Delayed Nucleation at a Weakly First-Order Transition

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The dynamics of the transformation out of a nonequilibrium metastable phase is discussed within a mean-field theory at temperatures below the transition temperature T_c. We show that fluctuations are important and lead to an unusual time dependence of the order parameter, in particular a sharp delay time for the onset of the stable phase. This model is applied to the dynamics of the paraelectric to ferroelectric transition in $BaTiO_3$ where the mediating forces arise from long-range strain fields.

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The dynamics of nucleation at a first-order transition is a venerable problem which has received much study over the years, particularly in the context of liquid-gas transitions.[1,2] In models with *short-range* interactions one considers nucleation and growth of domains whose size is determined by a competition between the volume-dependent free energy of transformation and a surface-energy cost.[1] In models with *long-range* interactions (e.g., when the order parameter is coupled to strain)[3] the latter becomes a volume-dependent term, and there is no meaningful critical radius.

An appropriate model to discuss nucleation from a metastable state in this case is a mean-field (infinite range) model, for example the double-well (soft-spin Ising) model with spin variable ϕ_i at site i in a field h, with the Hamiltonian

$$H/k_BT=\sum_i\{a[-\tfrac{1}{2}\phi_i^2+\tfrac{1}{4}\phi_i^4]-h\phi_i+\tfrac{1}{2}K(\phi_i-\bar{\phi})^2\}, \quad (1)$$

where $\bar{\phi}=(1/N)\sum_i\phi_i$. Conventionally, one assumes that fluctuations of ϕ_i about the mean $\bar{\phi}$ are small within mean-field theory, so that one can describe dynamics by an equation of motion for a single degree of freedom of the form $\dot{\bar{\phi}}=-\partial F/\partial\bar{\phi}$, where $F(\bar{\phi})$ is a Landau free-energy expansion.[4] Here we show that fluctuations in ϕ_i can be large, even within mean-field theory and at low temperatures, and that they lead to an unusual time dependence of the transformation with an apparent "delay time" before a sudden transformation out of a metastable phase. A straightforward extension of the double-well model allows us to compare our results to experiments in $BaTiO_3$ (where long-range strain coupling is known to be important). Recent measurements[3] have shown dramatic deviations from the behavior of traditional models for nucleation and growth.[1,2,4]

We assume that the transformation is slow enough that local thermal equilibrium is maintained, in which case the dynamical evolution of the system is governed by a Fokker-Planck equation.[5] At low temperature ($a\gg1$), we may assume a thermal distribution within each of the wells,[5] with an individual spin occupying the spin-down well (A) with probability p and the spin-up well (B) with probability $1-p$. Expanding the energy about the three extrema in the form $H(\phi)=H_J+\frac{1}{2}a_J(\phi-\phi_J)^2$ for $J=A,B,C$, where ϕ_C is the maximum, we have

$$dp/dt=-(\Gamma/2\pi)(-a_C)^{1/2}[a_A^{1/2}pe^{-(H_C-H_A)}-a_B^{1/2}(1-p)e^{-(H_C-H_B)}]. \quad (2)$$

We choose an initial state with $p=1$ and $h>0$, but as the spin-up state (B) acquires a small occupation, the barrier H_C-H_A is reduced, while H_C-H_B increases (see inset to Fig. 1) and the nucleation accelerates. The usual (hard-spin) Ising model is recovered by our letting $a\to\infty$, when Eq. (2) takes the familiar form

$$d\bar{\phi}/dt=\tilde{\Gamma}[(1-\bar{\phi})e^{(h+K\bar{\phi})}-(1+\bar{\phi})e^{-(h+K\bar{\phi})}], \quad (3)$$

where $\tilde{\Gamma}=(\Gamma a/\pi\sqrt{2})\exp(-\frac{1}{4}a+\frac{1}{2}K)$. While this equation is not new,[6] to our knowledge it has only ever been studied close to T_c ($K\approx1$), and with relaxation in a *single* well. At *low* temperatures ($K\gg1$), for $h<K$, the spin-down state $\bar{\phi}\approx-1$ is stable, but for $h>K$ it decays to the spin-up state. An asymptotic solution (valid for $\phi\lesssim0$) for the decay is

$$\bar{\phi}(t)=-1-(1/K)\ln(1-t/t_0),$$

where $t_0\sim(2K\tilde{\Gamma})^{-1}e^{-(h-K)}$.

Although the overall time scale is very long at low temperatures, the feedback from the mean field $K\bar{\phi}$ has a dramatic effect on the *shape* of the transformation curve. For large K, numerical integration of Eq. (3) confirms[7] that $\phi(t)$ has a steplike shape, with an apparent "delay

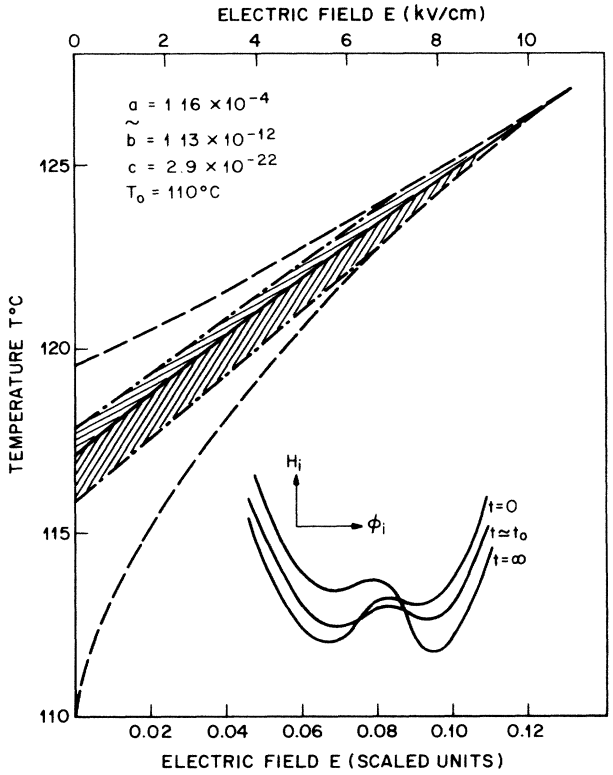

FIG. 1. Phase diagram for the cubic (paraelectric) to tetragonal (ferroelectric) transition in $BaTiO_3$ from Eq. (4), with data of Ref. 3. The solid line marks the phase boundary and the hatched regions are the regions of true metastability of the nonequilibrium phases for $\gamma=0.1$ and $\xi/a_0=70$. Inset: A schematic picture of the evolution of the local free energy with time.

time" t_0 for the transformation. An infinite-range model will always have a region in which the metastable state will never transform (in this case $h < K$). In finite-range models, the decay time of a metastable state will diverge exponentially with the range of interaction in this region (see, e.g., Griffiths *et al.*, Ref. 6).

We now generalize the model to study nucleation from the paraelectric to ferroelectric state in $BaTiO_3$. The static properties of the ferroelectric transitions in $BaTiO_3$ are well described by a Landau theory for the coupled order parameters of the polarization (P) and strain (s).[8] We consider here the high-temperature cubic (paraelectric) to tetragonal (ferroelectric) transition in a finite electric field E, neglecting transverse fluctuations. Thus, we take both P and s to be scalars, with s the uniaxial strain. The free energy (per unit volume) is written as[8]

$$F(P,s)=\tfrac{1}{2}a(T-T_0)P^2+\tfrac{1}{4}bP^4+\tfrac{1}{6}cP^6 - EP+\tfrac{3}{2}c_e s^2-qsP^2. \quad (4)$$

Here T_0 is the Curie temperature, E is the electric field, and $c_e=\frac{1}{2}(c_{11}-c_{12})$ is the shear elastic modulus. The coefficient b is positive; in the absence of coupling to strain a second-order transition at a temperature T_0 is expected. Equation (4) implies that polarization fluctuations are accompanied by spontaneous strain. The long-range strain interactions are approximated here by an infinite-range model, and we write for the total energy

$$F=V_0\textstyle\sum_i[F(P_i,s_i)+\frac{1}{2}K(S_i-\bar{s})^2]. \quad (5)$$

The subscript refers to individual "nuclei," each of volume $V_0=\xi^3$, and $\bar{s}=(1/N)\sum_i s_i$ is the average strain. The last term in Eq. (5) couples the individual strain fields to the average stress in the system so that $K\approx c_e$. We assume that the characteristic length scale for order-parameter fluctuations is given by ξ, comparable to the order-parameter correlation length $\xi_0\sim(T-T_0)^{-1/2}$ (measurements of the static dielectric constant indicate[8] that $\xi_0/a_0\sim 50$–100 close to T_c, with a_0 the lattice constant). Because we do not allow for any evolution of the distribution of nucleus sizes, our results (in particular the overall time scales) will be sensitive to our choice of ξ.[9]

Assuming that the *local* strain and polarization are strongly coupled, we solve for s_i and write the free energy in the form $F=\sum_i F_i(\phi_i)$, with a scaled variable $\phi_i=P_i/P_0$ and $P_0^2=-\tilde{b}/c$:

$$F_i=f_0[\tfrac{1}{2}\tilde{a}\phi_i^2-\tfrac{1}{4}\phi_i^4+\tfrac{1}{6}\phi_i^6-e\phi_i+\tfrac{1}{4}\gamma(\phi_i^2-\bar{\phi}^2)^2]. \quad (6)$$

Here $f_0=V_0cP_0^6$, and $\tilde{a}=a(T-T_0)/cP_0^4$;

$$\gamma=(1/cP_0^2)[2Kq^2/3c_e(3c_e+K)]\lesssim 0.5$$

for the parameters appropriate to $BaTiO_3$.[3,8] The coupling to strain renormalizes the fourth-order coefficient to be *negative* so that the transition is driven first order even with Landau theory (although weakly first-order behavior would be expected even if this were not the case).[4,10] The phase boundary can be crossed by application of a pulsed electric field at a temperature $T > T_c$. If fluctuations are neglected, no transition occurs until the spinodal line $e_s(T)$ (marked by the dashed line in Fig. 1) is crossed. Because of the large correlation length the energy scale is in the range $f_0/k_BT\sim 3\times10^3$–2×10^4, close to T_c. However, since $\tilde{a}$ is small close to T_c, the barrier height in the absence of coupling (i.e., $\gamma=0$) is of order $f_0\tilde{a}^2\sim(T-T_0)^{1/2}$ and is comparable to T_c, as should be expected. For finite γ, the barrier (and the relative heights of the two wells) is proportional to γf_0, which is large in comparison to thermal energies, and the *effective* temperature is low. Consequently, the previous analysis can be followed up to Eq. (2), but with use of the coarse-grained free energy F_i [Eq. (6)] instead of H_i and solving for $\bar{\phi}^2$ self-consistently. The rate constant Γ is also reduced and should be of order $\omega_0(a_0/\xi)^3$, with an optical phonon frequency ω_0 setting the microscopic scale.

Figure 2 shows the results of the numerical solution of Eq. (2) with the free energy of Eq. (6) for a sequence of electric field pulses at a temperature $T=116\,^\circ$C and for

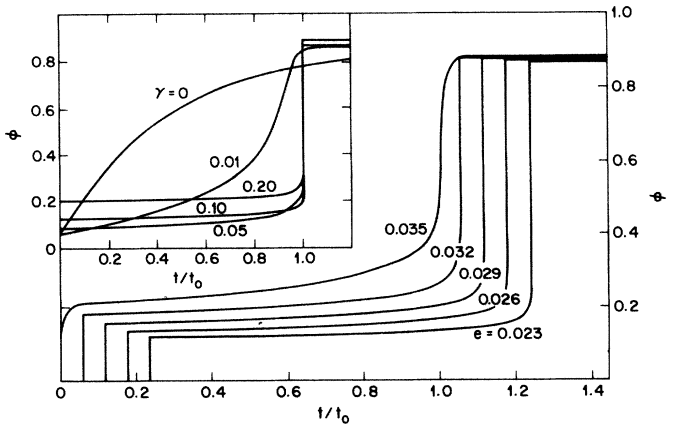

FIG. 2. Time evolution of the average polarization $\bar{\phi}$ for a sequence of electric fields e at a temperature $T=118\,^{\circ}\mathrm{C}$ for $\gamma=0.1$ and $\xi/a_0=70$. (The curves are displaced for clarity.) Inset: The change in shape of the curves for different γ at a fixed ratio $e/e_c=1.05$ (e_c is the boundary of the metastable region). Time is measured in units of the "delay time" t_0, which varies by several orders of magnitude between different curves.

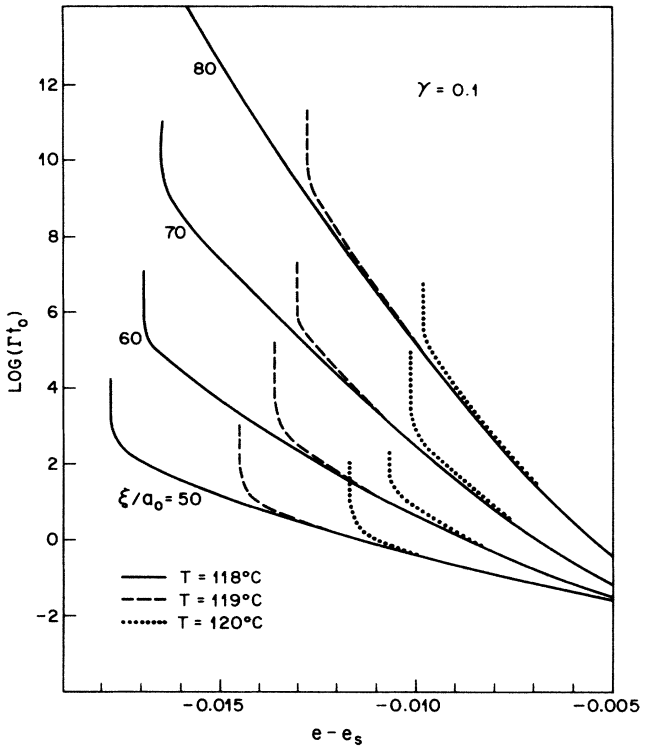

FIG. 3. Variation of the delay time t_0 with electric field for different values of ξ/a_0 and temperature. Fields are measured relative to the "spinodal" $e_s(T)$, marked by the dashed line in Fig. 1.

a value of $\xi/a_0=70$, with $\gamma=0.1$ The time in each case is scaled by the delay time t_0, which varies approximately exponentially with field in the form $t_0\simeq\exp(-e/e^*)$ over a sizable range (Fig. 3) in contrast to the power-law dependence of the time scale seen in the simple Landau theory.[4] The characteristic field e^* varies approximately inversely with the product γf_0; we believe that this accounts for the experimental observation that e^* *decreases* with hydrostatic pressure,[3] because the transition is being driven toward a tricritical point, increasing ξ and hence f_0.

The apparent phase diagram is changed in this model. For $\gamma=0.1$, above a temperature $T\approx 123\,^{\circ}\mathrm{C}$ (but still below the critical point) F_i [Eq. (6)] has only a single minimum, and the transition will not occur in the bulk until the "spinodal" line is crossed. The behavior in this region will be similar to that of the single-parameter mean-field theory which has been studied previously, and where a smoother time dependence than the steplike form of Fig. 2 is expected.[4] There are regions of the phase diagram in which the nonequilibrium phases are truly metastable ($t_0=\infty$) (shown by hatching in Fig. 1), which depend strongly on the value of γ. For smaller values of f_0/k_BT these regions are reduced as can be seen by inspection of Fig. 3. For increased γ, the boundary of the infinitely metastable regime moves to lower temperatures and larger fields; for $\gamma\geq 1$ the whole region above T_0 is metastable, and the conventional single-parameter theory is recovered (provided, of course, that $f_0/k_BT\gg 1$).

The measurements of McWhan *et al.*[3] are consistent with values of γ and ξ/a_0 of about 0.1 and 60–70, respectively, both well within their estimated range. The experimental range of t_0 is rather less than two decades, and so detailed comparison is difficult on account of uncertainties in the fit of the phase diagram. Note that the time scale of Fig. 3 is already considerably longer than microscopic time scales ($\sim 10^{-13}$ sec), because of the large correlation length. Delay times of the order of milliseconds are easily obtained.

We have considered here only the change in nucleation rate as the transformation proceeds. Once the ferroelectric state drops in energy *below* the paraelectric state the nuclei will be able to grow and the Kolmogorov-Avrami picture[2] will then be appropriate if the growth velocity is large enough. Indeed, a model of a constant nucleation rate provides a good description of the pressure-induced transition in RbI,[11] although these experiments were made on powder samples. Note that temperature quenching through the transition can be quite different because of the presence of domains of the three orthogonal orientations; these can screen the strain field at large distances, at the cost of large local stresses, a situation familiar in martensitic phase transitions.

In conclusion, we have presented a model for nucleation at a first-order transition in which the mediating forces are long range. We find that the long-range force induces a cooperative nucleation process, and that this feedback mechanism produces a well-defined delay time for the onset of nucleation which depends exponentially on the overdriving electric field, consistent with experi-

ment in $BaTiO_3$. We believe that the model has more general application, in that similar results will be obtained for any double-well model with a long-range coupling term.

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