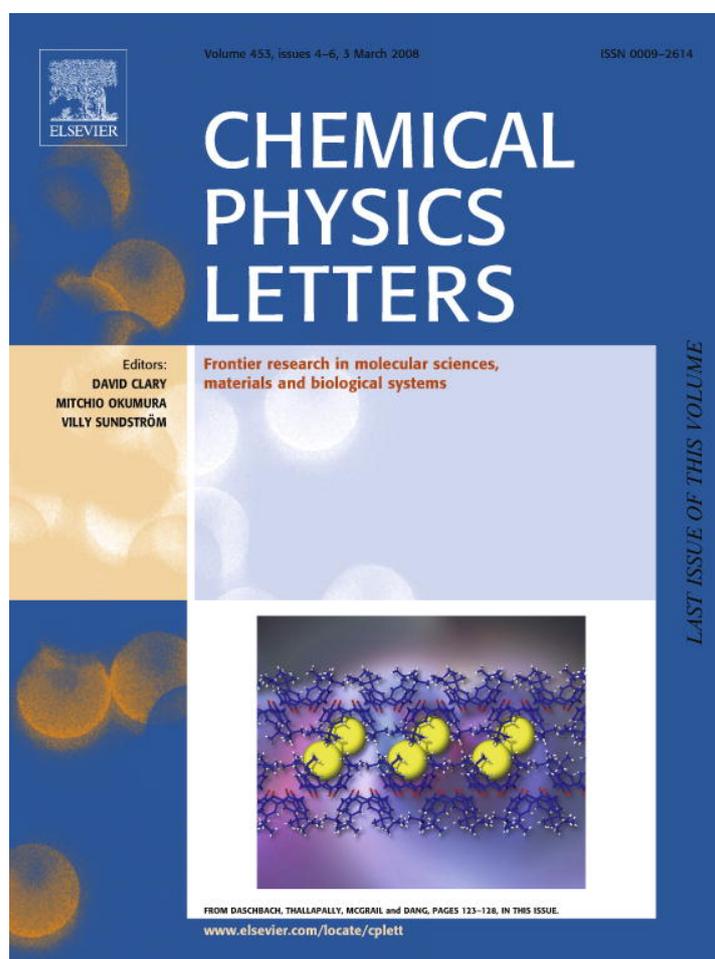


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Nematic transitions inside a film on substrates with stripe patterns of graded homeotropic anchoring

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Abstract

We investigate how a spatial pattern on substrates affects nematic-isotropic transitions inside a film deposited on them. The scales of the surface patterns and the film thickness of our interest are both dozens of nanometers. We considered simplified stripe patterns of graded homeotropic anchoring which induce uniaxial order with homogeneous director vectors. We discuss a naive approximation theory based on the Landau–de Gennes free energy, which provides simple physical pictures on the phase transitions inside the film. The reliability of the approximation are quantitatively confirmed by numerical calculations.

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Control over orientation of liquid crystal molecules by microtextured substrates has received a considerable attention [1–7]. The standard theoretical framework for this has been the Frank theory in which a distortion energy due to the spatial variation of the director vector is considered [8]. On the other hand, phase transitions of liquid crystal film of a finite thickness (as well as layer-thinning transitions in smectic films [9,10]) have been studied by the Landau–de Gennes free energy of the scalar order parameter S [11–13],

$$\varphi = \varphi_0 + LVS \cdot \nabla S + F(S) \quad (1)$$

where $F(S)$ is the standard Landau free-energy density with a negative cubic term for discontinuous transitions

$$F(S) = A(T - T^*)S^2 - BS^3 + CS^4 \quad (2)$$

In [11,12], the authors studied a liquid crystal film deposited on (non-textured) homeotropic substrate surfaces within this framework. Here, we examine phase transitions of liquid crystal film (of a finite thickness) on microtextured substrate surfaces using not the Frank energy but the scalar Landau–de Gennes energy in Eq. (1).

A more general energy for the tensorial order parameter Q unifies the Frank energy and the above scalar energy φ in the sense that both energies are recovered by the Landau–de Gennes expansion of it [8]. This generalized energy was studied by an extensive numerical analysis for a semi-infinite system (i.e., not a thin film with a finite thickness studied here) subject to inhomogeneous anchoring condition at the substrate [14,15]. In this context, what we carry out here is to assume uniaxiality and homogeneity of the director in the tensorial Q model, which reduces the generalized energy to the energy in Eq. (1), and to apply the reduced theory to a film of a finite thickness. The simplification of the tensorial Q theory to the scalar S theory allows us to obtain naive analytical results, whose appropriateness is confirmed by numerical study.

The texture on substrates considered below is specified by a wavy homeotropic anchoring at the substrate surface. The nematic order parameter $S(x, y, z)$ inside a film of thickness D (in the z direction) placed on the xy plane is set to

$$S(x, y, 0) = s_0(x) \equiv u + \Delta \sin kx \quad (3)$$

at the film bottom ($z = 0$) while the film surface at $z = D$ is kept free. Here, Δ and $\lambda = 2\pi/k$ are the amplitude and the wave length of the chemical modulation at the substrate

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surface (i.e., the film bottom) while $\Delta + u$ is less than unity. The average of director is assumed to point in the z direction inside the film.

Under this boundary condition, S is independent of y and the thermal equilibrium is determined by minimizing a functional of $S(x, z)$

$$\Phi[S] = AT_c \int_0^\lambda dx \int_0^D dz \phi \quad (4)$$

where ϕ is given by

$$\phi(S) = \xi^2(S_x^2 + S_z^2) + aS^2 - bS^3 + cS^4 \quad (5)$$

with dimensionless coefficients

$$a = (T - T^*)/T_c \quad (6)$$

$$b = B/AT_c \quad (7)$$

$$c = C/AT_c \quad (8)$$

Here, we have introduced the coherence length

$$\xi = (L/AT_c)^{1/2} \quad (9)$$

with using the bulk transition temperature $T_c = T^* + B^2/(4AC)$. Writing

$$S(x, z) = \sigma(z) + \delta(x, z) \quad (10)$$

where $\sigma(z)$ is the optimized solution for $\Delta = 0$, we define $\Delta\phi$ by the equation,

$$\phi(S) = \phi(\sigma) + \Delta\phi(\sigma, \delta) \quad (11)$$

for which $\Delta\phi = 0$ when δ is zero.

First consider the case of $\Delta = 0$, following Ref. [11] (but with spelling out some analytical results); this is necessary to make the extension described later to be understandable. Minimization of Eq. (4) when $\Delta = 0$ with respect to $S (= \sigma$ in this case) leads to

$$2\xi^2\sigma_{zz} = \frac{d}{dz}f(\sigma) \quad (12)$$

where σ_{zz} denotes the second derivative of σ with respect to z , which can be re-expressed as

$$\xi^2 \frac{d}{dz}\sigma_z^2 = \frac{d}{dz}f(\sigma) \quad (13)$$

where σ_z denotes the first derivative of σ with respect to z and

$$f(\sigma) = a\sigma^2 - b\sigma^3 + c\sigma^4 \quad (14)$$

Integrating Eq. (13) over z from $z = 0$ to $z = D$ with using the free-end condition $\sigma_z = 0$ at the film surface $z = D$, or, equivalently, the transversality condition (see also Appendix),

$$\frac{dS}{dz} = 0 \text{ at } z = D \quad (15)$$

as in [11], we obtain

$$\xi^2\sigma_z^2 = f(\sigma) - f(\sigma_D) \quad (16)$$

where $\sigma_D \equiv \sigma(z = D)$.

Eq. (16) implies $f(\sigma_D)$ is the minimum (but not necessarily the stationary point) of $f(\sigma)$ in the region $0 < z < D$

(i.e., inside the film). When u is close to one (homeotropic anchoring at the film bottom), since there is no reason that the molecules at the free film surface are ordered more than those at the film bottom, we expect that $d\sigma/dz$ is negative inside the film: $\sigma(z)$ is a monotonically decreasing function of z with

$$\frac{dz}{\xi} = - \frac{d\sigma}{\sqrt{f_u(\sigma) - f_u(\sigma_D)}} \quad (17)$$

Eq. (17) predicts how the order parameter $S(x, z) = \sigma(z)$ changes near the bottom and the surface of the film. Near $z = 0$ we obtain

$$\sigma(z) = u \left(1 - \frac{z}{u\xi_0} \right) \quad (18)$$

with

$$\xi_0 = \frac{\xi}{\sqrt{f(u) - f(\sigma_D)}} \quad (19)$$

This predicts the initial decay is predominantly governed by the length scale ξ . Near $z = D$, Eq. (17) guarantees $d\sigma/dz = 0$.

In the above, σ_D can be obtained by the minimization of

$$\Psi = \frac{D}{\xi} f(\sigma_D) + 2 \int_{\sigma_D}^u d\sigma \sqrt{f(\sigma) - f(\sigma_D)} \quad (20)$$

because differentiating the right-hand side with respect to σ_D leads to the equation obtained by integration of Eq. (17) over z from $z = 0$ to $z = D$.

The first term is dominant in the thick film limit ($D \gg \xi$) while the second term in the thin film limit ($D \ll \xi$). In the thin film limit, the minimization of the dominant second term leads to a trivial solution, $\sigma_D = u$. For a thick film where $D \gg \xi$, the minimization of Ψ is equivalent to that of $f(\sigma_D)$. In this thick film limit, the ordering σ_D at the film surface is exactly determined by the standard bulk transition theory; σ_D discontinuously jumps at a transition temperature, $T_c = T^* + B^2/(4AC)$, with a jump $\Delta\sigma_D = B/2C$, which are found from the conditions, $f(\sigma) = f(0)$ and $df(\sigma)/d\sigma = 0$. The σ_D is given from the condition $df(\sigma)/d\sigma = 0$ together with the transition temperature T_c given above

$$\sigma_D = \begin{cases} 0 & T > T_c \\ \frac{3B}{8C}(1 + \sqrt{K}) & T < T_c \end{cases} \quad (21)$$

where $K = 1 - \frac{32AC}{9B^2}(T - T^*)$.

In [11], the author examined a middle thickness region where two terms in Eq. (20) compete and he found a critical thickness D_c around 100ξ (i.e., around 100 nm because ξ is typically a few nanometers) where the original discontinuous transition becomes continuous. Below, we are interested in a bit thinner films of thickness around dozens of nanometers, but the physical picture in the thick film limit described above is helpful to understand numerical results shown below.

In summary, without modulation in the x -direction at the bottom $z = 0$, i.e., when $\Delta = 0$, ordering $\sigma(z)$ inside the film monotonically decreases towards the film-surface value σ_D from the fixed homeotropic value $u (> \sigma_D)$ at the bottom. In particular, for a film of micron thickness ($D \gg \xi$), the ordering σ_D at the film surface is determined by the standard bulk transition theory as in Eq. (21). For thinner films of our interest (but still $D > \xi$), σ_D is governed only indirectly by the bulk transition.

Based on the above understanding, we consider the case of $\Delta \neq 0$; we minimize the energy functional given in Eq. (4) with respect to $\delta(x, z)$ with regarding $\sigma(z)$ as a known function as above. The minimization with respect to δ of the integration of $\Delta\phi(\sigma, \delta)$ over x and z gives, after a cancellation due to Eq. (12),

$$2\xi^2(\delta_{xx} + \delta_{zz}) = G\delta \quad (22)$$

with

$$G = 2a - 6b\sigma + 12c\sigma^2 \quad (23)$$

where terms of the order higher than δ are neglected. We seek the solution to Eq. (22) of the form, $\delta = \Delta \exp(-\kappa z) \sin(kx)$, which satisfies boundary condition at the bottom given in Eq. (3), to find

$$\kappa^2 = k^2(1 + \alpha) \quad (24)$$

where

$$\alpha = \frac{\lambda^2}{\xi^2} \frac{G}{2(2\pi)^2} \quad (25)$$

We note here that in the limit $\lambda \rightarrow \infty$ this equation results in $\kappa^{-1} = 0$ so that $\delta = 0$ and thus the result for $\Delta = 0$ is recovered, as it should. By definition κ is independent of z , while α is z -dependent through σ . However, in the cases of our interest where λ is not too larger than ξ , the α term can be neglected since, as explicitly given below, the coefficient a , b , and c are small ~ 0.01 (see just before the concluding paragraph, for more detailed arguments on validity of this approximation). In such cases, the deviation field δ virtually satisfies the Laplace equation,

$$\delta_{xx} + \delta_{zz} = 0 \quad (26)$$

and the appropriate solution is given by

$$\delta(x, z) = \Delta \exp(-\kappa z) \sin(kx) \quad (27)$$

With this $\delta(x, z)$, the x -dependent order parameter inside the film is given by Eq. (10), under the conditions stipulated above. Namely, the x -dependence of the order parameter inside the film (at a given z) is similar to that at the bottom $z = 0$ but the amplitude of modulation $\delta(x, z)$ of ordering around an average value $\sigma(z)$ are decreased from that at the bottom. The decay of the amplitude $\delta(x, z) \sim e^{-2\pi z/\lambda}$ is dictated by the length scale λ . The average $\sigma(z)$ (of the order S over the x direction at a given z) decreases towards the free-surface value σ_D , which is, in particular for thick films, subject to the standard bulk transition theory.

To appreciate and extend our analytical results, we carried out numerical study, where we employed the following typical values as in [11]: $A = 0.045 \text{ J}/(\text{Kcm}^3)$, $B = 0.197 \text{ J}/\text{cm}^3$, $C = 0.307 \text{ J}/\text{cm}^3$, $T^* = 318.3 \text{ K}$ where the nematic-isotropic transition temperature is given by $T_c = 319 \text{ K}$. For these parameters and at temperatures relatively close to T_c ($T - T_c$ around a few K), as announced above, the coefficients a , b , and c are around 0.01 and δ practically satisfies the Laplace equation to give the deviation field δ in Eq. (27) if λ is not too larger than ξ , as we confirm below through numerical results.

In numerical study, we discretize the energy in Eq. (4) on a two-dimensional $N \times N$ grid on the x - z plane with using the fourth-order finite difference scheme and minimize the energy on the grid for the discretized set of S by using the conjugate gradient method with using analytical derivatives. We used the periodic boundary condition in the x direction and the boundary conditions at $z = 0$ and $z = D$ given in Eqs. (3) and (15), respectively. We confirmed for parameters we studied below the simulation size of $N = 50$ is enough for qualitative discussions by comparing the results with larger N : the results are virtually independent of the mesh size.

First, we examine the cases below the transition temperature at $T = 318 \text{ K}$. Fig. 1 shows a case where a film where $\lambda = 10\xi$, $D = 10\xi$, $\Delta = 0.3$, $u = 0.7$ (ξ is typically a few

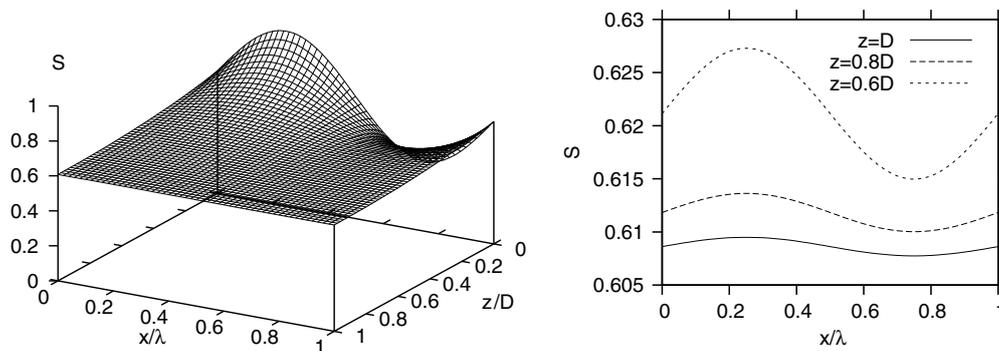


Fig. 1. (Left) The scalar order parameter S as a function of x and z at $T = 318 \text{ K}$ ($\lambda = 10\xi$, $D = 10\xi$, $\Delta = 0.3$, $u = 0.7$). (Right) The scalar order parameter S as a function of x at different depths of a film. The parameters are the same as in the left.

nanometer). As predicted (although λ is larger than ξ), the x -dependent profile inside the film for a given z is well characterized by the periodic function $s_0(x)$ imposed at the film bottom, with decrease in magnitude as z increases towards the film surface. If the wave length of the texture is increased to $\lambda = 50\xi$ with the other parameters fixed, as seen in Fig. 2, the decay towards the film surface of the wave amplitude decreases, as predicted (the decay rate is governed by the ratio D/λ) although λ is still larger than ξ .

Next, we discuss the cases above the transition temperatures. Although temperature in Fig. 3 is raised well above the transition temperature to $T = 325$ K while the other parameters are the same as in Fig. 1 ($\lambda = 10\xi$, $D = 10\xi$, $\Delta = 0.3$, $u = 0.7$), the order at the film surface in Fig. 3 does not drop to zero. This is because we cannot completely neglect the second term in Eq. (20) when $D/\xi = 10$; we checked that we need to raise temperature up to around 340 K to erase the order at the film surface for this parameter set. On the contrary, when the film thickness is increased five times to $D = 50\xi$, the film-surface order drops to zero even at 325 K, as shown in Fig. 4. This is also expected from our approximate theory because the boundary condition at the film bottom decays well due to the larger thickness: the decay is characterized by the length scale λ .

We confirmed that our simple approximate theory is quantitatively good for all the parameters used above. As seen from Eq. (24), the quality of our approximation is good when the quantity α in Eq. (25) is less than one. Rough estimates of α by setting $\sigma = 1$ (thus this is an overestimate) for parameters used in Figs. 1–4 are 0.04, 0.9, 0.06, 0.04, respectively, so that our approximation can be quantitatively good, which is numerically confirmed: we compared the approximate expression, Eq. (10) with Eq. (27), with numerical results and found that numerical differences among them are less than 5% even for parameters used in Fig. 2 for which the overestimated value of α is 0.9.

In conclusion, we demonstrated that graded homeotropic patterns of dozens-of-nanometer scales at substrate surfaces could affect significantly nematic-isotropic transitions inside a dozens-of-nanometer film deposited on a textured substrate in a naive framework. We established a simple approximate expression, Eq. (10) with Eq. (27). From this expression, the roles of the strip modulation on the substrate surface can be easily understood: the wavy pattern imposed at the film bottom is basically preserved inside the film till the film surface but the strength of the pattern diminishes when the film is thicker than the texture wave length ($D > \lambda$). In addition, when the film is thicker than the coherence length ($D > \xi$) the order at the free film

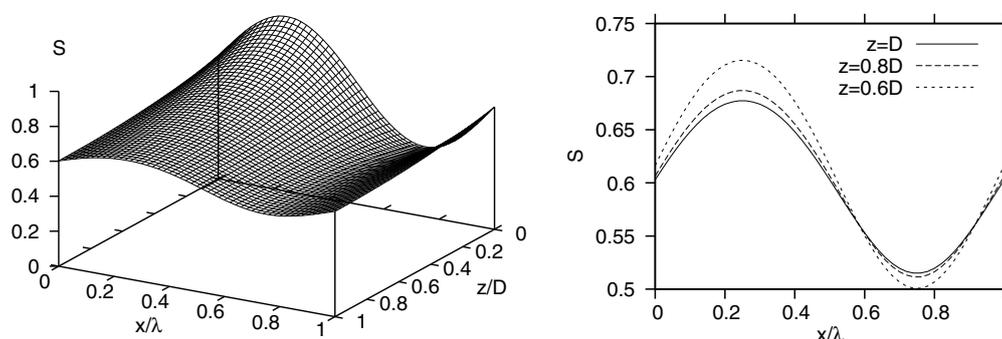


Fig. 2. (Left) The scalar order parameter S as a function of x and z at $T = 318$ K ($\lambda = 50\xi$, $D = 10\xi$, $\Delta = 0.3$, $u = 0.7$). (Right) The scalar order parameter S as a function of x at different depths of a film. The parameters are the same as in the left.

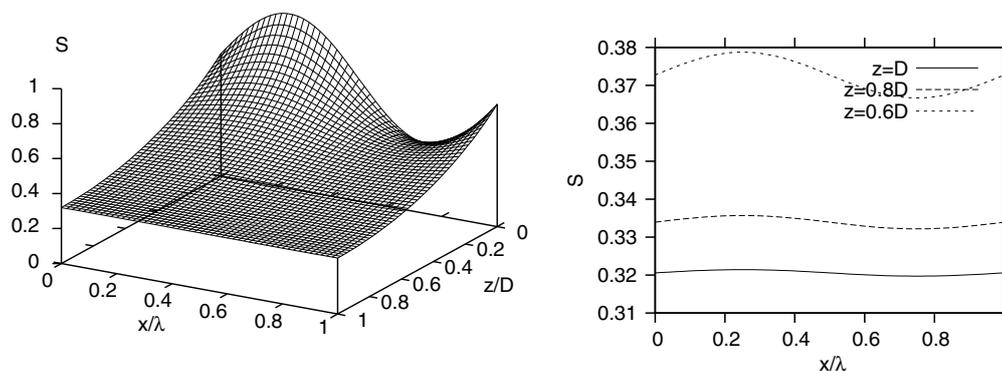


Fig. 3. (Left) The scalar order parameter S as a function of x and z at $T = 325$ K ($\lambda = 10\xi$, $D = 10\xi$, $\Delta = 0.3$, $u = 0.7$). (Right) The scalar order parameter S as a function of x at different depths of a film. The parameters are the same as in the left.

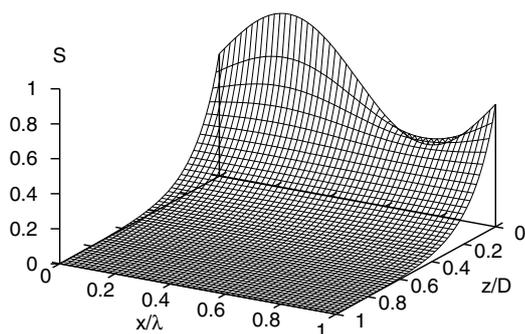


Fig. 4. The scalar order parameter S as a function of x and z at $T = 325$ K ($\lambda = 10\xi$, $D = 50\xi$, $\Delta = 0.3$, $u = 0.7$).

surface is (indirectly) governed by the standard bulk transition theory. We also performed numerical calculation to show that our approximate result is quantitatively good for a range of parameters of practical interest although the approximation is precise under limited conditions (i.e., $\xi < D$, $\Delta < 1$, $\lambda \simeq \xi$). In addition, we emphasize here that our present result can be directly applied to a film of thickness $2D$ sandwiched by two identical textured substrates with textures of the top and bottom substrates matched if we regard the depth $z = D$ corresponds to the middle position of the thickness of the film, because in the middle of the film the same ‘free surface’ boundary condition is appropriate due to the symmetry. Although our analysis is based on sinusoidal texture of graded homeotropic anchoring, we expect that the general tendency illustrated above could be tested even for experimentally more feasible textures such as non-wavy but stepwise stripe patterns.

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Appendix.

In this section, we describe the reason we required the boundary condition $dS/dz = 0$ at $z = D$ in the simplest case where $\Delta = 0$ where $S = \sigma$. We consider to minimize a functional of $u(z) = \sigma(z)$ (with $F = \xi^2 u_z^2 + f(u)$),

$$J[u] = \int_0^D dz F(z, u, u_z) \quad (28)$$

where $u_z = du/dz$, under a condition, $u = u_0$ at $z = 0$, and another condition that the value of u at $z = D$ is kept free. We denote the minimized solution $u = \bar{u}$ and then, for $u = u_\varepsilon$ where

$$u_\varepsilon(z) = \bar{u}(z) + \varepsilon \eta(z), \quad (29)$$

we obtain the condition that $dJ[u_\varepsilon]/d\varepsilon$ at $\varepsilon = 0$ should be zero, which results, after an integration by parts, in the form

$$\int_0^D dz \eta \left[\frac{\partial \bar{F}}{\partial u} - \frac{d}{dz} \frac{\partial \bar{F}}{\partial u_z} \right] + \left[\frac{\partial \bar{F}}{\partial u_z} \eta \right]_{z=0}^{z=D} = 0 \quad (30)$$

where an over-bar indicates that the quantity is evaluated at $u = \bar{u}$ and $u_z = \bar{u}_z$. As a matter of fact, from the first boundary condition, $u = u_0$ at $z = 0$, Eq. (30) is required to hold only when the function $\eta(z)$ satisfies $\eta(0) = 0$, because we seek the minimized function with u fixed at $z = 0$. From the second condition (free boundary for u at $z = D$), however, Eq. (30) should hold not only when $\eta(D) = 0$ (case 1) but also when $\eta(D)$ is free (case 2). In case 1, Eq. (30) results in the conventional Euler equation,

$$\frac{\partial \bar{F}}{\partial u} - \frac{d}{dz} \frac{\partial \bar{F}}{\partial u_z} = 0 \quad (31)$$

because the second square bracket in Eq. (30) vanishes due to the condition $\eta(0) = \eta(D) = 0$; the Euler equation should always hold for the minimized function, $u = \bar{u}$. Knowing this fact and considering case 2 where $\eta(D)$ is nonzero, we arrive at, from Eqs. (30) and (31), the transversality condition, in the simplest form,

$$\frac{\partial \bar{F}}{\partial u_z} = 0 \quad (32)$$

at $z = D$ when u is the solution of the above minimization problem. This simple analysis proves that the free boundary condition in a variational problem leads to the condition in Eq. (32), which corresponds to $dS/dz = 0$ in our specific problem. Even when Δ is nonzero and S becomes not only z -dependent but also x -dependent, because S as a function of x is a periodic function, the transversality condition emerges only in the z direction.

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