

Vogel-Fulcher freezing in relaxor ferroelectrics

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A physical mechanism for the freezing of polar nanoregions (PNRs) in relaxor ferroelectrics is presented. Assuming that the activation energy for the reorientation of a cluster of PNRs scales with the mean volume of the cluster, the characteristic relaxation time τ is found to diverge as the cluster volume reaches the percolation limit. Applying the mean field theory of continuum percolation, the familiar Vogel-Fulcher equation for the temperature dependence of τ is derived.

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Relaxor ferroelectrics (relaxors) have long been attracting considerable attention in view of their unique physical properties.¹ A key feature of relaxors is the appearance of a broad temperature and frequency dependent maximum of the dielectric permittivity $\epsilon(T, \omega)$ as well as the absence of long-range ferroelectric order in zero field at any temperature.² The high value of the quasistatic dielectric constant ϵ in a broad temperature range around the peak temperature T_m , and especially the giant piezoelectric effect,^{3,4} make relaxors attractive for various technological applications. Another characteristic relaxor property is the extremely slow relaxation below T_m , which signals the onset of relaxor freezing.⁵ The characteristic relaxation time diverges at the freezing temperature T_0 according to the well-known Vogel-Fulcher (VF) relation^{6,7}

$$\tau = \tau_0 \exp[U/k(T - T_0)], \quad (1)$$

where τ_0 represents the inverse attempt frequency, U the activation energy, and T_0 the VF or freezing temperature. For obvious reasons, Eq. (1) only makes sense for $T > T_0$.

The above empirical VF law (1) has been experimentally observed in a variety of other systems such as supercooled organic liquids, spin glasses, polymers, etc. Although many theoretical ideas about the origin of the VF law have been proposed in the past,⁸⁻¹⁴ a derivation of Eq. (1) at the mesoscopic level is still lacking.

Much of the experimental and theoretical research on relaxors has been focused on compositionally disordered perovskites such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) and related compounds.¹ Since only disordered ferroelectric systems show relaxor behavior, it is clear that disorder and/or frustration are key factors in producing a relaxor state. In particular, charge fluctuations are responsible for the formation of polar nanoregions (PNRs) below the so-called Burns temperature T_d .¹⁵ In PMN, for example, one has $T_d \sim 600$ K, while the dielectric maximum occurs at $T_m \sim 260$ K in the quasistatic limit. The PNRs can be regarded as a network of randomly interacting dipolar entities with the corresponding statistical distributions of their size and dipolar strength. The resulting collective state is reminiscent of a magnetic spin glass—or rather an electric dipolar glass—and it has been shown that its static properties can be described in terms of the spherical random bond-random field (SRBRF) model of relaxor ferroelectrics.^{16,17} Experiments performed by neutron scattering^{18,19} and NMR techniques²⁰ indicate that the aver-

age size of PNRs increases with decreasing temperature and saturates below T_m , suggesting the possibility of a percolation-type transition into a frozen relaxor state.^{1,21}

Relaxor dynamics is characterized by a broad distribution of relaxation times $g(\log \tau)$, and it appears that the freezing process is associated with the divergence of the longest relaxation time in $g(\log \tau)$.^{5,22} A typical empirical method used to analyze the dielectric permittivity $\epsilon(\omega, T)$ is to consider the dielectric maximum temperature $T = T_m$ as a function of frequency ω . One may then define a relaxation time $\tau = 1/\omega$, which is found to satisfy the above VF relation (1). For example, in PMN oriented along [001], the experimental parameter values determined in this manner are $\tau_0 = 10^{-12}$ s, $U/k = 911$ K, and $T_0 = 217$ K.²³ On the other hand, the longest relaxation time τ_{\max} was found to obey the VF relation (1) with similar parameter values, i.e., $\tau_0 = 4.3 \times 10^{-11}$ s, $U/k = 970$ K, and $T_0 = 224$ K.²²

The purpose of the present work is to present a simple physical mechanism for the VF-type relaxation process in relaxor ferroelectrics. We adopt a qualitative physical picture of the relaxor state below T_d based on a network of PNRs embedded in a highly polarizable medium.¹ One can imagine that the medium consists of a number of fluctuating reorientable dipoles and/or small size polar clusters. The first possibility corresponds to dipolar glasses and order-disorder-type relaxor ferroelectrics, whereas the second one applies to displacive-type relaxors; however, intermediate cases may as well exist. Each PNR will polarize the medium within a space region bounded by the correlation radius r_c . As the temperature is lowered, r_c is expected to increase; this process will continue until a number of PNRs of similar size start to merge, thus forming a polarization cluster. Eventually, freezing will occur due to the growth of both the size of PNRs and the correlations between them.²³

Let us now consider a PNR with a core radius r_0 and assume that the polarization cloud associated with it can be described by a power-law radial dependence,

$$\vec{P}(r) = \vec{P}_0 (r_0/r)^3, \quad r > r_0, \quad (2)$$

and $\vec{P}(r) = \vec{P}_0$ for $r \leq r_0$. The local electric field at some distance r is assumed to be proportional to the polarization,

$$\vec{\mathcal{E}} = \frac{\varphi}{3\epsilon_0} \vec{P}(r), \quad (3)$$

with a dimensionless local field factor φ .²⁴ The field $\vec{\mathcal{E}}$ couples to dipolar fluctuations of the surrounding medium and at a distance r induces an electric dipole moment

$$\vec{p} = \alpha \vec{\mathcal{E}}, \quad (4)$$

which is proportional to the polarizability α . For order-disorder relaxors one has $\alpha \approx \mu^2/kT$, where μ is the strength of the fluctuating dipole moment. Similarly, in the displacive case we can write $\alpha \approx e^*/(M\omega_0^2)$, where e^* is an effective charge, M the reduced mass, and $\omega_0^2 \approx a_0kT$ the frequency of a renormalized quasi harmonic mode, which becomes unstable at zero temperature. The associated change of the electrostatic energy is given by

$$\delta E = -\frac{1}{2} \alpha \mathcal{E}^2. \quad (5)$$

If $|\delta E| > kT$, the thermal fluctuations will be too weak to destroy the correlations between the dipole and the PNR and a bound state will exist. The correlation radius r_c then corresponds to the limiting distance for which $|\delta E| \approx kT$. Combining Eqs. (5), (2), and (3) we obtain

$$r_c^3 = r_0^3 \frac{T_d^*}{T}, \quad (6)$$

where $T_d^* = \varphi \mu P_0 / 3 \sqrt{2k\epsilon_0}$ for order-disorder relaxors and, similarly, $T_d^* = \varphi e^* P_0 / 3 \sqrt{2Ma_0k\epsilon_0}$ for the displacive case. Formally, we can require that $r_c \rightarrow r_0$ as $T \rightarrow T_d$, implying that T_d^* is of the order $\sim T_d$.

It follows that the correlation radius of each PNR in each case scales with temperature $t \equiv T/T_d^*$ as $r_c \sim t^{-1/3}$. Similarly, the correlation volume $v_c = 4\pi r_c^3/3$ scales as $\sim 1/t$, and the PNR dipole moment $p_c = (4\pi/3) \int_0^{r_c} P(r) r^2 dr$ as $p_c - p_0 \sim |\log t|$, where $p_0 = P_0 4\pi r_0^3/3$ is the core dipole moment.

As the temperature is lowered, the PNRs will grow in size and gradually start forming a connected polarization cluster. If n is the concentration of PNRs, they occupy a volume fraction $\eta = 4\pi n r_c^3/3 = 4\pi n T_d^*/3T$. When η reaches a threshold value η_p , the PNRs will merge into an infinite cluster—a familiar concept from the theory of percolation.²⁵ The temperature at which the infinite cluster appears is, therefore, $T_p = 4\pi n T_d^*/3\eta_p$. The percolation threshold for hard spheres on a lattice in three dimensions ($d=3$) is $\eta_p \approx 0.35$, and $\eta_p \approx 0.294$ for randomly overlapping spheres,²⁵ whereas $\eta_p = 1/3$ for random hard spheres in the effective medium approximation.²⁶ Experiments on PMN¹⁹ show that the volume fraction of PNRs saturates at ~ 0.3 below $T \sim 15$ K.

The theory of continuum percolation²⁷ predicts that the mean cluster volume v increases as η approaches η_p according to a power law $v \sim (\eta_p - \eta)^{-\gamma}$, or explicitly

$$v = v_0 (1 - \eta/\eta_p)^{-\gamma}, \quad (7)$$

where v_0 is the critical amplitude. Assuming that at high temperatures $T \sim T_d$ the mean cluster volume reduces to the average core volume, we obtain an estimate for the amplitude, i.e., $v_0 \sim 4\pi r_0^3/3$.

In the mean field case, which is applicable to systems with infinite effective dimensionality, one has $\gamma=1$. This may be a reasonable value for the present system, since the PNRs behave as a fully connected random-site network in view of the long-range character of dipolar interactions. Using the above expressions for η and η_p , we can rewrite Eq. (7) as

$$v = \frac{v_0}{(1 - T_p/T)}. \quad (8)$$

As the volume of the cluster grows, it becomes increasingly difficult for its total dipole moment to change direction, and eventually the reorientation will be suppressed completely as the mean cluster size reaches the percolation limit. The relaxation time τ for the reorientation of the dielectric polarization is usually described by the Arrhenius law $\tau = \tau_0 \exp(U/kT)$, where the activation energy U is determined by the potential barrier for the relaxing particle to jump out of the potential well. For magnetic clusters in disordered magnetic materials, Néel²⁸ suggested that the activation energy could be written as the product of mean cluster volume v and an anisotropy factor Q_{an} ,

$$\tau = \tau_0 \exp(v Q_{an}/kT). \quad (9)$$

As already noted by several authors^{1,5,29} an analogous relation should be applicable to PNRs in relaxors. Inserting the mean cluster size v from Eq. (8) into Eq. (9), we immediately obtain

$$\tau = \tau_0 \exp[v_0 Q_{an}/k(T - T_p)]. \quad (10)$$

This result has precisely the form of the VF equation (1) with $U = v_0 Q_{an}$ and $T_0 = T_p$.

The anisotropy constant Q_{an} in Néel's formula (9) has the dimensionality of energy density. Its magnitude can be estimated by assuming that the core radius r_0 is of the order, say, ~ 2 nm. Using the value $U/k = 970$ K for PMN,²² we thus find $Q_{an} \sim 2.3 \times 10^{-3}$ eV/(nm)³.

The VF relation (10) for the relaxation of dielectric polarization in relaxor ferroelectrics has been derived here on the basis of a plausible power-law model for the polarization distribution within the PNR. The principal mechanism responsible for relaxor freezing appears to be the growth and percolation of PNR clusters¹ culminating in the formation of an infinite cluster. Alternatively, the system could be described in terms of random normal modes, which are determined by the eigenstates and eigenvalues of the random interactions between PNRs;³² however, the relaxation time entering the equations of motion for these modes must again be associated with the growth of the PNRs discussed above and should, therefore, obey the same VF relation. Thus, according to our present model, the two physical pictures, namely, that of cluster growth and of the freezing of local modes,^{5,31} are essentially two parts of the same general scenario.

It should be noted that the above results are independent of any specific spin glass-type static model such as the SRBRF model. Of course, the SRBRF model remains applicable to true *static* phenomena, for example, the temperature

dependence of the quasistatic dielectric response as observed in a field-cooled (poled) sample.

An alternative mechanism of PNR formation and growth in relaxor ferroelectrics has recently been proposed by Vugmeister.³⁰ This mechanism is based on interacting short-range polar clusters existing within a PNR, which are due to off-center ions in highly polarizable materials. It would be interesting to compare the predictions of this model with the results of our semi-phenomenological approach, however, this is a nontrivial task which would go beyond the scope of the present paper.

The divergence of τ at T_p does not imply that the motion of all PNRs is completely frozen for $T < T_p$. Namely, the complex dielectric permittivity $\epsilon(\omega, T)$ remains finite below T_p , indicating that some degrees of freedom are still active at low temperatures. In fact, as already noted above, only $\sim 30\%$ of the PNRs are involved in the formation of the infinite cluster. Smaller PNRs in the remaining space may continue to undergo a similar process of growth and percolation, suggesting that at any temperature below T_p an analogous freezing mechanism may apply. One can thus introduce a probability distribution of VF temperatures $w(T_p)$ in the interval $0 < T < T_p$ which could, in principle, be transformed into a nontrivial distribution of relaxation times. A simple linear shape of $w(T_p)$ ³² then reproduces the main physical features, i.e., the finite value of $\epsilon(\omega, T)$ at temperatures below T_p and a frequency dispersion of its real and imaginary parts, although the agreement with the observed behavior of $\epsilon(\omega, T)$ is, admittedly, only qualitative.

At present, it is not yet clear whether the above approach is applicable in a straightforward manner to analogous systems such as random ferromagnets and spin glasses, super-

cooled organic liquids, structural glasses, etc. In magnetic systems, the magnetic dipolar interactions are much weaker than the short-range exchange interactions, which are responsible for the formation of superparamagnetic clusters. However, in spin glasses the RKKY interactions actually fall off as $\sim r^{-3}$ up to some oscillatory prefactor, and magnetic dipolar interactions are believed to be relevant in some spin glass systems.³³ Thus the present model may serve as a convenient starting point for these systems. Meanwhile, in relaxor ferroelectric polymers, the above physical picture seems to be applicable without serious limitations.¹⁷ For structural glasses and supercooled organic liquids, the possibility of elastic deformations and their interactions playing a leading role in the growth of correlated clusters should be explored.

In conclusion, we have derived the Vogel-Fulcher (VF) relation in relaxor ferroelectrics by introducing a mesoscopic mechanism for the growth of PNRs. The basic idea is that thermodynamic stability of the polarization density with a power-law distribution $P(r) \sim r^{-3}$ entails a temperature dependence of the correlation radius $r_c \sim T^{-1/3}$. Thus a cluster of PNRs is formed on lowering the temperature, and its mean volume v increases until the percolation limit is reached at some temperature T_p . Using the mean field theory of continuum percolation, we have shown that $v \sim (1 - T_p/T)^{-1}$ and, since according to Néel the activation energy U for the re-orientation of the cluster polarization is proportional to v , the VF relation follows immediately.

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