Subsurface growth of smectic liquid crystals

V. I. Marchenko
Institute of Solid State Physics, Russian Academy of Sciences, 142432, Moscow Oblast, Chernogolovka, Russia

(Submitted 17 September 1992)
Pis'ma Zh. Eksp. Teor. Fiz. **56**, No. 8, 406–408 (25 October 1992)

A new mechanism is proposed for the growth of an atomically smooth face of a smectic liquid crystal. If the smectic dislocation energy is smaller than $\sqrt{2}$ of the energy of a surface step, the growth results from the nucleation, growth, and coalescence of loop dislocations in an exponentially large layer below the surface of the smectic crystal.

The growth of an ideal, atomically smooth crystal surface occurs through the nucleation, growth, and coalescence of new atomic layers.[1] This "layer-by-layer" growth mechanism should also operate in smectic liquid crystals, in which the density is a periodic function of one coordinate. In smectics, however, there is another growth mechanism which could operate, in the direction of the atomically smooth surface. The dislocations in smectic crystals differ from those in crystals in having a finite energy per unit length.[2] The nucleation of new layers on the surface is thus in competition with the nucleation and growth of loop dislocations in the interior of the smectic crystal. As a result, a subsurface mechanism of layer-by-layer growth can operate, as is shown below.

Let us first "turn off" the nucleation of new layers, both at the surface and in the interior. As the temperature moves away from the transition point, there can accordingly be a phase and mechanical liquid–smectic equilibrium if the interface is oriented parallel to the smectic layers. A state with anisotropic stresses is thus set up in the smectic crystal: The stress along the normal to the boundary is equal to the pressure in the liquid, while the stress in the tangential plane reaches a level such that the

 0021-3640/92/000347-03$03.00

chemical potentials of the phases become equal. This equilibrium can be established because of a diffusive transport of molecules between the smectic layers and between the liquid and the first surface layer.

This state of the smectic crystal is metastable: Conditions favor a change in the number of layers through a change in the 2D density of molecules in the layers in such a way that the system goes into the normal state, with an isotropic pressure. These ideas obviously lead to the following possible growth mechanism for the smectic crystal. The coexistence of the liquid and the anisotropically stressed smectic crystal is established at the boundary. Below the surface, in some layer of macroscopic size, new layers grow as the result of a nucleation of loop dislocations (a corresponding effect is known to occur in crystals supersaturated with vacancies or interstitial atoms; Ref. 3, for example). This growth of new layers relieves the stress anisotropy far from the surface.

As a measure of the deviation of the local state of the smectic crystal from the equilibrium state (which prevails far from the surface), we adopt the deviation ($\delta\rho$) of the 2D density of molecules in the smectic layer. The value of $\delta\rho$ directly beside the boundary corresponds to the phase equilibrium described above. Far from the surface, the state of the smectic crystal tends toward equilibrium. Upon a small deviation of the temperature from the transition temperature, the boundary conditions for the $\delta\rho$ profile can thus be written

$$\delta\rho|_{z=0}=\gamma\delta T; \quad \delta\rho|_{z=\infty}=0. \tag{1}$$

The equation describing the transport of molecules away from the surface into the smectic crystal reduces to the following mass conservation law:

$$\partial_t\rho - D\partial_z^2\rho = I, \tag{2}$$

where I is the drainage of the molecules into the newly nucleated and growing layers, and D is the diffusion coefficient. The growth mechanism which we are proposing here differs from ordinary layer-by-layer growth only in that new layers form between layers in the interior, rather than exclusively in a surface layer. Making use of the obvious analogy with layer-by-layer growth,[1] we can thus write the following relation for I:

$$I \propto \exp(-U_c/3T), \tag{3}$$

where U_c is the formation energy of a critical nucleation center of the new layer. We restrict the present letter to a calculation of the argument of this exponential function for the growth rate, so we ignore the pre-exponential factors in (3) and below.

The energy of a circular nucleating region of a new layer is

$$U(\delta\rho,R) = -\pi R^2 A\delta\rho + 2\pi R\alpha, \tag{4}$$

where R is the radius of the region. The first term gives the energy benefit resulting from the formation of a new layer in the metastable state of the smectic crystal. The second term is the boundary energy of the nucleation center (a ring dislocation). The energy of a critical nucleation center corresponds to an extremum of (4):

$$U_c(\delta\rho)=\pi\alpha^2/A\delta\rho. \tag{5}$$

Ignoring the rate of change of the density, we multiply Eq. (2) by $\partial_z\rho$. Using (3) and (5), we find a first integral within the accuracy stated above:

$$(\partial_z\rho)^2 \propto \exp(-U_c(\delta\rho)/3T). \tag{6}$$

The smectic crystal growth rate V is evidently determined by the flux of molecules toward the surface:

$$V \propto D\partial_z\delta\rho|_{z=0} \propto \exp\left(-\frac{\pi\alpha^2}{6AT\gamma\delta T}\right). \tag{7}$$

The expression for the growth rate for the ordinary (surface) layer-by-layer mechanism [expression (83) in Chap. I in Ref. 1] differs from (7) only in that the dislocation energy α is replaced by the energy of a step, and a coefficient of 3 appears instead of a 6 in the denominator of the argument of the exponential function. Accordingly, if the energy of a smectic dislocation is less than $\sqrt{2}$ of the energy of a surface step, the growth of the smectic crystal should occur by the subsurface mechanism which we are proposing here.

This change in coefficient (from 3 to 6) occurs because an exponentially large skin layer is participating in the layer-by-layer growth. Integrating Eq. (6), we find the profile of the density deviation:

$$\delta\rho=\frac{\pi\alpha^2}{6AT}\left(\ln\frac{b+z}{a}\right)^{-1}; \quad b=a\exp\frac{\pi\alpha^2}{6AT\gamma\delta T}, \tag{8}$$

where the length parameter a depends on both kinetic and equilibrium parameters of the problem. It furthermore depends (in a power-law fashion) on the distance from the transition point.

Let us now assume that the growth rate is controlled by the ordinary surface layer-by-layer mechanism. In this case the phase-transition boundary is also accompanied by a tail on the density deviation. In determining it we can ignore diffusion. We seek a solution in the form of a steady-state profile in a coordinate system which is moving at the velocity of the boundary. Equation (2) then reduces to

$$-V\partial_z\rho=I. \tag{9}$$

For boundary conditions (1) we thus find

$$\delta\rho=\frac{\pi\alpha^2}{3AT}\left(\ln\frac{c+z}{V\tau}\right)^{-1}; \quad c=V\tau\exp\frac{\pi\alpha^2}{3AT\gamma\delta T}, \tag{10}$$

where τ depends on the drainage pre-exponential factor I and on the parameter α^2/AT.

Clearly, a corresponding subsurface perturbation occurs in ordinary crystals also. The mass transport in this case results from a diffusion of vacancies and interstitial atoms. Because of the logarithmic nature of the dislocation energy, however, the growth rate may be determined exclusively by the ordinary surface mechanisms of layer-by-layer or normal growth.

I wish to thank E. A. Brener and S. V. Iordanskiĭ for a useful discussion. This study was supported financially in part by a grant from the American Physical Society.

[1] *Modern Crystallography: Formation of Crystals*, Vol. 3, Nauka, Moscow, 1980.
[2] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, Nauka, Moscow, 1987, §45 (earlier editions of this book have been published in English translation by Pergamon, New York).
[3] J. Friedel, *Dislocations*, Pergamon, New York, 1964, Chap. 5, §4.1.

Translated by D. Parsons