Surface smecticity in chiral liquid crystals

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A stability range of the surface smectic A-phase is predicted to exist in the vicinity of the cholesteric-smectic A^* phase transition line. This surface smecticity must precede the recently discovered[1] structure with periodic density modulation in the plane of the smectic layer. Surface smecticity may produce an apparent smearing of the phase transition in experiment.

1. De Gennes[2] was the first to call attention to the analogy between a normal metal-superconducting phase transition and a nematic-smectic A transition. According to this analogy, the director $\vec{n}$ functions as the vector-potential, while the tortional strain proportional to curl $\vec{n}$ functions as the magnetic field. The most natural source of such a strain is the chirality of the cholesteric liquid crystal. Hence, if we are discussing a mixed state, it is necessary to consider a cholesteric-smectic A phase transition. The spontaneous helicity of the cholesteric (whose ground state is given by the condition $\vec{n}$ curl $\vec{n} = k_0$, where $\vec{n}$ is the director, and k_0 is the wave vector of the cholesteric helix) is also a magnetic field source.

Until recently, type-I smectics, in which the Ginzburg parameter $\kappa < 1/\sqrt{2}$, were the only known smectics. However, type-II smectics, in which the Ginzburg parameter $\kappa > 1/\sqrt{2}$, were discovered quite recently[1] and the structure of their mixed state was determined. This structure was found to be different from the regular structure of the Abrikosov vortices in superconductors and is consistent with the structure predicted previously for liquid crystals with periodic density modulation in the plane of the smectic layer.[3] This difference stems from the fact that dislocations are the analog of

vortices in the smectics, while a regular dislocation lattice is not suitable due to the rise in elastic energy.

In our study we analyzed the nucleation process of the smectic A phase in the cholesteric phase. We will show that the nucleation energy of the smectic A phase is always lower near the boundary of the cholesteric than in the bulk. In this sense, we can state that a type-II cholesteric-smectic A transition always corresponds to a superconductor in a magnetic field parallel to the surface of the sample.

It is necessary to find the minimum eigenvalue of the De Gennes–Landau functional for this transition[3] in order to investigate the stability of the cholesteric phase relative to nucleation of the smectic A phase. This procedure corresponds to solving the Schrödinger equation:

$$\hat{H}\Psi = E\Psi, \tag{1}$$

where

$$\hat{H} = -\frac{1}{2m}\frac{d^2}{dz^2} + \frac{1}{m}q_0^2[1 - \cos k_0(z - z_0)].$$

The parameter z_0 corresponds to the localization site of the wave function of the ground state, m is the effective mass (assumed to be isotropic for simplicity), and q_0 is the wave vector of smectic density modulation.

Boundary conditions must be imposed on Eq. (1). We consider a semi-infinite system and assume that at the boundary $z = 0$ we have

$$\frac{d\Psi}{dz} = 0. \tag{2}$$

Such a boundary condition corresponds to fixing the orientation of the liquid crystal at the surface $z = 0$. It is also convenient in that the solution of Eq. (1) with boundary condition (2) is equivalent to a solution of the Schrödinger equation in all space (from $-\infty$ to $+\infty$), but with a potential V of the type

$$V = \begin{cases} \frac{1}{m}[1 - \cos k_0(z - z_0)], & \text{for } z > 0 \\ V(-z), & \text{for } z < 0 \end{cases}. \tag{3}$$

Here the wave function of the ground state will automatically satisfy all necessary symmetry requirements and boundary condition (2).

It is most convenient for our purpose to utilize the variational principle. We will seek the solution of the non-normalized wave function of the ground state in the form

$$\Psi = \exp(-rz^2). \tag{4}$$

We will use the parameters r and z_0 as the variational parameters in which the ground state energy E_0 is minimized. The matrix elements of Hamiltonian (1) with the functions (4) are calculated explicitly and can be expressed in terms of hypergeometric functions. It is therefore more convenient to find directly only a single number that defines the reduction of the eigenvalue of the ground state energy of the semi-infinite

problem (1), (2) compared to the infinite case.

In the critical-field terms, this reduction means that in a semi-infinite sample nucleation occurs in a field

$$h_{c3} = 1,48 h_{c2}. \tag{5}$$

We note that the number appearing in (5) is larger [1.695 (Ref. 4)] in the superconducting problem (where the potential in the Schrödinger equation is a harmonic oscillator).

In liquid crystals the effective factor is the transition temperature, rather than the field h which is, in fact, the constitutive constant. Relation (5) means that in the semi-infinite case of smectics of the second kind ($\kappa > 1/\sqrt{2}$) nucleation centers of the surface smectic phase are always formed at a temperature

$$T_s = (T_c + 1,48 \frac{k_0 q_0}{m}). \tag{6}$$

At temperatures in the range from T_s to T^* the intermediate phase, which was predicted in Ref. 3, with a density modulation in the smectic-layer plane, is stable:

$$T^* = T_c + \frac{k_0 q_0}{m}. \tag{7}$$

Finally, a homogeneous (normal) smectic A phase is formed at a temperature T_c.

In conclusion, let us briefly discuss whether the surface smectic phase can be observed. X-ray diffraction, a simple method, makes it possible to identify the smectic structure from the Bragg peak. The ultrasonic method is also very sensitive, in principle, to the presence of a smectic phase. A unique second-sound propagating mode occurs in a smectic phase. A fluctuation contribution to the low-frequency acoustic absorption also occurs in a smectic phase. It is interesting to note that fluctuation effects are important only at scales smaller than the cholesteric helix step in the smectic A phase with a density modulation in the layer (which is a layered crystalline phase by virtue of its global symmetry).

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