

Electric-field dependent freezing in relaxor ferroelectrics

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The concept of polar nanoregions (PNRs) in relaxor ferroelectrics has recently been discussed in several numerical and theoretical studies for the special case of barium zirconate-titanate $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (BZT). Here we present a semiphenomenological model of relaxation in BZT and related systems in order to show that the correlation radius of a PNR is determined by the condition that the surrounding medium undergoes a local phase transformation into a correlated polar state. The model describes the growth and percolation of the PNRs on lowering the temperature or under the application of an electric field, leading to a generalized Vogel-Fulcher-type dielectric relaxation time. It is suggested that the above condition might be applied to discriminate between the relaxor state and the analogous dipolar glass state.

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I. INTRODUCTION

Relaxor ferroelectrics (relaxors) are inorganic as well as organic compositionally disordered ferroelectric systems, which are characterized by strong frequency dispersion and a broad temperature peak of the dielectric permittivity, and by the absence of spontaneous ferroelectric long range order at all temperatures [1,2]. In view of their excellent dielectric, electrostrictive, and piezoelectric properties relaxors have long been of special interest for numerous practical applications, especially in electromechanical [3,4] and electrocaloric devices [5,6]. Typical representatives of inorganic relaxors are mixed ABO_3 perovskites, such as lead magnesium niobate $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ or PMN and mixed barium zirconate-titanate $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ or BZT in the concentration range $0.25 \lesssim x \lesssim 0.75$ [7]. Since the ionic charges of Zr^{4+} and Ti^{4+} in BZT are the same, this system is an example of isovalent relaxors. BZT has recently been the subject of several theoretical [8–12] and experimental [13–16] studies. In particular, in Ref. [8] it has been shown by means of Monte Carlo simulations based on a first-principles model of BZT ($x = 0.5$) that below $T \sim 250$ K the so-called polar nanoregions (PNRs) represented by areas of correlated Ti displacements appear, and on further lowering the temperature they grow in size and gradually coalesce into larger entities. Moreover, it has been argued [8] that contrary to common belief random electric fields and random strains are not needed to explain the microscopic origins of relaxors.

In a subsequent paper [9], it was shown that when an electric field is applied at fixed temperature, the PNRs also grow in size along the field and percolate through the sample. Similarly, strain-induced rotation and elongation of the PNR dipoles as well as an increase of the PNR size has been predicted to occur in epitaxial BZT films [10]. Recently, it has been argued [11,12] that the onset of PNRs and ergodicity found in first-principles-based simulations can be understood by mapping the system on a soft pseudospin glass model.

Relaxors share many common features with the dipolar glasses (DGs) [1,2], the latter being a physical realization of fixed-length reorientable electric dipoles randomly distributed in a dielectric medium. Actually, there are binary systems

that can show either relaxor or DG behavior depending on the concentration x of the constituents, for example, $\text{CuInP}_2(\text{S}_x\text{Se}_{1-x})_6$ [17], and in fact BZT has also been claimed to be a DG for concentrations $0.45 < x < 0.75$ [14,16].

From a microscopic point of view, a distinction between DGs and relaxors appears to be trivial. Namely, in DGs one is dealing with randomly interacting individual dipoles, whereas in relaxors some clustering of the dipoles occurs, giving rise to the above-mentioned PNRs [18]. This view is supported by the probability distribution of local polarization $W(p)$, which can be measured by NMR; it has a Gaussian shape at all temperatures in relaxors [19], but develops two or more side peaks in DGs at low temperatures [20,21]. This behavior can be quantitatively explained by the random bond–random field (RBRF) model in the case of DGs [22], and by the spherical random bond–random field (SRBRF) model for relaxor ferroelectrics [23].

On the other hand, the actual probability distribution of dielectric relaxation times $f(\log \tau)$, as extracted from the complex permittivity by the Tikhonov regularization method [24], shows a single-peak structure in DGs, whereas in relaxors it develops a second peak at low temperatures [21,25,26]. This suggests that the relaxation processes in relaxors may be more complex than in DGs, as realized in the framework of the extended polarizability model of ferroelectricity in perovskites [27]. In this way the two-component relaxation can be related to the flipping and breathing of the PNRs, corresponding to the in-gap local modes and discrete breathers in the anharmonic lattice model [28,29]. Recent neutron scattering experiments on PMN with 30% PT (PMN-30PT) by Manley *et al.* [30] have established the existence of in-gap localized phonon modes as the origin of PNRs, thus confirming the predictions of the lattice dynamical model of relaxors [27–29].

Both in DGs and relaxors [26], the longest relaxation time diverges on approaching the freezing temperature T_0 according to the Vogel-Fulcher (VF) law, namely,

$$\tau = \tau_0 \exp[U/(T - T_0)], \quad \text{for } T > T_0, \quad (1)$$

and $\tau = \infty$ for $T \leq T_0$. This means that ergodicity is effectively broken at $T = T_0$ both in DGs and in relaxors, although the relaxation mechanism in the two cases may not be the same. The first application of Eq. (1) to relaxors

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was for the ceramic system PMN with 10% PT (PMN-10PT) by Viehland *et al.* [31], who also discussed how the leading edge of $f(\log \tau)$ extends towards macroscopic times as T_0 is approached from above.

It has also been found empirically that in relaxors a macroscopic ferroelectric domain state can be induced by applying a sufficiently large electric field, whereas in prototypical DGs this could not be achieved [14,20,32]. It should also be noted that in 1994 Dai *et al.* [33] studied the spontaneous relaxor to normal ferroelectric transition in 12/40/60PLZT and concluded that the relaxor state differs from a dipolar or spin glass state in that at low temperatures the long-range ordered state in a relaxor is thermodynamically achievable due to a competition between short- and long-range order. The above considerations suggest that the existence of PNRs in relaxors might be instrumental for the appearance of a field-induced long range ordered ferroelectric state, but not in DGs where the response is due to uncorrelated single dipoles.

In the present paper, we formulate a quantitative thermodynamic criterion in terms of a phenomenological Landau model for the polarizable medium into which the elementary dipolar entities in relaxors (i.e., PNRs) and in DGs (isolated fixed-length dipoles) are embedded. Specifically, we will show that the growth of PNRs in relaxors is due to a local phase transformation occurring in the medium within a certain correlation volume, which is a function of temperature and of the applied field. On the other hand, in DGs the polarizability of the medium does not allow a local phase transition into a correlated polarization cloud to occur, and a different freezing mechanism is needed.

II. MECHANISM OF GROWTH OF POLAR NANOREGIONS

In the following we consider a typical perovskite relaxor such as BZT. On a microscopic scale, three distinct types of chemical regions can be identified, namely, those corresponding to clusters of (i) barium titanate (BTO), (ii) barium zirconate (BZO), and (iii) mixed BTO-BZO regions. In a schematic picture, an isolated BTO region will be represented by a spherically shaped PNR, which is embedded in a polarizable dielectric medium, i.e., a BTO-BZO region. Let us assume that the PNR is fully polarized inside a core radius r_0 , but its dipolar density falls off with distance according to the theory of diffusion-limited aggregation [34]. Thus at large distances the density is expected to obey the universal power law [34] $P(r) \sim r^{-\alpha}$, and we can write

$$\vec{P}(r) = \vec{P}_0 \left(\frac{r_0}{r} \right)^\alpha, \quad \text{for } r > r_0, \quad (2)$$

and $\vec{P}(r) = \vec{P}_0$ for $r \leq r_0$. For illustration purposes, we will choose in the following the trial value $\alpha = 3$, which has been found earlier to reproduce the empirically observed behavior [35]. Also, we will consider only one polarization component, say, $P = P_z$.

The Landau free energy density of the medium in the BTO-BZO region at some distance r from the PNR center can be written as

$$f = \frac{1}{2}ap^2 + \frac{1}{4}bp^4 + \frac{1}{6}cp^6 + \dots - gpP - pE, \quad (3)$$

where p is the polarization of the medium and g the coupling [36] between p and the PNR polarization cloud P , and E is the external field. We will assume that the PNR is oriented along the direction of the field; however, it should be noted that this assumption may be valid only for sufficiently strong fields [9]. In general, the coefficients a, b, c, \dots, g may depend on the concentration x .

In a paraelectric medium, the first coefficient in Eq. (3) is given by

$$a = \frac{T}{\Theta}, \quad (4)$$

where $\Theta = \Theta(x)$ is the Curie constant, and the coupling g is essentially a local-field factor.

The equilibrium condition $(\partial f / \partial p)_T = 0$ leads to the relation

$$ap + bp^3 + cp^5 - h = 0, \quad (5)$$

where we have introduced an effective field

$$h = gP(r) + E. \quad (6)$$

Equation (5) can be solved numerically; however, only those solutions that correspond to stable minima of Eq. (3) are relevant. Therefore, to eliminate any unstable solutions, $p(h, T)$ has been determined by direct numerical minimization of the free energy (3).

The behavior of $p(h, T)$ will crucially depend on the sign of the coefficient b . If $b > 0$, the solutions $p(h, T)$ simply increase with h and decrease with T , as expected for a normal paraelectric medium. On the other hand, for $b < 0$ and an infinitesimally small value of h a jump in $p(T)$ occurs. This corresponds to a local first-order field-induced phase transition from a paraelectric to a ferroelectric state, in which the Ti dipoles are correlated with the core of the PNR. The solutions $p(h, T)$ for the case $b < 0$ are shown in Fig. 1 for $b = -1/3$,

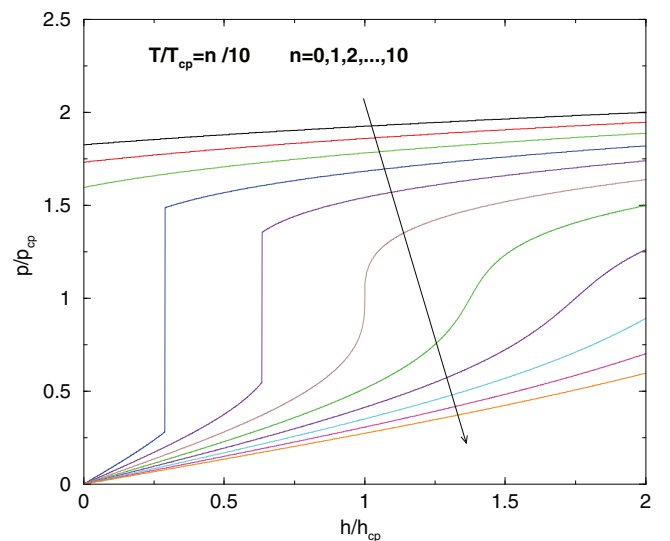


FIG. 1. (Color online) Polarization of the medium as a function of effective field h/h_{cp} for several values of temperature, calculated by numerical minimization of the free energy. p_{cp} , h_{cp} , and T_{cp} are values of polarization, field, and temperature at critical point, respectively.

$c = +1/3$, $0 \leq T/T_{cp} \leq 2$, and h in the range $0 \leq h/h_{cp} \leq 2$, where the scale parameters T_{cp} and h_{cp} are specified below. As h increases, the jump in p decreases, and eventually vanishes at a critical point (cp), where the derivative $(\partial p/\partial a)_E$ diverges. This is analogous to the occurrence of a critical point in normal ferroelectrics as well as in relaxors [37–39]. The value of a at the critical point is $a_{cp} = 9b^2/20c$, corresponding to a critical temperature $T_{cp} = (9b^2/20c)\Theta$, whereas the polarization p_{cp} and the field h_{cp} are given by [37,39]

$$p_{cp} = \left(\frac{3|b|}{10c}\right)^{1/2}, \quad h_{cp} = \frac{6b^2}{25c} p_{cp}. \quad (7)$$

For the above values of b and c we find $p_{cp} = 0.548$ and $h_{cp} = 0.0438$. For $T > T_{cp}$ and/or $h > h_{cp}$ the medium is in a “supercritical” state, characterized by a continuous evolution of $p(h, T)$, where the Ti dipoles are essentially uncorrelated with the PNR core.

Since h depends on the distance r according to Eqs. (6) and (2), we can define a correlation radius r_c such that for $r \leq r_c$ the Ti dipoles are part of the PNR, i.e., they remain correlated with the PNR core, but for $r > r_c$ they are uncorrelated and thus part of the paraelectric medium. Thus r_c is a measure of the size of the PNR. At a given temperature, r_c corresponds to the field $h_1(T)$ at which the field-induced first-order phase transformation into a polarized state occurs. From Eqs. (2) and (6) we have the relation

$$gP_0r_0^3/r_c^3 + E = h_1(T). \quad (8)$$

The function $h_1(T)$ can be found numerically by determining the value of h at which a jump of p appears for a given value of T (see Fig. 2). It turns out that $h_1(t)$ can be rather well approximated by a linear function

$$h_1(T)/h_{cp} \cong \kappa_0(T - T_m)/T_{cp}, \quad \text{for } T > T_m, \quad (9)$$

and $h_1 = 0$ for $0 \leq T \leq T_m$. For the above values of b and c we find $T_m/T_{cp} \cong 0.418$ and $\kappa_0 \cong 1.72$.

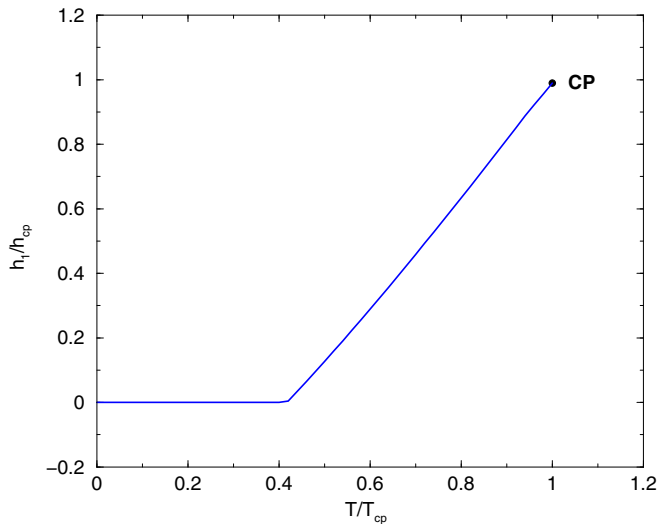


FIG. 2. (Color online) Relation between effective field h_1 and temperature T at first order phase transitions, evaluated numerically from the positions of polarization jumps (see Fig. 1). CP: critical point.

The corresponding correlation volume $v_c = 4\pi r_c^3/3$ can now be written in the form

$$v_c = v_0 \frac{gP_0}{\kappa(T - T_m) - E}, \quad (10)$$

where $v_0 = 4\pi r_0^3/3$ is the core volume and $\kappa = \kappa_0 h_{cp}/T_{cp}$. As T approaches the value

$$T_m(E) = T_m + E/\kappa, \quad (11)$$

the correlation volume formally diverges; physically this means that a single PNR has reached the size of the system. Thus T_m is just a symbolic minimum temperature and, as discussed below, the relevant parameter limiting the growth of PNRs is the volume fraction occupied by a cluster of PNRs, which diverges in the percolation limit.

In principle, one can have $r_c > r_0$ only when the condition $T < T_{cp}$ is satisfied. Obviously, for $T \geq T_{cp}$ the PNR volume is limited by the core radius r_0 and no growth can occur.

The above estimate for the size of a PNR is based on the strong condition that a local phase transition into a field-induced ferroelectric phase should occur at a given distance (i.e., radius) from the PNR center. Such a transformation is only possible when the Landau coefficient b of the medium is negative. In general, we can distinguish between two cases: (i) $b < 0$ corresponding to relaxors, where the growth of PNRs is possible, and (ii) $b > 0$ representing any other systems, tentatively the DGs, where the medium remains uncorrelated with the isolated dipoles at all temperatures and fields. A negative value of the coefficient b in relaxors is likely due to the strong electrostrictive coupling between the polarization and lattice strains [39].

III. PERCOLATION OF POLAR NANOREGIONS IN RELAXORS

As the temperature is lowered or the electric field increased, the volume of the PNRs increases according to Eq. (10) and a connected polar cluster is gradually formed. The volume fraction η occupied by the PNRs is given by the sum over all correlation volumes v_c divided by the total volume V , namely,

$$\eta = \frac{g[v_0 P_0]_{av}}{\kappa(T - T_m) - E}, \quad (12)$$

where the average is defined as the sum over all PNRs per unit volume, i.e., $[v_0 P_0]_{av} = \sum_i^N v_0^i P_0^i / V$. Obviously, the minimum value of η is $\eta_{min} = [v_0]_{av}$; this corresponds to a limiting temperature

$$T^*(E) = T_m + \frac{g[v_0 P_0]_{av}}{\kappa[v_0]_{av}} + E/\kappa. \quad (13)$$

The second term can be estimated as $\sim g\bar{P}_0/\kappa$ with $\bar{P}_0 = \sum_i^N P_0^i / N$ representing the average core polarization. Thus, for $T > T^*(E)$, the medium is effectively uncorrelated with the PNRs.

In general, at a given value of E the correlation exists for $T_m(E) < T < T^*(E)$, as illustrated in Fig. 3. In this correlation region the volume will increase with decreasing temperature and when η reaches a threshold value η_p , the PNRs will form an “infinite” percolation cluster. This occurs at a percolation

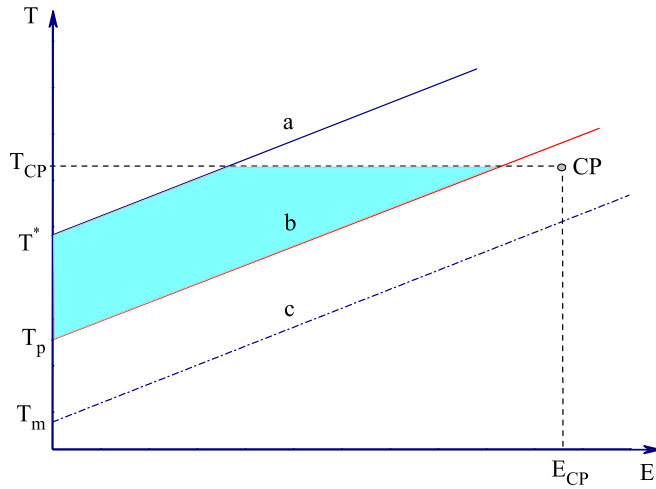


FIG. 3. (Color online) Schematic presentation of the correlation region between lines (a) and (c), and $T < T_{cp}$, $E < E_{cp}$. Shaded area: cluster growth region. The lines are as follows: (a) $T^*(E)$, Eq. (13); (b) $T_p(E)$, Eq. (14); (c) $T_m(E)$, Eq. (11). CP: critical point.

temperature

$$T_p(E) = T_m + \frac{g[v_0 P_0]_{av}}{\kappa \eta_p} + E/\kappa. \quad (14)$$

The value of η_p is close to $\eta_p \sim 0.3$ for a number of theoretical models [35]. It was shown by Viehland *et al.* [40] that quasielastic neutron scattering data for PMN-10PT reveal a temperature dependent correlation length, which was found to increase on lowering the temperature and saturate near the freezing temperature. Subsequently, an analogous result was reported by Jeong *et al.* [41] for PMN, where the mean cluster volume was observed to saturate at a value $\eta \sim 0.3$ at low temperatures, in agreement with the above estimate for η_p from percolation theory.

As η approaches η_p the mean cluster volume increases according to the power law [42]

$$v = \frac{\bar{v}_0}{(1 - \eta/\eta_p)^\gamma}, \quad (15)$$

where $\bar{v}_0 = \sum_i^N v_0^i/N$ is the average core volume. The exponent γ depends on the dimensionality and structure of the lattice [9] and has the value $\gamma = 1$ for mean field systems [42], which we adopt here. Since $[v_0]_{av} \ll 1$ and $\eta_p \sim 0.3$, we conclude that $T_m(E) < T_p(E) < T^*(E)$ (see Fig. 3).

The reorientation time for overturning a large magnetic cluster, or in our case a percolation cluster of PNRs with volume v , is given by the Néel formula [35,43]

$$\tau = \tau_0 \exp(v Q_{an}/kT), \quad (16)$$

where Q_{an} is the anisotropy factor and τ_0 the inverse attempt frequency. Inserting v from Eq. (15) and using the relations(14)–(16) we obtain after some rearranging the result:

$$\tau = \tau_0 \exp \left\{ w_1 \frac{Q_{an} \bar{v}_0}{kT} + w_2 \frac{Q_{an} \bar{v}_0}{k[T - T_p(E)]} \right\}. \quad (17)$$

Here we have introduced two weighting factors

$$w_1 = \left(\frac{E_m}{E_p + E_m} \right), \quad w_2 = \left(\frac{E_p}{E_p + E_m} \right), \quad (18)$$

with $E_m \equiv E + \kappa T_m$ and $E_p \equiv g[v_0 P_0]_{av}/\eta_p$.

The exponent in Eq. (17) contains two terms as follows. The first of these corresponds to a standard Arrhenius-type relaxation process with a potential barrier $U_1 = w_1 Q_{an} \bar{v}_0$, which exists even in zero field. The second process describes a Vogel-Fulcher-type relaxation with a field-dependent VF temperature $T_0(E) = T_p(E)$ and potential barrier $U_2 = w_2 Q_{an} \bar{v}_0$.

When the dipolar relaxation occurs in the presence of a bias field E , the energy difference between the states parallel and antiparallel to the field gives rise to an asymmetry parameter $A = p_{dip} E$, where p_{dip} is the total dipole moment of the system. Thus the dielectric relaxation time $\tau_d(E)$ acquires an additional factor, i.e., $\tau_d(E) = \tau/[2 \cosh(A)]$ [44]; however, the extra field dependence due to this factor is much weaker than that of the singular VF term in the exponent of Eq. (17), and can be ignored as T approaches $T_p(E)$.

Note that at a fixed value of E the relaxation time for the PNR cluster is given by Eq. (17), which is valid in the temperature range $T_p(E) < T < T^*(E)$, i.e., in the cluster growth region (see Fig. 3). When $T \leq T_p(E)$, however, Eq. (17) is not applicable and the corresponding relaxation time for this relaxation channel is infinite. This simply means that the percolating PNR cluster cannot rotate any more, but some alternative relaxation processes may, of course, still be active. On the other hand, for $T > T^*(E)$ the growth of the correlation radius is not possible and some alternative relaxation mechanism should be considered (see the following section).

The electric-field dependence of the VF temperature T_0 has been studied experimentally in relaxor ferroelectric ceramics 9/65/35PLZT [45] and in PMN [111] single crystal [46]. In PLZT, at small field values a weak variation of the VF temperature $T_0(E)$ with E was found, but for $E > 4$ kV/cm a stronger increase with E was observed. The nonlinear E dependence of $T_p(E)$ could be attributed to an extra field dependence of the core polarization $P_0(E)$, which is related to the nonlinear dielectric susceptibility χ_3 [45]. Another possibility is that in real systems the PNR polarization does not align along the field unless the field exceeds a certain threshold value E_{tr} [9]. Thus it seems that, in PLZT, $E_{tr} \sim 4$ kV/cm, but for $E > E_{tr}$ the relaxation time may increase faster than linearly with E , in qualitative agreement with Eq. (14) (see Fig. 4).

Earlier experiments in PMN-10PT ceramics [47] revealed a field dependence of $T_0(E)$, which initially decreases with E until a minimum at $E_{min} \sim 4$ kV/cm is reached, and then starts to increase faster than linearly, similar to the case of PLZT in Fig. 4. Furthermore, the activation energy U was found to increase slightly with the field until it reaches a maximum at $E_{max} \sim 4$ kV/cm, and then starts to decrease, in qualitative agreement with Eq. (18) for w_2 , which yields an effective activation energy $U_{eff} = w_2 Q_{an} \bar{v}_0$.

Meanwhile, in single crystal PMN [111], $T_0(E)$ initially decreases with E , reaches a minimum at $E_{min} \sim 5$ kV/cm, and finally recovers the original value $T_0(0)$ at $E \sim 7$ kV/cm

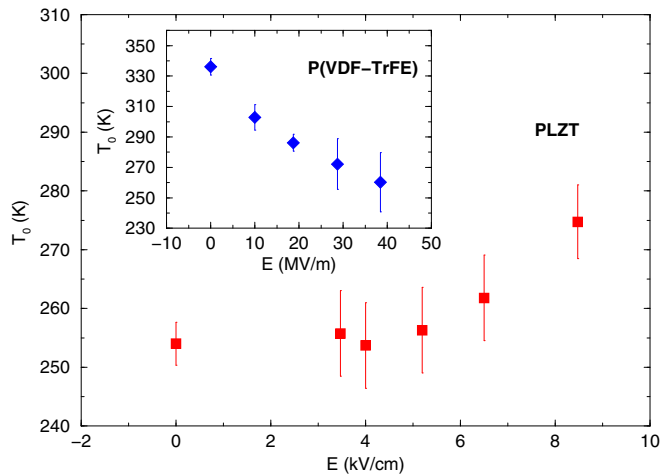


FIG. 4. (Color online) Experimental data for the electric-field dependence of freezing temperature T_0 in 9/65/35PLZT ceramics (extracted from Ref. [45]). Inset: same for relaxor polymer P(VDF-TrFE) [45].

[46]. It should be noted, however, that the critical field in PMN [111] is of the order $E_{cp} \sim 3.5$ kV/cm [48]; thus $E_{min} > E_{cp}$ and again Eq. (14) cannot be applied. Therefore, to explain the unusual field dependence of $T_0(E)$ another mechanism of relaxation should be considered. On the other hand, in PMN [110] the critical field is much larger, ~ 8 kV/cm, but the field dependence of $T_p(E)$ has not yet been determined. Clearly, more experiments on different relaxor systems are needed in order to test the predictions of the above theory.

In contrast to inorganic relaxors, the VF temperature $T_0(E)$ in the organic relaxor copolymer P(VDF-TrFE) [45] was found to be a decreasing function of E (see the inset of Fig. 4). This was attributed to the sign of χ_3 , which implies a positive sign of the bulk Landau coefficient b . However, as already stated above, for $b > 0$ the percolation mechanism is not applicable. Thus Eqs. (14) and (17) cannot be used to interpret the field dependence of the VF temperature $T_0(E)$ in P(VDF-TrFE).

Monte Carlo simulations on the first-principles model of BZT in a field [9] indicate that the strength of the percolation cluster P_∞ is nearly constant for fields below a threshold value E_{tr} , but starts to increase sharply for $E > E_{tr}$. This suggests that the behavior of $T_p(E)$ in PLZT ceramics might be analogous to that of P_∞ in percolation theory.

IV. RELAXATION MECHANISM IN DIPOLAR GLASSES

As already stated in the Introduction, in DGs the polarization of the dielectric medium in which the individual dipole moments are embedded is uncorrelated with the dipoles. Thus, in contrast to relaxors, a ferroelectric phase cannot be induced by applying an external electric field. In the framework of the model discussed in Sec. II, this means that the fourth-order Landau coefficient is positive, $b > 0$, and no field-induced critical point exists.

It has been found experimentally in several DG systems that the dielectric relaxation time also obeys the VF law (1) [1,2]; however, it is clear that the relaxation mechanism introduced in Sec. II for the case of relaxors is inapplicable to DGs. A

possible alternative mechanism is based on the so-called cooperative rearrangement of dipolar clusters [49]. The essential idea is that the dipole moments can undergo a collective rotation within the dielectric medium, which is analogous to the collective motion of molecules in a supercooled glass-forming liquid. The relaxation mechanism can then be formulated in the framework of the Adams-Gibbs (AG) molecular-kinetic theory [50]. The crucial quantity is the so-called configurational or excess entropy $S_{ex} = S_{para} - S_{ferro}$, i.e., the difference between the entropies of the paraelectric and ferroelectric phase [49,51]. The relaxation time depends on S_{ex} according to the exponential relation [52]

$$\tau = \tau_0 \exp(A/TS_{ex}), \quad (19)$$

where A is a thermodynamic potential barrier.

The details of this mechanism have already been described in several papers [49,51]; therefore, we only review here the main ideas. The essential point is that as the temperature is lowered, S_{ex} tends to vanish at the Kauzmann temperature T_K [53]. Thus, for $T < T_K$, S_{para} would become negative (the ‘‘Kauzmann paradox’’); however, the impending entropy crisis is averted by the appearance of a frozen DG phase. By assuming a hyperbolic temperature dependence of the excess specific heat $C_{ex} = B/T$ [52] the excess entropy is trivially obtained by integration, i.e., $S_{ex} = B(T - T_K)/T_K T$. Inserting this into Eq. (19) immediately leads to the VF relaxation time (1) with $U = AT_K/B$ and $T_0 = T_K$.

An extension of the Adam-Gibbs theory to the case including external electric fields acting on the dipole moments has not yet been attempted. Thus, at this moment, we do not have the means to compare the field-dependent relaxation time for relaxors (17) with the corresponding expression for DGs.

V. CONCLUSIONS

Following the physical picture originally proposed by Samara [1,2], we have formulated a mechanism of growth and percolation of polar nanoregions (PNRs) in relaxor ferroelectrics in the presence of an external electric field E , which leads to a temperature and field dependent dielectric relaxation time near the freezing transition. Here we have applied a thermodynamic criterion for the correlation radius of a PNR based on the Landau free energy of the medium in which the PNRs are embedded. If the fourth-order anharmonic Landau coefficient is negative, $b < 0$, the polarization of the medium at a distance r from the PNR center undergoes a transition into a field-induced ferroelectric state and thus becomes correlated with the PNR.

The line of phase transitions in the E, T plane terminates at a field-induced critical point, beyond which the correlations do not exist. The volume fraction of the PNRs η increases as the temperature is lowered or the field is increased until it reaches the percolation limit η_p , where an infinite cluster of PNRs is formed. The reorientation time τ of the infinite cluster obeys the Néel formula [43] for overturning large magnetic clusters in rock magnets, which leads to a Vogel-Fulcher (VF) type expression for τ with a field-dependent VF freezing temperature $T_0(E, T)$. In the percolation limit, $T_0(E, T)$ is predicted to increase quasi-linearly with E .

We also discussed the freezing in dipolar glasses (DGs), in which the elementary dipolar entities are believed to be isolated electric dipoles rather than PNRs and a field-induced ferroelectric state does not exist. In the above context, the polarizable medium in DGs can be described by a Landau free energy function with a positive value of the anharmonic coefficient, i.e., $b > 0$. This may provide a simple thermodynamic criterion for discriminating between relaxors ($b < 0$) and DGs ($b > 0$).

The freezing mechanism in DGs has been described earlier using the analogy with the Adam-Gibbs theory of glass forming liquids [50] by introducing the concept of cooperative rearrangement of dipolar clusters [49]. This approach again leads to the VF-type expression for the relaxation time τ with

a VF temperature T_0 ; however, it should be stressed that to present this result is only applicable in the zero-field case. Thus an extension of the Adam-Gibbs theory to nonzero fields acting on the dipoles is clearly needed.

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