Brief Reports

Nonlinear field-induced dynamics of interphase boundaries at some diffusionless phase transitions

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Magnetic- and electric-field effects on the width, surface tension, and velocity of the interphase boundary are calculated for solid-solid and nematic-isotropic first-order phase transitions described by the Landau expansion with a cubic term. The exact solution of the Ginzburg–Landau–de Gennes equation including an external field is obtained. The results are compared with the experimental data in nematic liquid crystals and ferroelectrics.

A significant fraction of solid-solid and nematic-isotropic phase transitions are first-order diffusionless ones.[1] Many such transformations can be described by the Landau expansion of the free energy density as a function of the order parameter including the cubic term. In recent years there has been increasing interest in the rates and mechanisms of interfacial kinetics for first-order phase transitions.[2–6] The growth process is usually associated with the propagation of interfaces separating the high-temperature parent phase and low-temperature product phase. The phase transition proceeds by interphase boundary migration. By means of this process one phase grows at the expense of another one. The temperature kinetics of the diffusionless first-order phase transitions have been considered as a kink-type movement of the interphase boundary and studied experimentally and theoretically in Refs. 2–11. Unlike a presence of the theoretical consideration of the thermally induced interface propagation, there exists so far no quantitative description of the kinetics of a diffusionless transformation in external electric and magnetic fields. In this paper we examine the nonlinear dynamics of an interphase boundary which arises under the influence of electric and magnetic fields. We carry out the estimates for nematic-isotropic and ferroelectric phase transitions.

The model outlined here assumes that the interfacial dynamics are governed entirely by the evolution of the order parameter. The relaxation of the metastable system to equilibrium provides the propagation rate of the phase transition front. We use the time-dependent Ginzburg–Landau–Gennes equation[12,13] for the evolution of the order parameter Q:

$$\partial Q / \partial t = -\Gamma \delta F / \delta Q , \quad (1)$$

where Γ is the Landau-Khalatnikov transport coefficient which sets the time scale of the relaxation process and is assumed to depend noncritically on a temperature. In the case of nematics $\Gamma = 1/\tau A$, where τ is the relaxation time. F is the free energy

$$F[Q(r,t)] = \int \{ f[Q(r,t)] + D[\nabla Q(r,t)]^2 \} d^3 r , \quad (2)$$

where

$$f(Q) = \tfrac{1}{2} A Q^2 - \tfrac{1}{3} B Q^3 + \tfrac{1}{4} C Q^4 - H Q , \quad (3)$$

where coefficients B and C are positive, coefficient A is a temperature-dependent one: $A = a(T - T_0), T_0$ is the temperature of the stability limit of the high-temperature phase; coefficient a does not depend on temperature. D is the positive coefficient of the inhomogeneity term. The functional derivative $\delta F / \delta Q$ is a term tending to restore the value of Q to its thermal equilibrium value. It is the thermodynamic force that drives the system towards equilibrium. H is the external field. This expansion for the order parameter can be applied for structural, ferroelectric, martensitic, nematic-isotropic and quasicrystalline phase transitions.[14–18] For example, in ferroelectrics Q is the spontaneous polarization, H is the electric-field strength. In nematics $Q = \tfrac{3}{2} \langle \cos^2\theta - \tfrac{1}{3} \rangle$, where[17] θ is the angle between the long axis of a molecule and the local optic axis, the angular brackets denote a statistic average. $D > 0$ describes the extra free energy due to a distortion in Q. If the long axis of molecules is parallel $(\theta = 0)$ and antiparallel $(\theta = \pi)$ to the optic axis, $Q = 1$ (the completely aligned material). If the orientation of the molecules is chaotic, then $\langle \cos^2\theta \rangle = \tfrac{1}{3}$ and $Q = 0$. The term Q^3 arises because of the quadrupole symmetry

of the ordered state. If Q is positive the molecules order with their long axes parallel to the optic axis. The external field H may be an electric or magnetic one

$$H = \tfrac{1}{3}\Delta\chi h^2 , \tag{4}$$

where $\Delta\chi$ is the coefficient of the anisotropy in the diamagnetic susceptibility,[17] $\Delta\chi = \chi_p - \chi_t$, χ_p and χ_t are the diamagnetic susceptibilities parallel and transverse to the optic axis. The external magnetic field h interacts with the nematic liquid crystal through the anisotropy of its diamagnetic susceptibility tending to align the director parallel to the magnetic field. If h is an electric field, $\Delta\chi$ is the volumetric susceptibility anisotropy.

The equilibrium value of the order parameter Q is the one that provides the lowest possible free energy. Minimizing the free energy density with respect to Q gives the equation of state for the uniform state

$$AQ - BQ^2 + CQ^3 - H = 0 . \tag{5}$$

For the zero-field case, when Eq. (5) has three real roots, two of them correspond to minima in the free energy. At temperatures well above T_0 and in zero field the free energy is lowest when $Q = 0$, but at $T = T_c = T_0 + 2B^2/9aC$ the free energy becomes lower for the minimum at finite Q. A first-order transition then occurs to the ordered state at T_c. The discontinuity in order parameter at T_c is $Q_c = 2B/3C$, and the latent heat is $\tfrac{1}{2}T_c Q_c^2$. The first-order phase transition exists for fields which are lower than the critical field $H_c = B^3/27C^2$. In the case of a nematic-isotropic phase transition the critical field is equal to $h_c = (B/3C)(B/3\Delta\chi)^{1/2}$ at which the boundary between the isotropic and the nematic phases becomes vague.

The theory of the kinetics of diffusionless first-order phase transitions for $H = 0$ based on Eqs. (1)–(3) was proposed by Chan.[9] We develop here a theory of the external field effect on the interphase boundary dynamics.

Variating the functional (2), (3) and substituting the result into Eq. (1), we obtain the following expression for the uniaxial or strongly anisotropic cases:

$$\partial Q/\partial t + \Gamma(AQ - BQ^2 + CQ^3 - H) - 2\Gamma D \partial^2 Q/\partial x^2 = 0 . \tag{6}$$

Using $s = x - vt$, we have

$$2\Gamma D\, d^2Q/ds^2 + v\, dQ/ds - \Gamma(AQ - BQ^2 + CQ^3 - H) = 0 . \tag{7}$$

Equation (7) was solved in Refs. 8 and 9 for $H = 0$. We solve it for $H \neq 0$ for the boundary conditions characteristic of the interphase boundary. Then we derive the following equation for the interphase boundary profile:

$$Q = Q_2 + (Q_1 - Q_2)/[1 + \exp(s/\Delta)] , \tag{8}$$

where Q_1, Q_2, and Q_3 are solutions of Eq. (5):

$$Q_1 = (B/3C)[1 + 2(1 - 3\alpha)^{1/2}]\cos(\phi/3),$$

$$Q_2 = B/3C[1 - 2(1 - 3\alpha)^{1/2}]\cos[(\pi - \phi)/3] , \tag{9}$$

$$Q_3 = (B/3C)[1 - 2(1 - 3\alpha)^{1/2}]\cos[(\pi + \phi)/3] ,$$

where $\alpha = AC/B^2$ is the temperature factor and

$$\phi = \arccos\{[(H/2H_c) + (1 - 9\alpha/2)]/(1 - 3\alpha)^{3/2}\} . \tag{10}$$

In nematics we have $\tfrac{1}{2}(h/h_c)^2$ instead of $\tfrac{1}{2}(H/H_c)$ in Eq. (10). Δ is the width of the interphase boundary given by

$$\Delta = (3DC)^{1/2}/B(1 - 3\alpha)^{1/2}\cos(\phi/3 - \pi/6) . \tag{11}$$

The solution (8) exists when the velocity of the interphase boundary is equal to

$$v = 2\Gamma B(D/C)^{1/2}(1 - 3\alpha)^{1/2}\cos[(\pi + \phi)/3] . \tag{12}$$

To analyze the interface dynamics described by Eq. (12) we present Eq. (3) as follows:

$$f(Q) = f'(Q')B^4/C^3 , \tag{13}$$

where

$$f'(Q') = \tfrac{1}{2}\alpha Q'^2 - \tfrac{1}{3}Q'^3 + \tfrac{1}{4}Q'^4 - (H'/27)Q' , \tag{14}$$

where $Q' = (C/B)Q$ and $H' = H/H_c$.

In Fig. 1(a) the interphase boundary velocity v is shown as a function of the dimensionless field H' for the temper-
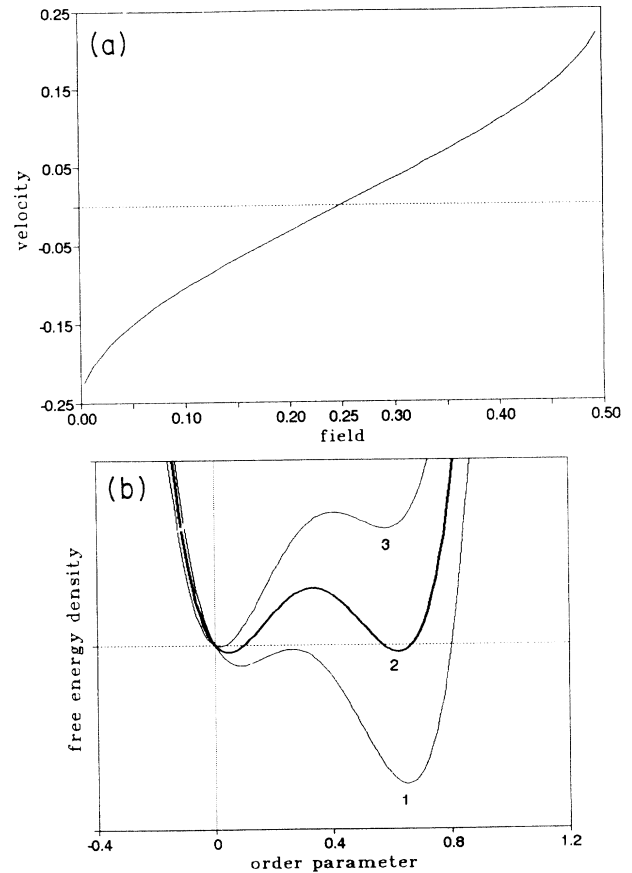

FIG. 1. (a) The interphase boundary velocity v [in units of $2\Gamma B(D/C)^{1/2}$] as a function of the strength of the dimensionless field H' for the dimensionless temperature factor $\alpha = 0.25$ [Eq. (12)] (the phase transition occurs at $\alpha = 0.25$ and $H' = 0.25$). (b) The free energy density as a function of the order parameter at $\alpha = 0.25$ for three values of H': $1 \rightarrow H' = 0.4$; 2 (the heavy solid line describes the phase transition point) $\rightarrow H' = 0.25$; $3 \rightarrow H' = 0.1$ [Eq. (14)].

ature at which $\alpha=0.25$. In Fig. 1(b) the free energy density [Eq. (14)] is demonstrated as a function of the order parameter for $\alpha=0.25$ and for three fields: curve 1 corresponds to $H'=0.4$; curve 2 (the heavy solid line) corresponds to the field $H'=0.25$ for which the phase transition point is reached because the two minima describing the two coexisting phases are at the same level; curve 3 corresponds to $H'=0.1$. At the phase transition point ($\alpha=0.25$ and $H'=0.25$) the interphase boundary stops because of the equality of free energy densities of coexisting phases. For fields $H'=0.4$ and $H'=0.1$ the interphase boundary moves in two opposite directions depending on the "direction" of the asymmetry of the free energy density. As is known, for $H'=0$ the temperature factor $\alpha=\frac{2}{9}$. Thus, Fig. 1(b) reflects the fact that the phase transition temperature depends on the external field strength. It is seen from Fig. 1(a) that the curve of the interphase boundary velocity exists at the range of coexistence of two phases. In Fig. 2(a) the interphase boundary velocity is shown as a function of the dimensionless temperature factor α for $H'=0.3$. At the point for

which $\alpha=0.255$ the phase transition occurs and the interphase boundary stops. It is seen that at the phase transition temperature the interface changes the direction of its motion in Fig. 2(b) which presents the dependence of the free energy density on the order parameter according to Eq. (14): curve 1 corresponds to $\alpha=0.24$; the heavy solid curve 2 (which describes the phase transition for this field) corresponds to $\alpha=0.255$; curve 3 corresponds to $\alpha=0.27$. The direction of the interphase boundary motion is determined by the "direction" asymmetry of the free energy density. The velocity curve exists at the range of coexistence of two phases. In Fig. 3 the interphase boundary width is shown as a function of the field for $\alpha=0.25$. The interface narrowing at the phase transition point (here $\alpha=0.25$ and $H=0.25$) is explained by the fact that on approaching the phase transition at which the minima of the free energy density have the same depth the system overcomes the lowest barrier.

To our knowledge, there are no experimental data on the field influence on the interphase boundary motion in nematics. However, we can check our approach calculating the surface tension coefficient of the interphase boundary. The data on the magnetic field effect on the surface tension are available in p-methoxy benzylidene p-n-butylaniline (MBBA): $\sigma=(2.3\pm0.4)\times10^{-2}$ erg/cm^2,[19] for the magnetic-field strength $h=0.3$ T. The data[20] were obtained for $h=0$: $\sigma=1.6\times10^{-2}$ erg/cm^2. Let us calculate σ in the external field. Using Eq. (8) and integrating we obtain

$$\sigma=2D\int_{-\infty}^{\infty}(dQ/dx)^2dx=(D/3\Delta)(Q_1-Q_2)^2 . \qquad (15)$$

For the estimate of the surface tension of the interphase boundary in magnetic fields in MBBA we use the following experimental values: $a=6.2\times10^5$ erg K^{-1} cm^{-3},[21] $B=4.7\times10^6$ erg cm^{-3},[21] $C=7.9\times10^6$ erg cm^{-3},[21] $D=6.1\times10^{-7}$ dyn,[22] $\Delta x=1.25\times10^{-7}$ erg G^{-2} cm^{-3},[21] $h=3000$ G. For $T_c-T_0=1$ K we obtain $\sigma=10^{-2}$ erg/cm^2, which is very close to the experimental value.[20] Within this range of fields the surface tension of the interphase boundary is not changed. It corresponds to the result obtained by using Eq. (15).

We can check our results by considering the two known limited cases. For $H=0$ we obtain in Eq. (6) the
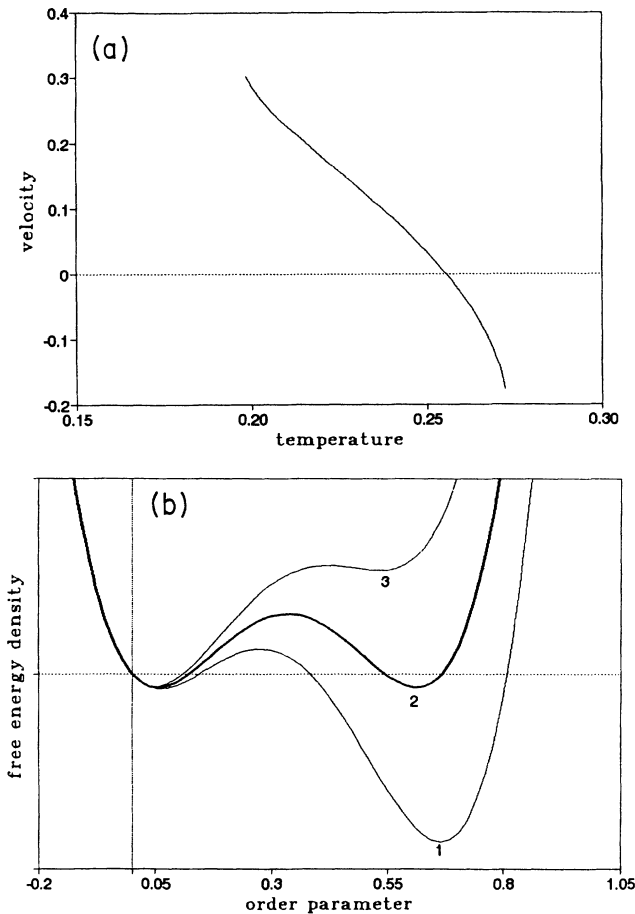
FIG. 2. (a) The interphase boundary velocity v [in units of $2\Gamma B(D/C)^{1/2}$] as a function of the temperature factor α for $H'=0.3$ [Eq. (12)]. The phase transition takes place at $\alpha=0.255$ and $H'=0.3$. (b) The free energy density as a function of the order parameter at $H'=0.3$ for three values of α: $1\to\alpha=0.24$; 2 (the heavy solid line describes the phase transition point) $\to\alpha=0.255$; $3\to\alpha=0.27$ [Eq. (14)].
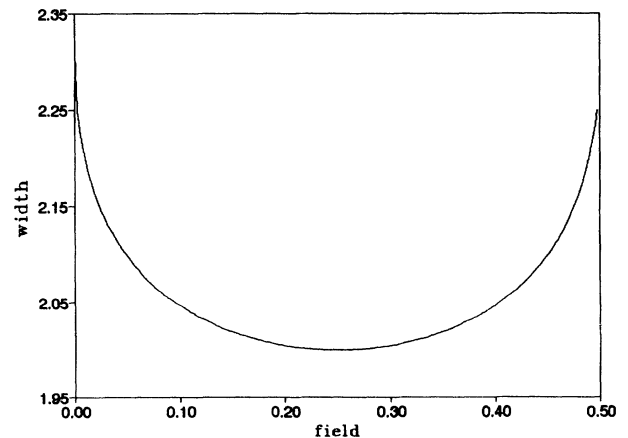
FIG. 3. The interphase boundary width Δ as a function of the field H' for $\alpha=0.25$ in units of $(3DC)^{1/2}/B$.

equation describing the temperature-induced motion of the interphase boundary[9] giving the following profile for this type of phase transitions:

$$Q = Q_2 / 1 + \exp[-(x - vt)/\Delta] , \tag{16}$$

which follows from Eq. (8) when $Q_1 = 0$. For $v = 0$ we obtain the known equation for the interphase boundary in the static case from Eq. (8)

$$Q = \tfrac{1}{2}(Q_1 + Q_2) + \tfrac{1}{2}(Q_1 - Q_2)\tanh(x/2\Delta) , \tag{17}$$

where $Q_1 = 0$.[23]

Let us compare our results with the experiment on the electric-field-induced motion of the interphase boundary in the ferroelectric substance SbSI.[24] In Ref. 24 a constant electric field applied to the crystal caused the interphase boundary to move toward the cathode. The rate of interphase boundary displacement in one of the investigated crystals was $v = 10^{-3}$ cm/s for the external electric-field strength $H = 300$ V/cm, which is much lower than the critical electric field in SbSI. For this reason we use Eq. (13) for the estimate. We use the following experimental values: $\Gamma = 11$ cm^{-1},[25] $a = 3.31$

$\times 10^{-5}$ K^{-1},[26] $B = 3.2 \times 10^{-13}$ cgs,[26] $C = 7.4 \times 10^{-23}$ cgs.[26] We estimate the coefficient D according to[27] $D = (\pi/15)\ d^2$, where d is the lattice parameter: $d = 8.49$ A.[28] For temperatures close to $T_c = 20\,°$C ($\Delta T \sim 1\,°$C) we obtain $v = 0.7 \times 10^{-3}$ cm/s. The light difference between the experiment and the theory can arise from the fact that we use the Landau expansion with the cubic term instead of the expansion with the sixth term. The expansion including the cubic term can be used for the ferroelectric $(NH_4)_2BeF_4$,[29] for Ag_3AsS_3,[30] Ag_3SbS_3,[31] and other "divertible ferroelectrics"[32] in which the polarization cannot be reversed but can only be turned in another direction: the states $+Q$ and $-Q$ are not equivalent and this permits the existence of the Q^3 term. The same expansion of the free energy can be used in structural phase transitions,[14] in martensitic phase transitions,[16] and in quasicrystals.[18] This means that our results can be applied in these cases.

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