Paraelectric and Ferroelectric States in a Model for Relaxor Ferroelectrics

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We study the free energy landscape of a minimal model for relaxor ferroelectrics. Using a variational method which includes leading correlations beyond the mean-field approximation as well as disorder averaging at the level of a simple replica theory, we find metastable paraelectric states with a stability region that extends to zero temperature. The free energy of such states exhibits an essential singularity for weak compositional disorder pointing to their necessary occurrence. Ferroelectric states appear as local minima in the free energy at high temperatures and become stable below a coexistence temperature $T_c$. We calculate the phase diagram in the electric field-temperature plane and find a coexistence line of the polar and non-polar phases which ends at a critical point. First-order phase transitions are induced for fields sufficiently large to cross the region of stability of the metastable paraelectric phase. These polar and non-polar states have distinct structure factors from those of conventional ferroelectrics. We use this theoretical framework to compare and to gain physical understanding of various experimental results in typical relaxors.

I. INTRODUCTION

The unusual linear and nonlinear dielectric response of relaxor ferroelectrics make them both technologically important and scientifically remarkable.¹⁻⁵ Typical relaxors such as PbMn$_{1/3}$Nb$_{2/3}$O$_3$ (PMN) and PbZn$_{1/3}$Nb$_{2/3}$O$_3$ (PZN) show extended regions of fluctuations (often called diffuse phase transitions) with several special energy scales: for temperatures above the so-called Burns temperature $T_B$ their dielectric constant follows the Curie-Weiss law with a characteristic Curie-Weiss temperature $T_{CW}$. Below $T_B$, it deviates from the Curie-Weiss behavior and reaches a broad, frequency dependent maximum at a temperature $T_{max}(\omega)$ without any signature of a global broken symmetry.⁶⁻¹¹ $T_{max}(\omega)$ follows the Vogel-Fulcher law.¹² At low temperatures, no macroscopic structural changes are observed¹³,¹⁴ unless large enough electric fields are applied, which reveal an additional energy scale $T_\epsilon$.¹⁵⁻¹⁸ Very significantly, neutron scattering experiments observe the onset of elastic diffuse scattering at a temperature $T^*$ with unusual temperature dependence.¹⁹⁻²² and non-Lorentzian line shapes.²² It is found that $T^* \approx T_{CW}$ within experimental uncertainty.²¹,²³ Under static conditions, $T_\epsilon$ and $T^*$ are the only temperature scales observed in elastic X-ray and neutron scattering experiments.²¹,²²,²⁴ Solid solutions of relaxors with conventional ferroelectrics such as PbMn$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ (PMN-PT) and PbZn$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ (PZN-PT) also show relaxor behavior for small PT content and well defined ferroelectric transitions for sufficiently large PT.²⁵⁻²⁷ Transitions of structurally distinct ferroelectric phases across a morphotropic phase boundary occur for intermediate PT concentrations.²⁸⁻³²

Though relaxors were first synthesized more than 50 years ago,³³,³⁴ and several models have been proposed to describe their dielectric behavior,³⁵⁻⁴⁰ several aspects of their properties are not well understood. A common problem is that it is difficult to assign the parameters of a model to their characteristic temperatures in a universal fashion.¹ An additional difficulty has been to identify the ground state or glassy metastable states of relaxors due to their skin effect. For PMN, a cubic-to-rhombohedral distortion is observed at about $T_c$ in the near-surface region (the skin) while the bulk remains cubic down to low temperatures.²⁴,⁴¹ The skin is macroscopically large (a few tens of micrometers) and thus it is not clear whether the skin or the bulk is in a thermodynamic stable state. Similar skin effects have been observed in PZN,⁴² PMN-PT and PZN-PT.⁴³,⁴⁴

Compositional disorder is essential to observe relaxor behavior.⁴⁵ In the heterovalent relaxor PMN, for instance, disorder arises from the different charge valencies and atomic radii of Mg$^2+$ and Nb$^3+$ on the octahedrally coordinated site.¹ Such disorder leads to (i) quenched random electric fields and (ii) quenched random bonds.⁴⁵ It is expected that (i) introduces effects similar to those in magnets with quenched random magnetic fields⁴⁷,⁴⁸ while (ii) is the classic ingredient of spin glasses if the bonds are frustrated.⁴⁹ If they are not, this is the random local transition temperature model in Landau theory of phase transitions.⁵⁰ Quite generally, it is understood in the theory of phase transitions that fields which couple linearly to the order parameter affect the properties much more strongly than random bonds which couple to the order parameter quadratically. This point has been appreciated in connection with relaxors.¹ Therefore, the effects of (i) must be understood before including (ii). Experiments on the non-ergodic behavior of relaxors,¹⁸,⁴⁶,⁵¹ their skin effect,⁴²,⁴¹,⁴⁴ and their structure factors²¹,²² provide support for this view as similar effects have been observed in magnets with quenched random fields.⁵²,⁵³
The purpose of this paper is to study the effects on quenched electric random fields in a simple displacive model with which conventional ferroelectrics were first understood.\textsuperscript{54,55} This model was recently used in Ref. [56] to show that the broad region of fluctuations (a hallmark of relaxors) is the result of dipolar interactions (already present in the displacive model) acting together with compositional disorder. This point can be appreciated from the fact noted by Onsager,\textsuperscript{37} that due to intrinsic fluctuations a model with dipolar interactions alone has no phase transition down to the lowest temperature. Similar models with further extensions have been studied earlier, however, they have almost exclusively been studied by numerical methods.\textsuperscript{37,38} Analytic solutions often help in finding general features of the solution, therefore we consider the minimal model of Ref. [56]. Though by no means exhaustive, this analysis allows an analytic account of microscopic aspects of the physics of relaxors. In this paper we introduce a method more general than that used in Ref. [56] and also study the effects of static applied electric fields.

The essential physical points in the simplest necessary solution of the model are to formulate an approximation which considers thermal and quantum fluctuations at least at the level of the Onsager approximation,\textsuperscript{57} and treats compositional disorder at least at the level of a replica theory.\textsuperscript{58} Here, we do so with a variational method which extends the self-consistent phonon approximation\textsuperscript{59} to incorporate disorder.\textsuperscript{60} This variational method leads to the self-consistent equations of the earlier approximation, but also allows us to explore the energy landscape and the competition between states with and without spontaneous polarization. We show that there are metastable paraelectric states in the free energy that persist down to zero temperature. Within our approximation, the free energy of the disordered state exhibits an essential singularity for weak disorder. Ferroelectric states appear as local minima in the free energy above a coexistence temperature $T_c$ and become stable below it. We calculate the electric field-temperature ($E - T$) phase diagram for moderate disorder and find a coexistence line of the polar and non-polar phases which ends at a critical point. First-order phase transitions are induced for fields sufficiently strong to cross the stability line of the metastable paraelectric phase. These ordered and disordered states are unusual, as their structure factors differ from those of conventional ferroelectrics.

This paper is organized as follows: in Sections II and III we present our model Hamiltonian and variational solution, respectively; the results and discussion are presented in Section IV; and a comparison to experiments is provided in Section V. A summary and conclusions are given Section VI.

### II. MODEL HAMILTONIAN

We consider the model for relaxor ferroelectrics of Ref. [56] and add an applied field. We focus on the relevant transverse optic mode configuration coordinate $u_i$ of the ions in the unit cell $i$ along the polar axis (chosen to be the $z$-axis). $u_i$ experiences a local random field $h_i$ with probability $P(h_1, h_2, ...)$ due to the compositional disorder. The model Hamiltonian is

$$H = \sum_i \left[ \frac{\Pi_i^2}{2M} + V(u_i) \right] - \frac{1}{2} \sum_{i,j} v_{ij} u_i u_j - \sum_i h_i u_i - E_0 \sum_i u_i, \quad (1)$$

where $\Pi_i$ is the momentum conjugate to $u_i$, $M$ is an effective mass, and $E_0$ is a static applied electric field. We assume the $h_i$'s are independent random variables with Gaussian probability distribution with zero mean and variance $\Delta^2$,

$$P(h_1, h_2, ...) = \prod_i \frac{1}{\sqrt{2\pi}\Delta^2} e^{-\frac{1}{2} (\frac{h_i}{\Delta})^2}, \quad (2)$$

$V(u_i)$ is an anharmonic potential,

$$V(u_i) = \frac{\kappa}{2} u_i^2 + \frac{\gamma}{4} u_i^4, \quad (3)$$

where $\kappa$, $\gamma$ are positive constants. $v_{ij}$ is the dipole interaction,

$$v_{ij} / e^2 = \begin{cases} 3 \left( \frac{Z_i - Z_j}{R_i R_j} \right)^2 - \frac{1}{|R_i - R_j|^2}, & R_i \neq R_j, \\ 0, & R_i = R_j, \end{cases} \quad (4)$$

where $e^*$ is the effective charge and $Z_i$ is the $z$-component of $R_i$.

The Hamiltonian of Eq. (1) presents long ranged (anisotropic) dipolar interactions, compositional disorder, and anharmonicity. We do not consider cubic symmetry, coupling to strain fields and disorder in the bonds $v_{ij}$ expected in relaxors.\textsuperscript{1,35,37,38} As we stated above, our purpose is to study the effects of quenched random fields alone in a displacive model for ferroelectrics.

### III. VARIATIONAL SOLUTION

In this section, we present a variational framework to study the statistical mechanics of the problem posed by the Hamiltonian (1).

We consider a trial pair-probability distribution,

$$\rho^{tr} = \frac{1}{Z^{tr}} e^{-\beta H^{tr}}, \quad (5)$$

where $H^{tr}$ is the Hamiltonian of coupled displaced harmonic oscillators in a random field,

$$H^{tr} = \sum_i \frac{\Pi_i^2}{2M} + \frac{1}{2} \sum_{i,j} (u_i - p)G_{i,j} (u_j - p) - \sum_i h_i u_i, \quad (6)$$
and \( Z^{tr} \) its normalization,
\[
Z^{tr} = \text{Tr} e^{-\beta H^{tr}} = \left( \prod_q \left[ 2 \sinh \left( \frac{\beta \Omega_q}{2} \right) \right]^{-1} \right) \times \left( \prod_{i,j} e^{\frac{\beta \hbar \gamma_i \gamma_j}{2} \psi_i \cdot \psi_j + \beta \hbar \gamma_i} \right).
\]
(7)

Here, \( p \) is an uniform order parameter: it is the displacement coordinate averaged over thermal disorder \((\ldots)\) first, and then over compositional disorder \((\ldots)\),
\[
p = \langle u_i \rangle = \int_{-\infty}^{\infty} dh_1 dh_2 \cdots P(h_1, h_2, \ldots) \text{Tr} \rho^{tr} u_i. \quad (8)
\]

In the standard variational scheme of the self-consistent phonon approximation, the Fourier transform of the function \( G^{-1}_{i-j} \) is the frequency of the transverse optic mode \( M_{ij} = \sum_{i,j} e^{iq(R_i-R_j)} \) at wavevector \( q \). We define \( G^{tr-1}_{i-j} = (1/N) \sum_q (M^{tr}_{ij}q^2)^{-1} e^{-iq(R_i-R_j)} \) where the summations over \( q \) extend over the first Brillouin zone. \( p \) and \( \Omega_q \) are variational parameters and are determined by minimization of the free energy.

Using Eqs. (1)-(8), we calculate the free energy, \( \bar{F} = \langle H \rangle + T(k_B \ln \rho^{tr}) \). The result is given as follows,
\[
\frac{\bar{F}}{N} = \frac{k}{2} \left[ p^2 + \eta + \Delta^2 \psi \right] + \frac{\gamma}{4} \left[ p^4 + 6p^2 \Delta^2 \psi + 3\Delta^2 \psi^2 + 6\eta \left\{ p^2 + \Delta^2 \psi \right\} + 3\eta^2 \right]
- \frac{1}{2N} \sum_q v_q^2 \frac{\hbar}{2M \Omega_q} \coth \left( \frac{\beta \Omega_q}{2} \right) - \frac{1}{2} \frac{v_0^2}{\Omega_0^2} - \frac{1}{2N} \sum_q v_q^2 \frac{\Delta^2}{(M^{tr}_{ij}q^2)^2}
- \frac{1}{2} \frac{\Omega_0^2}{\Omega_0^2 - E_0 p}
- \frac{1}{4N} \sum_q \hbar \Omega_q \coth \left( \frac{\beta \Omega_q}{2} \right) + \frac{k_B T}{N} \sum_q \ln \left[ 2 \sinh \left( \frac{\beta \hbar \Omega_q}{2} \right) \right].
\]
(9)

where \( v_q/(ne^2) = 1/(ne^2) \sum_{i,j} v_{ij} e^{iq(R_i-R_j)} = \frac{4\pi}{3} \left( 1 - 3a^2 \right) - \zeta |q|^2 + 3\zeta (q_0 a)^2 \) is the Fourier component of the dipole interaction \( v_{ij} \) for cubic lattices in the long-wavelength limit; \( \zeta \) is a dimensionless coefficient that depends on the structure of the lattice;\(^6\) \( a \) is the lattice constant; and \( v_0^2 = 4\pi ne^2/3 \) the \( q = 0 \) component of \( v_q \) in the direction transverse to the polar axis (\( v_q \) is non-analytic for \( q \rightarrow 0 \)). \( \eta \) are mean squared fluctuations averaged over compositional disorder,
\[
\eta = \left\langle (u_i - \langle u_i \rangle)^2 \right\rangle = \frac{1}{N} \sum_q \frac{\hbar}{2M \Omega_q} \coth \left( \frac{\beta \Omega_q}{2} \right),
\]
(10)
and \( \psi \) is defined as follows,
\[
\psi \equiv \frac{1}{N} \sum_q \frac{1}{(M^{tr}_{ij}q^2)^2}.
\]
(11)

We have ignored terms independent of \( p \) and \( \Omega_q \) in Eq. (9).

Minimization of the free energy with respect to \( p \) and
\[
\Omega_q \text{ gives the result,}
\]
\[
E_0 = \left[ M(\Omega_0^2) - 2\gamma \right] p \quad (12a)
\]
\[
M(\Omega_0^2) = \left( M(\Omega_0^2) - \eta \right) \quad (12b)
\]
\[
M(\Omega_0^2)^2 = \kappa + 3\gamma \left[ \eta + \Delta^2 \psi + p^2 \right] - \eta_0^2. \quad (12c)
\]

Equations (12a)-(12c) together with Eqs. (10) and (11) are self-consistent equations that determine the temperature dependence of the zone-center soft mode \( \Omega_0^2 \) and the order parameter \( p \). The temperature dependence of \( \Omega_q \) is determined through \( \Omega_q^2 \). For \( E_0 = 0 \) and \( p = 0 \) they correspond to those derived in Ref. [56]. For no disorder \( (\Delta = 0) \), they correspond to those of the self-consistent phonon approximation for pure ferroelectrics.

We now compute the structure factor \( S_q \). The structure factor is obtained from the Fourier transform of the correlation functions \( \langle u_i u_j \rangle \). With the help of Eqs. (5)-(7), we obtain the following result,
\[
S_q = p^2 \delta_q + \frac{\hbar}{2M \Omega_q} \coth \left( \frac{\beta \hbar \Omega_q}{2} \right) + \frac{\Delta^2}{(M^{tr}_{ij}q^2)^2},
\]
(13)
where \( p, \Omega_q \) are given by Eq. (12). This expression corresponds to the structure factor derived in Ref. [56].
with an additional contribution from the order parameter $p$. We identify the correlation length $\xi$ from the structure factor of the pure system: in the classical limit and for no compositional disorder, we recover the structure factor for conventional ferroelectrics, $S_\mathbf{q} = p^2 \delta_\mathbf{q} + k_B T / (M_0^2 \omega_\mathbf{q})$, with $M_0^2 \omega_\mathbf{q} = \frac{v_0^2 \zeta_0^2}{4\pi^2} \left( \xi^{-2} + |\mathbf{q}|^2 \right)$ for wavevectors $\mathbf{q}$ in the $x$ and $y$ directions. We recognize $\xi$ as the correlation length

$$\xi/a = \sqrt{\frac{\zeta(4\pi/3)}{M_0^2 \omega_\mathbf{q}^2 / v_0^2}}, \tag{14}$$

which diverges at the onset of the ferroelectric transition for the pure system.

IV. RESULTS AND DISCUSSION

A. No Applied Electric Field, $E_0 = 0$.

Figures 1 (a)-(b) show the temperature dependence of the order parameter and the the zone-center transverse optic frequency obtained from Eq. (12) for $E_0 = 0$. For no disorder, we obtain the well-known results of the self-consistent phonon approximation: a paraelectric-to-ferroelectric second order phase transition at a critical temperature $T_c^0$ with a transverse optic phonon frequency that softens as $(\Omega_0^2)^2 \propto |T - T_c^0|$, with logarithmic corrections. For finite disorder, ordered states with opposite polarization appear below a superheating temperature $T_1 < T_c^0$ (only the state with positive polarization is shown). The paraelectric states persist down to zero temperature for small $((\Delta^2/\omega_0^2))/(k_B T_c^0) \lesssim 0.01$ and moderate disorder $(0.01 \lesssim (\Delta^2/\omega_0^2))/(k_B T_c^0) \lesssim 0.02)$. For small disorder, we now show that the non-polar states have an essential singularity: for $T = 0$ and $p = 0$, we solve in the classical limit the Euler-Lagrange equations (12) for the zone-center transverse optic mode frequency,

$$M(\Omega_0^2) = \frac{3\gamma}{2} \left( A_0/v_0^4 \right) \left( \Delta^2/\omega_0^2 \right) B^2 Q^2 \times W_0 \left[ \frac{4B^4Q^4v_0^4}{(3\gamma/2) (A_0/v_0^4)} (\Delta^2/\omega_0^2) e^{v_0^4} \right], \tag{15}$$

Here, $W_0(z)$ is the zeroth branch of the Lambert function,$^{65}$

$$A_0/v_0^4 \equiv (1/N) \sum_q (v_0^4 - v_0^4)^{-1} = \left( 4\pi/\sqrt{3} \right) B Q^{-1}, \quad B^2 = \frac{(\zeta_0^2)/4\pi^2}{\Delta^2}, \quad k_B T_c^0 = \left( v_0^4 - \gamma \right) / (3\gamma_0 A_0/v_0^4),$$

and $Q$ is a wavevector cut-off. Using that for $W_0(z) \sim z + O(z^2)$ for $z \to 0$, we obtain in the limit of small disorder,

$$M(\Omega_0^2) \approx \left( 4B^2 Q^2 v_0^4 e^{-1} \right) \left[ 0.5 \left( \frac{k_B T_c^0}{\Delta^2} \right) \right], \tag{16}$$

which is an essential singularity. This points to the necessary occurrence of non-polar states with a stability region that extends to zero temperature. First-order phase transitions are expected, nonetheless, as the paraelectric state is close to a saddle point in the free energy for small disorder and well below $T_1$, as shown in Fig. 1.

![Fig. 1. (Color online) Temperature dependence of (a) the order parameter $p$ and (b) the zone-center soft mode frequency $\Omega_0^2$. Inset: Temperature dependence of the correlation length $\xi$. There is an essential singularity for small compositional disorder. Solid lines correspond to stable and metastable states. Dashed lines correspond to a saddle point in the free energy. Here, $h/(M v_0^4 a^4)^{1/2} = 4.5 \times 10^{-6}$, $(v_0^4 - v_0^4) = 1.98 \times 10^{-3}$, $\gamma a^2/v_0^4 = 1.98 \times 10^{-1}$, $k_B T_c^0/v_0^4 a^2 = 5.70 \times 10^{-5}$. These model parameters were obtained from fits to transition temperature, Curie-Weiss constant, polarization, and phonon dispersion of PT at $\Delta = 0.63,64$](https://example.com/f1.png)

Fig. 2 shows the free energy landscape $(p, \Omega_0^2)$ for several temperatures. For $T > T_1$ the paraelectric phase is stable. At $T_1$, ordered ferroelectric states appear as local minima. At a temperature $T_2 < T_1$ there is a coexistence region of disordered and ordered states. For $T < T_2$, the ordered states are stable and the disordered state is metastable down to $T = 0$. Two saddle points with opposite polarization appear at $T_1$. The temperature dependence of these saddle points is shown by the dashed line in Figs. 1 (a)-(b).

The temperature dependence of the correlation length $\xi$ is shown in the inset of Fig. 1 (b). For finite disorder, $\xi$ remains finite at all temperatures in the disordered
states, though it becomes very large for weak disorder as a consequence of the essential singularity (16). For the ferroelectric states, $\xi$ grows as it approaches the superheating temperature $T_1$.

Figure 4 shows the temperature-disorder phase diagram. Paraelectric metastable states extend from the coexisting temperature $T_c$ down to zero temperature for small and moderate disorder. First-order phase transitions are expected in the small disorder regime since the saddle points in the free energy are very close to the metastable paraelectric states at low temperatures, as stated above. For intermediate disorder, no transition occurs for $T \rightarrow T_c$: the saddle and paraelectric points remain well separated (see Fig. 1) Nucleation of polar domains may occur within the paraelectric phase as stable ferroelectric states are present in the free energy. For large disorder $((\Delta^2/\nu_0^0)/(k_B T_c^0) \gtrsim 0.02)$, there is only a global paraelectric minimum in the free energy, as shown in Fig. 3.

B. Applied Electric Field, $E_0 > 0$.

Figures 5 (a)-(b) show the temperature dependence of the order parameter and the zone-center transverse optic frequency obtained from Eq. (12) for finite applied fields and moderate compositional disorder. For clarity, only the states with polarization parallel to $E_0$ are shown. For small field strengths $E_0 a/(k_B T_c^0) \lesssim 0.002$, the paraelectric states acquire a tiny polarization parallel to $E_0$ and persists down to zero temperature. The stable ferroelectric state does not change significantly from that without applied fields. For moderate field strengths $0.002 \lesssim E_0 a/(k_B T_c^0) \lesssim 0.007$, first-order phase transitions are induced as the the paraelectric states merges with the saddle point in the free energy.
Upon increasing $E_0$, the transition smears out for fields greater than a critical field $E_c$, $E_c a/(k_B T_c) \approx 0.007$, thus revealing a critical point. The free energy landscape for moderate disorder is shown in Fig. 6.

Figure 7 shows the $E-T$ phase diagram for moderate disorder. The coexistence line $T_c$ ends at the critical point $(E_c, T_c)$ above which the transition is smeared out. The spinodal curves $T_0$ and $T_1$ indicate the end of the stability region of the paraelectric and ferroelectric phases, respectively. As opposed to pure ferroelectrics where it is observed that the spinodal curve $T_0$ of the paraelectric phase is close to the coexistence line and crosses the $T$-axis, $T_0$ extends to zero temperature and does not cross the abscissa for finite disorder.

V. COMPARISON TO EXPERIMENTS

We compare our model with experiments in PMN and PMN-PT.

A. No applied electric field, $E_0 = 0$

In the absence of applied electric fields and for moderate compositional disorder, our model shows that there is no symmetry-breaking down to low temperatures, as observed in PMN. This disordered state is metastable and is not that of a simple paraelectric, as their structure factors are distinct, see Eq. (13).

We now estimate the Curie-Weiss temperature $T_{CW}$ and Curie-Weiss constant $C_{CW}$ for PMN from our model. By calculating the inverse dielectric susceptibility of our model, $\chi^{-1} = M (\Omega_0^2/\nu_0)^2/(k_B T_c) \approx 0.014$ (see Sec. V B), we estimate by linear extrapolation that $T_{CW} \approx 300 \text{K}$ and that $C_{CW} \approx 5 \times 10^5 \text{K} (T_c \approx 720 \text{K})$. This $T_{CW}$ is lower than the observed value ($\gtrsim 400 \text{K}$) but it is consistent with a temperature higher than $T_c$. The calculated $C_{CW}$ is slightly higher than that of experiments ($\approx 1.2 \times 10^5 \text{K}$). As opposed to $T_c$ and $T_1$, we find that $T_{CW}$ does not correspond to any special temperature in the free energy of our model: it
FIG. 6. (Color online) Contour plots of the free energy for moderate disorder and moderate applied electric fields. (a) For high temperatures there is a global paraelectric minimum with a polarization parallel to $E_0$. (b) At a temperature $T_1(E_0)$ a ferroelectric metastable state appears with a polarization parallel to $E_0$. (c) At $T_2(E_0)$, the paraelectric and ferroelectric states coexist. (d) Below $T_3(E_0)$, the paraelectric state becomes a local minimum while the ferroelectric state is now stable. (e) For low temperatures, a new local ferroelectric minimum appears in the free energy with polarization opposite to $E_0$. Free energies are measured with respect to global minimum in units of $k_B T_e^0$. Here, $(\Delta^2/\nu_0^2)/(k_B T_e^0) = 0.018$ and $E_0 a/(k_B T_e^0) = 0.003$. 

$T = 0.2 T_c$ 

$T = 0.16 T_c$ 

$T = 0.15 T_c$ 

$T = 0.13 T_c$ 

$T = 0$
is simply the onset temperature of critical fluctuations of polarization of a paraelectric state which do not undergo a phase transition.

Well defined ferroelectric transitions are observed in PMN-PT with sufficiently large PT content (≥ 30%). This is consistent with our model as transitions to polar stable states are expected for small disorder \((\Delta^2/v_0^c)/(k_B T_c^0) \gtrless 0.010\). From Fig. 4, we find that \(T_c/T_c^0 \approx 0.48\) (or \(T_c \approx 350\) K) for \((\Delta^2/v_0^c)/(k_B T_c^0) = 0.010\). This is slightly lower but consistent with the observed transition temperature of about 400 K in PMN-PT with 30%PT.

B. Applied electric field, \(E_0 > 0\)

In comparing to experiments in PMN in the presence of applied fields, we must distinguish between the observed behavior of the skin and that of the bulk. Since the skin is macroscopically large (a few tens of micrometers) we compare our model to the skin and the bulk separately.

We first compare to the skin of PMN. Our model shows that there is a field induced first-order phase transition for applied fields that are large enough to cross the stability limit of the paraelectric phase, see Fig. (7). Upon increasing the applied field, the transition smears out above a critical field \(E_{cr}\), as observed in PMN\(^{17}\). We can estimate \(E_{cr}\) from our model: by fitting the superheating temperature \(T_1\) to that of field-cooled-zero-field-heating experiments in PMN \((T_1 \approx 210\) K\),\(^{15,18}\) we find that the corresponding disorder strength is of about \((\Delta^2/v_0^c)/(k_B T_c^0) = 0.014\), according to Fig. 4. For this disorder strength, the transition is smeared at about \(E_{cr}a/(k_B T_c^0) = 0.004\), which corresponds to about 5 kV/cm.\(^{68}\) This is close to the observed value of about 4 kV/cm.\(^{17}\) Morphotropically distinct ferroelectric phases are observed in the skin of PMN-PT for PT concentrations of about 30–35%\(^{28–31}\). We cannot discuss this effect within our approximation as we do not consider cubic symmetry.

We now compare to the bulk of PMN. Bulk PMN does not go through any macroscopic structural phase transition under applied fields,\(^{24}\) which is in disagreement with our model. We believe this discrepancy arises because we ignore coupling to strain fields. Despite there is no observation of global broken symmetries, neutron scattering experiments reveal a smooth peak in the diffuse scattering upon application of an electric field precisely at about \(T_c \approx 200\) K\(^{24}\). This is suggestive of clamping effects\(^{69}\) for which there are two possible scenarios: (i) the bulk is clamped and remains in the metastable disordered state while the skin can relax to access the stable states with spontaneous polarization; or (ii) clamping effects are such that the disordered phase is stable down to \(T = 0\) and the skin is in a metastable ordered state. Previous theoretical studies consider coupling to acoustic modes but do not address this point.\(^{37,38}\)

VI. CONCLUSIONS

We have studied the effects of quenched random fields in a simple displacive model for ferroelectrics using a variational method. We show that for small and moderate disorder there are metastable paraelectric states in the free energy with a stability region that extends to zero temperature. For small disorder, these states exhibit an essential singularity in their free energies. Ferroelectric states appear as local minima below a superheating temperature \(T_1\) and above a coexisting temperature \(T_c\). Below \(T_c\), the ferroelectric states become stable. No global symmetry breaking occurs for moderate disorder as the saddle points and disordered states remain well separated down to zero temperature. First-order phase transitions are induced for electric fields large enough to cross the stability limit of the paraelectric phase. These paraelectric and ferroelectric states have distinct structure factors from those of conventional ferroelectrics.

Based on our results, we present our view of the static thermodynamic behavior of heterovalent relaxors. Pure relaxors such as PMN and PZN are in a stable paraelectric state for temperatures above \(T_c\); below \(T_c\), they remain in a metastable disordered state with a stability region that extends down to zero temperature. Nucleation of local polar domains within the non-polar phase may occur as there are stable ferroelectric states in the free energy. First-order transitions are induced for applied fields large enough to cross the stability region of the metastable paraelectric phase. Upon increasing the applied field, the coexisting region approaches a critical point. The paraelectric and ferroelectric states are not those of conventional ferroelectrics as their structure factors differ. \(T_{CW} (\approx T^*)\) is the onset temperature.
of critical fluctuations of polarization of a paraelectric state which does not undergo a phase transition. It does not correspond to a special temperature in the free energy within the variational solution of our model. Ferroelectric transitions occur in PMN-PT and PZN-PT with sufficiently large PT content as they fall in the weak disorder regime where the metastable disordered state is close to an instability point.

We suggest that clamping effects are responsible for the lack of macroscopic symmetry breaking in the bulk of PMN and PZN upon application of electric fields. Extensions of this model to incorporate cubic symmetries and coupling to acoustic phonons are needed to validate or refute this point.

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