabla \cdot \frac{\partial F}{\partial(\nabla \theta)} = 0 \tag{3'}$$

for the bulk, and

$$\mathbf{N} \cdot \nabla S = 0 \tag{4}$$

on the surface Equation (4) is the transversality condition Of course in the case in which a « surface » energy f_s imposing some values of S on the surface is present, boundary condition (4) becomes

$$(3/2)\, L_1\, \nabla S \cdot \mathbf{N} + \partial f_s / \partial S = 0\,. \tag{4'}$$

In the BG model, S was implicitly assumed to be uniform and equal on the surface to its bulk equilibrium value S_b whatever may be S_b In our model, S is now a continuous function $S(z)$. We must also remember that S is physically defined by volume averaging over a size $\sim \xi$ defined properly later. In principle, we could assume that the surface would impose a well defined value S_s of $S(0)$, leading to a finite surface normal ∇S to reach the bulk value S_b. In fact, we must chose for S_s a boundary condition which matches the BG one, i.e. $S_s = S_b$, in the limit of weak curvature This condition must be valid for any S_b The only way to fullfill these constraints is to assume that f_s is independent of S. This results in the transversality condition (4)

This condition has also the advantage to demonstrate that curvature alone is able to decrease the surface ordering Our free boundary condition is different from the Sheng one, who postulated [14] an S dependent surface energy. More generally other hypotheses on the S anchoring could have been made. We expect them to give the same general result, since the averaging procedure previously described erases the unphysical details of the $S(z)$ behavior. By substituting equation (3) into equation (3') we obtain the Euler-Lagrange equations

$$\Delta S - [(2/3\, L_1)(\mathrm{d}f/\mathrm{d}S) + 3\, S(\nabla\theta)^2] = 0\,, \tag{5}$$

$$2\, S(\nabla S)\,.\,(\nabla\theta) + S^2\, \Delta\theta = 0\,. \tag{6}$$

These two coupled differential equations are non-linear and need in general a numerical integration

Before trying to solve equations (5) and (6), we can directly understand what happens close to a rough surface, from the simple inspection of the free energy density F given by (3). At constant S, a surface induced curvature $q\theta_0$ creates an increase of F of the order of $L_1\, S^2\, q^2\, \theta_0^2$. On the contrary a surface melting, releasing the undulation, increases F by, approximatively, $L_1\, S^2\, \xi^{-2}$, by definition of the usual coherent length ξ [3] (redefined properly later) One immediately sees that, for $q^2\, \theta_0^2\, \xi^2 > 1$ i.e. for a « rough » surface, it costs less energy to melt than to undulate the nematic orientation. Let us try to estimate this « melting » effect, in the two possible limits, the weak and the strong roughness cases.

2 1 THE WEAK ROUGHNESS CASE ($q\theta_0 \xi < 1$). — In this case, one expects S not to vary too much, i.e. $s = S - S_b < 1$. In this limit equation (6) always gives

$$\Delta\theta = 0 , \tag{7}$$

since $s \ll S$. This gives the solution

$$\theta(x, z) = Aq \cos (qx) \exp(- qz) , \tag{8}$$

where Aq is the maximum surface tilt θ_0 previously defined, as in the standard BG model. The linearized equation (5) is now written as

$$\Delta s - [\xi^{-2} + 3(\nabla\theta)^2] s = 3(\nabla\theta)^2 S_b \tag{9}$$

where ξ is defined as usual, by

$$\xi^{-2} = (2/3 L_1)(d^2 f/dS^2)_{S_b} , \tag{10}$$

from the known curvature of $f(S)$ around $S = S_b$.

The θ curvature, which has been propagated in the bulk up to the distance $2\pi/q$, now gives two effects. First it decreases the melting temperature, since from equation (10), the term $3(\nabla\theta)^2$ in the l.h.s. of (9) can be associated with a decrease $9 L_1(\nabla\theta)^2/2 a$ of T_c (a is the usual first coefficient of the Landau expansion of the free energy of the nematic phase [13]) In addition, $(\nabla\theta)^2$ appears in the r.h s. of equation (9) as the source of spatial variation for S. From (8), $(\nabla\theta)^2$ is :

$$(\nabla\theta)^2 = A^2 q^4 \exp(- 2 qz) = (1/3 \xi_0^2) \exp(- 2 qz) \tag{11}$$

where $\xi_0^{-2} = 3 A^2 q^4$ Note that $(\nabla\theta)^2$ is now independent of x It will then induce (from Eq. (9) an order parameter variation s depending only on z Equation (9), by taking into account equation (11), is written as

$$d^2 s/dz^2 - [\xi^{-2} + \xi_0^{-2} \exp(- 2 qz)] s = \xi_0^{-2} \exp(- 2 qz) S_b . \tag{12}$$

Furthermore, since $s = s(z)$ only, boundary condition (3) implies

$$ds/dz = 0 , \quad \text{at} \quad z = 0 . \tag{13}$$

In our weak roughness case, $\xi_0 > \xi$. In this limit equation (12) becomes

$$d^2 s/dz^2 - \xi^{-2} s = \xi_0^{-2} \exp(- 2 qz) S_b , \tag{14}$$

whose solution, satisfying boundary condition (13) is

$$s(z) = \{(\xi/\xi_0)^2/[(2 q\xi)^2 - 1]\} S_b[\exp(- 2 qz) - 2 q\xi \exp(- z/\xi)] . \tag{15}$$

This order parameter variation extends on the thickness $z = 2\pi/q$ where the angular distortion appears. s is of order $(\xi/\xi_0)^2$, i e negligible, as expected. Whence S is practically uniform and the purely elastic BG model is valid.

2 2 THE STRONG ROUGHNESS CASE ($q\theta_0 \xi \sim 1$) — We are now interested to estimate what happens in the « large » roughness limit $Aq^2 \xi \sim 1$ With our assumption of weak surface tilt

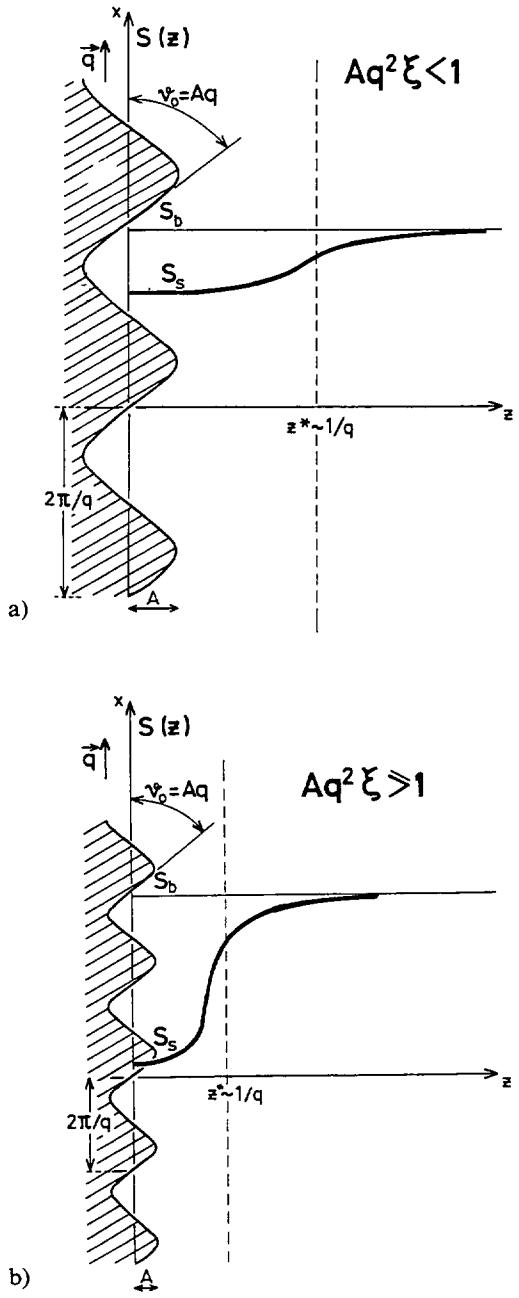

Fig 1. — Sketch of the order parameter dependence for a) The weak roughness case ($Aq^2\xi < 1$) b) Strong roughness case ($Aq^2\xi > 1$). The maximum surface angle $\theta_0 = Aq$ is the same for the two cases. The only difference is the wave number q In both cases, there exists a surface layer $z < z^* < q^{-1}$ where the curvature and the S variation are concentrated

$\theta_0 = Aq \leqslant 1$, this implies $q\xi \geqslant 1$ We now expect S to become weak at the surface, and to increase toward S_b far from the surface. To solve (5) and (6), the standard procedure would be to decompose S and θ in Fourier components nq ($n = 0, 1, .$) along x At first sight, these

components are coupled, without any apparent cut-off for large n. This is due to the chosen free energy density (3), which is valid only in the $q\xi < 1$ limit, inadequate for our purpose Higher order missing gradient terms would force this cut-off It is a generally accepted, although an incorrect procedure, to guess the shape of the boundary profile by keeping the form (3) In this approximation, (3) can just describe the coupling of the lowest order Fourier components $S(q = 0)$ and $\theta(q)$, assuming all other components to be zero Physically, this is equivalent to work only with an x-averaged S order parameter. S is now a function of z only In equation (6), the first term $(\nabla S) . (\nabla\theta)$ remains to zero close the surface, since the only component of ∇S is zero, from equation (4). $\theta(x, z)$ remains then harmonic ($\Delta\theta = 0$). As we expect S to be small close to the boundary, we rewrite equation (5) as

$$d^2S/dz^2 - [\xi^{-2} + \xi_0^{-2} \exp(-2qz)]\, S = 0 \tag{16}$$

There exists now a boundary layer of thickness z^*, defined by

$$\xi^{-2} = \xi_0^{-2} \exp(-2qz^*), \quad \text{i.e.} \quad z^* = (1/q) \ln(\xi/\xi_0). \tag{17}$$

For $z > z^*$ equation (5) is written as

$$d^2s/dz^2 - \xi^{-2} s = 0, \quad \text{where s can become as large as } S_b. \tag{18}$$

Equation (18) represents an exponential relaxation of S, from some low value S^* close to the surface, toward S_b imposed by the thermodynamics in the bulk. For $z \ll z^*$, on the other hand, equation (16) becomes

$$d^2S/dz^2 - \xi_0^{-2} S = 0, \tag{19}$$

since the curvature is the dominant contribution In this boundary, the solution is

$$S(z) = S_s \cosh(z/\xi_0), \tag{20}$$

where S_s is the unknown weak surface order parameter To fix S_s, we must match this solution to the one of the curvature free region $z > z^*$ We now use equation (5), where we neglect the curvature term $3(\nabla\theta)^2$ An obvious integration gives

$$[(dS/dz)^2]_{z=z^*} = (2/3\, L_1)[(f(S^*) - f(S_b))]. \tag{21}$$

In practice, in the limit of small S^* the r.h.s is approximately $-(2/3\, L_1) f(S_b) \sim + S_b^2 b/\xi^2$. This shows that the slope $(dS/dz)_{z=z^*}$ is the same as that of an exponential decay from $S = 0$ toward $S = S_b$ From equation (21) we find for S_s the estimate

$$S_s = (\xi_0/\xi)\, S_b/\sinh(z^*/\xi_0) \sim S_b/[3\, A^2 q^3 \xi \ln(\xi/\xi_0)]. \tag{22}$$

For large roughness, S_s would tend towards zero Note, of course, that this estimate is itself « rough », as the assumptions made, but the decreases of S_s follows the expected trend. The new result is that the surface melting appears inside a melting boundary layer of thickness $z^* \sim q^{-1}$. The general trend of $S(z)$ is sketched in figure 1

3. Surface energy.

We now calculate the total surface energy, G, as the sum of the energies of the two boundary layers $0 < z < z^*(G_1)$ and $z > z^*(G_2)$

3.1 WEAK ROUGHNESS — For a weakly rough surface ($Aq^2\xi < 1$), using equation (15) in equation (3), we find

$$G_1 = \int_0^{z^*} F \, dz \sim (3/2) A^2 q^3 L_1 S_b^2, \tag{23}$$

for the curvature layer, and

$$G_2 = \int_{z^*}^{\infty} F \, dz \sim 0 \tag{24}$$

for the S-damped transition region G_1 is, obviously, the classical BG elastic energy. The quadratic dependence in S results from our hypothesis that the undulated surface acts only on the director orientation

3 2 STRONG ROUGHNESS. — For a rough surface we find, for $z < z^*$, that $S(z)$ is given by equation (20), in which S_s is given by (22) For $z > z^*$, $S(z)$ is found to be

$$S(z) = S_b - (S_b - S^*) \exp[-(z - z^*)/\xi] \tag{25}$$

where, as follows from matching conditions, $S_b - S^* \sim S_b$ Hence, we have now :

$$G_1 = (3/8)(L_1 S_s^2/\xi_0) \sinh(2 z^*/\xi_0) = (3/4)(L_1 S_b^2/\xi)(1/q\xi) \ln(\xi/\xi_0), \tag{26}$$

if we take equation (22) into account

For large roughness, $G_1 \to 0$ This is normal, since it is the energy of the isotropic phase By using (25), G_2 is then found to be

$$G_2 = (3/8) L_1 (S_b - S^*)^2/\xi = (3/8) L_1 S_b/\xi . \tag{27}$$

G_2 is now independent of the curvature source, since it represents only the surface energy of an isotropic-nematic interface

4. Application to real surfaces.

To apply this model to a real rough surface, we can Fourier decompose the surface irregularities Each mode of wave vector $\mathbf{q}$ can be characterized by an amplitude $A(\mathbf{q})$ Let us discuss simply the isotropic case $A(\mathbf{q}) = A(q)$ In this case, one can estimate a melted boundary layer thickness z^* defined by :

$$\xi^{-2} = \frac{1}{2} \sum_q \xi_0^{-2}(q) \exp(-2 qz^*) \tag{28}$$

where $\xi_0^{-2}(q) = 3 A^2(q) q^4$ Each mode adds its curvature contribution to the surface order quasi melting.

For practical cases, S is observed to be nearly zero at the surface, as shown in references [9, 12, 15, 16] and $|\nabla S| \sim S/\xi$ We are now in a situation comparable to that of a nematic-isotropic interface, already discussed [17]. One can then expect the onset of an order electric polarization, proportional to ∇S The electric energy associated with the order electric polarisation is minimum for a tilt angle of the order of the « magic » angle. This gives rise in the nematic orientating surface energy to a new term describing the attraction towards the magic angle cone This term has been used to explain the continuous change of orientation

observed on SiO surfaces, *versus* the surface roughness [18] since, in this case, the amplitude and the period $L/2\ \pi$ of surface irregularities, ~ (1 000/2 π) Å compares with ξ ~ 100-200 Å The observed anisotropy of the alignment on SiO evaporated surfaces is probably as much related to the surface roughness anisotropy as to the « valley » effect of the BG model.

5. Conclusion.

In conclusion, we have resumed the Berreman-de Gennes model which discusses the orientating effect of a grooved surface on a NLC liquid crystal. We have shown that when the surface undulation becomes rapid enough ($Aq^2\xi \sim 1$), a nematic constrained to undulate would better melt Of course, if the real surface were a smooth cylinder, this melting would never occur, since the nematic would just orientate itself along the grooves of the cylinder. In the case of a rough surface, on the other hand, there is no possibility to escape by a uniform rotation the crossed and disordered undulations associated with the roughness. A more or less large surface melting of the nematic order parameter is the only way to release curvature energy The mean orientation of the partially melted nematic depends on the anisotropy of the bidimensional surface undulation modes. For an isotropic distribution of strong roughness, a total melting is expected, with an azimuthal degeneracy This allows for a conical anchoring of the nematic liquid crystal, because of the order electric energy In all cases, we find the reasonable physical result that the isotropic phase wets a rough solid surface.

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