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LETTER TO THE EDITOR

## Dynamic criterion in the kinetics of ferroelectric phase transitions

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**Abstract.** The rate of the latent heat transfer at first-order phase transitions is calculated. A dynamic criterion to determine the dominating process in kinetics of phase transitions is obtained. It is shown that in ferroelectric perovskites of the  $ABO_3$ -type the relaxation of the order parameter governs the phase transition kinetics. The electric field dynamics of interphase boundaries is studied as an example of the applicability of the relaxation kinetics and the front velocity appears to be of the threshold field type.

The kinetics of first-order phase transitions is an active branch of research which deals with the dynamics of metastable and unstable phases. These phase transitions in various systems are often accompanied by pretransitional or precursor phenomena, when drastic changes of system properties occur displaying substantial changes in the behaviour of observable quantities. The origin of these phenomena is the appearance of nuclei of competing thermodynamic phases inside a host phase [1]. In recent years interest has grown considerably in studying the nature of metastable states and first-order phase transitions. Relaxation of a metastable system to a thermodynamically stable state may take place due to motion of a phase transition front. In the solid diffusionless transformations the growth may be slow enough for the observation by polarization microscope technique. In particular, in ferroelectrics sharp interphase boundaries can be observed [2–6, 9–14]. Usually the interphase dynamics are governed entirely by the time evolution of the order parameter [15–22] and the temperature can be considered to be a constant. Thus the heat is assumed to be removed rapidly enough so that no temperature change occurs as the latent heat of the phase transition appears at the interphase boundary. However the moving interface can act as a heat source giving rise to a jump in the thermal gradient. The heat generated during the interphase boundary motion can accelerate the interface which, in turn, increases the heat production rate. If one deals with substances which conduct heat very well, the temperature may be treated as a constant and so no kinetic equation additional to that for the order parameter is necessary. For materials which do not conduct heat so well, we may need a second equation to determine the temperature distribution. Therefore the interphase boundary motion can be determined by the rate of heat transfer in the system. In a recent review [14] our theory of the kink motion of the interphase boundary [16, 18, 19] has been examined. The necessity to consider processes of dissipation of energy released or absorbed during the time of transition has been pointed out in [14].

This paper concerns the effect of the dynamics of a phase transition, specifically the dynamics of a propagating interface on the degree of order in a phase. We also consider

the inversional problem: how the order in a phase can affect the dynamics of an associated transition and in particular on its growth rate. We obtain a criterion of necessity to consider the heat transfer effect on the interphase boundary propagation. Thus, we justify the conditions when only the Ginzburg–Landau equation may be used to study the kinetics of phase transformations. We show here that at first-order phase transitions in ferroelectric semiconductors the thermal conductivity is not a controlling process and the interface movement is determined by the kinetics of the phase transition. As an example the electric field dynamics of interphase boundaries are considered for the case when they are governed by the polarization evolution.

The electric-field driven kinetics of ferroelectric interphase boundaries have not been studied up to now. We estimate conditions of the applicability of the mean-field Landau theory for the study of the ferroelectric–paraelectric phase transition in low electric fields. We discuss how the volume strain-induced elastic energy contribution leads to existence of the threshold electric field in the phase transition investigated. We start our analysis with the discussion of the conditions when the propagation rate of the phase transition front is determined only by a non-activated process. For this purpose we compare the velocities of interphase boundary conditioned by heat transfer and by relaxation kinetics. The velocity of the interface caused by the latent heat transfer may be found from the following considerations. The heat flowing across the interphase boundary is  $k\nabla T S \Delta t$ , where  $k$  is the thermal conductivity coefficient,  $\nabla T$  is the temperature gradient,  $S$  is the square of the area of the interface and  $\Delta t = \Delta R/v_T$ , where  $\Delta R$  is the change of size of the new phase during the interface motion with a velocity  $v_T$ . This heat per unit mass is the latent heat  $L = k\nabla T \Delta V / \Delta m v_T$ , where  $\Delta m / \Delta V$  is the density,  $\rho$ . Thus, the propagation rate of the phase transition front due to the latent heat transport is given by

$$v_T = \frac{k\nabla T}{\rho L}. \quad (1)$$

The velocity of the interphase boundary movement caused by the kinetic process  $v$  was calculated in [16]. It has been derived from the time-dependent Ginzburg–Landau equation (GL) with  $\Gamma$ , the Landau–Khalatnikov kinetic coefficient, independent of temperature. The free energy  $F$  may be written in the Landau-type form:

$$F(P) \int \left( D(\nabla P)^2 + \frac{1}{2}A(T)P^2 - \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + f_{coupl}\{P, \epsilon_{\alpha\beta}\} + f_{elast}\{\epsilon_{\alpha\beta}\} \right) dV \quad (2)$$

where  $V$  is the volume,  $D$  is the inhomogeneity coefficient,  $B$  and  $C$  are constants,  $A = A'(T - T_0)$ ,  $T_0$  is the stability limit of the paraelectric phase,  $A'$  is a constant and  $\epsilon_{\alpha\beta}$  are the strain tensor components. As was discussed in [7, 8] the  $f_{coupl}$  is the additional free energy describing the coupling of polarization and strain. This  $f_{coupl}$  contains terms which are proportional to  $P^2$  and only affect the  $T_0$  value.  $f_{elast}$  is the elastic free energy that does not influence the relaxation kinetics of the phase transformation because it is polarization-independent and does not contribute to the GL equation. We will use experimental values for  $T_c - T_0$  that already account for the coupling contributions and which renormalize the coefficient  $A$  from equation (2). Here  $T_c$  is the Curie temperature.

For a moving phase transition front the GL equation holds at the interphase boundary provided the interphase boundary width,  $\Delta$ , is considerably greater than the interatomic distances. This equation cannot be solved exactly in the three-dimensional case but if the size,  $R$ , of clusters of the new phase inside the old one is much larger than the width of the interphase boundary  $\Delta$ ,  $R \gg \Delta$ , the exact solution can be obtained [16]. Thus, the theory works at  $R \gg \Delta \gg d$ , where  $d$  is the lattice parameter.

Now the relation between a critical size,  $R_c$ , of the product transformed region and the growth rate,  $v$ , can be established. The profile for the front may be found from the exact solution of the GL equation in the equilibrium limit. The spatial dependence of the polarization  $P(r)$  is approximately given by [16]:

$$\begin{aligned} P &= P_F & (|r| \leq R) \\ P &= (P_F/\sqrt{2}) \left[ 1 - \tanh\left(\frac{r-R}{2\Delta}\right) \right]^{1/2} & (R \leq r \leq R + \Delta) \\ P &= 0 & (|r| \geq R + \Delta) \end{aligned} \quad (3)$$

where  $P_F^2 = (B/2C)[1 + (1 - 4AC/B^2)]$ . Equation (3) gives a radial symmetric cluster of the nucleating phase embedded in a spatially uniform metastable background. Using (3) and integrating in (2) for  $R \gg \Delta$  one obtains

$$F = -\frac{4\pi R^3 f(P_F)}{3} + \frac{\pi R^2 D P_F^2}{\Delta} + \frac{4\pi R^3 Q}{3} \quad (4)$$

where  $Q$  is the elastic energy density and  $f(P_F)$  is the density of the free energy given by the GL functional.

From (4) it is seen that the surface tension  $\sigma = DP_F^2/4\Delta$ . The last term in equation (4) is the result of integration of  $f_{elast}(\epsilon_{\alpha\beta})$  over volume in the assumption that  $\epsilon_{\alpha\beta}$  are independent of  $r$ .

According to the classical theory of nucleation, the new phase nucleus whose radius corresponds to the maximum of the free energy is the critical nucleus  $R_c$ . Let us suppose that  $Q \ll f(P_F)$ . Then neglecting the third term in equation (4) after maximization we derive

$$R_c = \frac{6D}{\Delta|4A - BP_F^2|}. \quad (5)$$

Combining the interface velocity [18] and (5) we obtain

$$v = \frac{4\Gamma D}{R_c}. \quad (6)$$

The propagation of the interphase boundary is determined by the kinetics of the order parameter, if  $v_T \gg v$ . Comparing the velocity of the interphase boundary from [18] and (6) and supposing that  $\nabla T \approx (\Delta T/R_c)$ , where  $(\Delta T)$  is the supercooling or superheating, one obtains that this criterion is fulfilled for

$$\gamma = \frac{k\Delta T}{4\rho L\Gamma D} \gg 1. \quad (7)$$

This condition does not depend on the critical size  $R_c$ . Let us check the criterion for ferroelectric perovskite semiconductors for which many measurements of interphase boundary dynamics have been carried out [2–6, 9–14]. We used the following experimental values, which are typical for  $ABO_3$  ferroelectric perovskites:  $L = 8.96 \times 10^6 \text{ erg g}^{-1}$  ( $50 \text{ cal mol}^{-1}$ ) [23],  $k = 11 \times 10^{-3} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$  [24],  $\rho = 5.9 \text{ g cm}^{-3}$  [24],  $\Gamma = 1.61 \times 10^{10} \text{ Hz}$  [12],  $D = 3.3 \times 10^{-16} \text{ cm}^2$  [18],  $\Delta T = 0.25 \text{ K}$  [12],  $A' = 9.09 \times 10^{-6} \text{ K}^{-1}$  [18],  $B = 1.27 \times 10^{-12} \text{ esu}$  [25],  $C = 5.73 \times 10^{-23} \text{ esu}$  [25] and  $T_c - T_0 = 43 \text{ K}$  [26]. The required ratio is then about 100. Thus, the heat transfer process is more rapid than the kinetics of the order parameter relaxation. For this reason, the latter process determines the interface propagation in the above ferroelectric semiconductors. Consequently, the release of the latent heat of the phase transition does not play an important role in the dynamics of interphase boundaries in the perovskites under consideration.

However, if  $\gamma \approx 1$ , the two processes must be taken into account. The theory of the kink-type motion for interphase boundaries [16, 18, 19] is suitable for perovskite ferroelectric semiconductors because the criterion (7) is fulfilled. This is due to the comparatively high thermal conductivity and comparatively low latent heat.

As was mentioned above the velocity of relaxation growth may be obtained in a compact form of equation (6) if the condition  $Q \ll f(P_F)$  is fulfilled. The density of the homogeneous strain energy for typical perovskite ferroelectric–paraelectric phase transition (cubic–tetragonal structure transformation) is given by

$$Q = 0.5C_{11}^0 (\epsilon_{xx}^2 + \epsilon_{yy}^2 + \epsilon_{zz}^2) + C_{12}^0 (\epsilon_{xx}\epsilon_{yy} + \epsilon_{yy}\epsilon_{zz} + \epsilon_{zz}\epsilon_{xx}) + 0.5C_{44}^0 (\epsilon_{xy}^2 + \epsilon_{xz}^2 + \epsilon_{yz}^2) \quad (8)$$

where  $C_{11}^0$ ,  $C_{12}^0$  and  $C_{44}^0$  are the elastic constants of the paraelectric phase. Assuming only uniform deformation we may neglect the non-uniform inhomogeneous contribution to the elastic energy. At the same time we may assume that  $\epsilon_{xy} \sim \epsilon_{xz} \sim \epsilon_{yz} \sim 0$ . This is confirmed, for example, by the first-principles calculations for BaTiO<sub>3</sub> (see for example [7]). As follows from [7] the values of  $\epsilon_{xx}$ ,  $\epsilon_{yy}$  and  $\epsilon_{zz}$  are of the same order, thus we use their equality in estimations. Under these conditions and using the definition of  $\epsilon_{\alpha\alpha}$  ( $\alpha = x, y, z$ ) and the Clausius–Clapeyron equation we obtain

$$\epsilon_{\alpha\alpha} = \frac{dT_c}{dp} \frac{L}{3\Omega T_c}. \quad (9)$$

Here  $p$  is pressure, and  $\Omega$  is a primitive cell volume. The density of the elastic energy is then given by

$$Q = \frac{1}{2} \left( \frac{dT_c}{dp} \right)^2 B \left( \frac{L}{\Omega T_c} \right)^2 \quad (10)$$

where  $B$  is the bulk modulus.

Let us analyse the situation for the ferroelectric phase transition in a low electric field when the approximation of the linear response may be used. In this case the relaxation kinetics of polarization also dominate the thermal conduction-driven mechanism for motion of the phase transition front. For instance in [27] the front velocity is  $10^{-3}$  cm s<sup>-1</sup> even at an electric field of  $E = 300$  V cm<sup>-1</sup>. Thus, the criterion (7) is fulfilled. The appearance of a nucleus of the new phase results in a free energy change which is given by

$$-\frac{4\pi R^3 E P_F}{3} + \frac{4\pi R^3 Q}{3} + 4\pi R^2 \sigma$$

in the linear field approximation, where  $\sigma$  includes both the electric field induced and the elastic terms. The first term was introduced in [28]. The second term presents the volume strain energy contribution [29]. Comparing the densities  $E P_F$  and  $Q$  in the above mentioned way one may estimate when it is possible to neglect  $Q$ . In the ferroelectric semiconductors under investigation the polarization charge at the interphase boundary can be easily compensated so that the depolarization energy is much smaller in comparison with the elastic energy [3] and may be neglected in our consideration. Then after maximization we derive

$$R_c = \frac{2\sigma}{P_F(E - E_c)}$$

where  $E_c = Q/P_F$ . The latter formula reflects the fact that at first-order phase transitions the volume and shape change associated with the transition cause a strain energy contribution to the free energy suppressing the nucleation process [30]. Thus, we arrived at an electrical

modification of the known Laplace formula [31] in which  $(P_F E - Q)$  yields the difference between the pressures in the two phases. To find the velocity of the interface motion in the presence of  $E - E_c$  in the linear field approximation, we should compare the power lost by the system due to damping and the power input, i.e. the work per time unit done by the electric force. Using the dynamic form of the front profile (3) [16], calculating  $\partial F/\partial t$ , integrating and equating the powers we obtain

$$v = \frac{2\Gamma D P_F (E - E_c)}{\sigma}. \quad (11)$$

Equation (11) implies that the interphase boundary would move if the electric field is larger than the threshold electric field  $E_c$ . This result is known from measurements of velocities of the electric field-induced motion of ferroelectric interphase boundaries in SbSI [32] and domain walls in BaTiO<sub>3</sub> [33], Rochelle salt [34] and NaNO<sub>2</sub> [35]. Observations in [32] indicated the existence of some critical value of the electric field below which the boundary did not react to the presence of the electric field. The boundary began to move in fields somewhat larger than the critical value. In [33–35],  $v \propto (E - E_c)$ .

The present study of criterion for separating two mechanisms for the front motion—the latent heat transfer and the relaxation of the order parameter—provides an encouraging test of the accuracy of the theory of the kink-type motion for interphase boundaries [16, 18, 19] for perovskite ferroelectrics. Fulfilling the criterion obtained emphasizes the dominating process of the order-parameter relaxation in the dynamics of perovskite phase transition fronts due to relatively high thermal conductivity of ABO<sub>3</sub>-type perovskites. It is anticipated that it will be very important to study the strain contributions in kinetics of ferroelectric–paraelectric phase transitions in perovskites, which should clarify the role of stress and stress anisotropy in this process. The study of electrical field response in phase transition kinetics demonstrates the method of application of the proposed approach.

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