COEXISTENCE OF THE CRITICAL SLOWING DOWN AND GLASSY FREEZING IN RELAXOR FERROELECTRICS

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We have developed a dynamical model for the dielectric response in relaxor ferroelectrics which explicitly takes into account the coexistence of the critical slowing down and glassy freezing. The application of the model to the experiment in PbMg\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3} (PMN) allowed for the reconstruction of the nonequilibrium spin glass state order parameter and its comparison with the results of recent NMR experiment (Blinc et al., Phys. Rev. Lett 83, No. 2 (1999)). It is shown that the degree of the local freezing is rather small even at temperatures where the field-cooled permittivity exceeds the frequency dependent permittivity by an order of magnitude. This observation indicates the significant role of the critical slowing down (accompanying the glass freezing) in the system dynamics. Also the theory predicts an important interrelationship between the frequency dependent permittivity and the zero-field-cooled permittivity, which proved to be consistent with the experiment in PMN (A. Levstik et al., Phys. Rev. B 57 11204 (1998)).

I. INTRODUCTION

Relaxor ferroelectrics which are disordered perovskite ferroelectrics like PbMg\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3} (PMN) or PbSc\textsubscript{1/2}Ta\textsubscript{1/2}O\textsubscript{3} (PST) represent a new class of materials which have been a subject of numerous investigations (see, for example, Refs. 1–13). Relaxor ferroelectrics manifest themselves in the extraordinary low frequency dispersion of their dielectric permittivity compared with regular ferroelectrics. The position and the height of the permittivity maximum plotted as a function of temperature depends on the frequency of the probe field and shifts to lower temperatures when the frequency decreases.

The latter behavior is accompanied by the observed splitting between the field-cooled (FC) and zero-field-cooled (ZFC) permittivity and the existence of long lived remanent polarization. However, as has been emphasized recently, the bulk of the relaxation spectra in relaxors remains active even far below the temperature \(T_f\) where the FC and ZFC permittivity split, and the nonlinear susceptibility does not diverge at \(T_f\). All these findings indicate nonequilibrium phenomena and quasi-nonergodicity ("freezing"), rather than a true thermodynamic dipole spin glass transition.

On the other hand, the existence of the very high dielectric constant indicates that these systems are close to ferroelectric instability, and, therefore, one could expect the manifestation of the critical slowing down of dynamics and a competition between the critical slowing down and the dipole spin glass freezing. Such a dichotomy makes it a non-trivial task to extract from the experiment quantitative characteristics of the freezing.

One of the important characteristics of spin glass freezing is a value of the Edwards-Anderson order parameter \(q\), which in relaxors is a time dependent quantity. We will show that this quantity can be extracted from the experimental results on the frequency dependent permittivity, with the use of the model discussed below. Also the theory predicts an important interrelationship between the frequency dependent permittivity and the zero-field-cooled permittivity, which proved to be consistent with the experiment.

II. MODEL

It has been recently proposed \[12\] that relaxor behavior is a common characteristic of the collective dynamics of localized giant dipole moments distributed in highly polarizable crystals, and a necessary condition of relaxor behavior is the simultaneous existence of the broad distribution of the local field and the broad distribution of dipole relaxation frequencies. Also experiments \[10,11,4\] favor the hypothesis that the physical origin of localized dipole moments is the off-center shift of the atom even at high temperatures. In this model the large values of the dipole moments are associated with the polarization cloud (cluster) formed by the simultaneous displacements of the other atoms adjacent to a given off-center ion.

A convenient approach to describe dynamical behavior of relaxor ferroelectrics is to start from the Bloch type equations widely explored in the theory of regular ferroelectrics possessing Debye relaxation. We write the Bloch equation in the form

\[
\frac{\partial P_{cl}}{\partial t} = \frac{1}{\tau}(P_{cl} - P_{cl}^{eq}(E)). \tag{1}
\]

Eq.(1) describes the relaxation of polarization of each cluster to its quasiequilibrium value \(P_{cl}^{eq}(E)\) which depends on the value of the local field \(E\) induced by other clusters at any moment of time. In general the local field \(E\) is a time dependent random field. It includes also the
contribution from the applied field $E_{ex}$ and the contribution from the static random field caused by material imperfections. Note that Eq. (4) is quite general and, although the explicit form of $P_{cl}(E)$ and the precise definition of the polar clusters are model dependent, it effects only the coefficients of the theory discussed below.

In order to apply Eq. (4) to relaxor ferroelectrics one should perform an average over the distribution of relaxation times $\tau$ and the random local field $E$. We assume that the distribution function $f(E, P)$ of the local field, which depends parametrically on the average polarization of the system $P(t)$, has the form $f(E, P) = \tilde{f}(E - \gamma P - \gamma_0 E_{ex}/4\pi)$. This form of $f(E)$ is consistent with the mean field approximation $f(E, P) = \delta(E - \gamma P - \gamma_0 E_{ex}/4\pi)$, where $\delta$ is the Dirac $\delta$-function and $\gamma$ is the local field phenomenological parameter. The effect of the local field fluctuations corresponds to the replacement of the $\delta$-function by the function $\tilde{f}$ with finite width. The value $\gamma_0 E_{ex}/4\pi$ is the local field induced by the external field at the location of each off-center ion in a dielectric media with the dielectric constant $\epsilon_0 >> 1$, i.e., we assume that the localized dipole moments are distributed in crystals with large lattice permittivity caused by the existence of the soft modes. This assumption is consistent with the observation in relaxors of the soft optical modes (remaining finite at all temperatures), frequencies of which are of the same order of magnitude ($\sim 50 \text{cm}^{-1}$) as those in highly polarizable dielectrics such as $\text{K-TaO}_3$, $\text{SrTiO}_3$.

It is known that the existence of the broad distribution of relaxation times leads to non-exponential behavior in the polarization relaxation. In order to reproduce this effect within the proposed formalism we rewrite Eq. (4) in the integral form and then take the average with respect to $\tau$, $E$, and the initial cluster polarization $P_{cl}(0)$. Thus, we obtain

$$P(t) = P(0)q(t) - k(T) \int_0^t dt' \frac{dq(t')}{dt'} [P(t - t')] + \frac{\epsilon_0}{4\pi} E_{ex}(t - t').$$

(2)

In Eq. (2) we assumed a linear response of the polarization to the applied electric field, and $T > T_c$ where $T_c$ is the temperature of a possible ferroelectric phase transition,

$$k(T) = \int dE dP_{cl}(E) \frac{\partial f(E, P)}{\partial P} |_{P=0},$$

(3)

and for second order phase transitions $k \rightarrow 1$ as $T \rightarrow T_c$. The function $q(t)$ is equal to

$$q(t) = \int_{\tau_0}^{\tau_m} d\tau \tilde{g}(\tau)e^{-t/\tau} \approx \int_{\tau}^{\tau_m} d\tau \tilde{g}(\tau)$$

(4)

where $\tilde{g}(\tau)$ is a distribution function of relaxation times and the right hand side expression of Eq. (4) is valid for smooth functions $\tilde{g}(\tau)$. The variable $q(t)$ describes the fraction of clusters effectively frozen at time $t$ and therefore has the meaning of the Edwards-Anderson spin glass order parameter on a finite time scale. Note that, as we assumed above, $q(t) \rightarrow 0$ at $t \rightarrow \infty$.

### III. FREQUENCY DEPENDENT PERMITTIVITY

The steady state frequency dependent permittivity can be easily obtained from Eq. (2) assuming $E_{ex}(t) = E_{ex}^{(1)} e^{i\omega t}$ and using the definition

$$\epsilon(\omega, T) = 4\pi \frac{\partial P(\omega)}{\partial E_{ex}} + \epsilon_0.$$  

(5)

Thus we obtain

$$\epsilon(\omega, T) = \frac{\epsilon_0}{1 - k(T)Q(\omega, T)}$$

(6)

where

$$Q(\omega, T) = \int_{\tau_0}^{\tau_m} d\tau e^{i\omega \tau} \frac{\tilde{g}(\tau)}{\tau} \approx \int_{\tau}^{1/\omega} d\tau \tilde{g}(\tau)$$

$$= 1 - q(\omega^{-1}, T).$$

(7)

(8)

The relation (8) between the functions $q(t)$ and $Q'(\omega, T)$ will be employed below to obtained information on the degree of local freezing in relaxors from the frequency dependent dielectric constant using the fact that usually $Q'' < Q'$. At $\omega = 0$ Eq. (8) defines the static or field-cooled permittivity

$$\epsilon_{FC} = \frac{\epsilon_0}{1 - k(T)}.$$  

(9)

On the other hand, at $\omega \tau_m >> 1$ the function $Q(\omega, T) \rightarrow 0$ and therefore $\epsilon(\omega) \rightarrow \epsilon_0$. Thus, in our model $\epsilon_0$ can be regarded as a high frequency permittivity $\epsilon_{\infty}$. Combining equations (6) and (8) we obtain

$$Q(\omega) = \frac{\epsilon(\omega) - \epsilon_0}{\epsilon_{FC} - \epsilon_0} \cdot \frac{\epsilon_{FC}}{\epsilon_0}.$$  

(10)

Note that in a number of recent publications on relaxors [12, 13] the analysis of the relaxation spectrum $Q(\omega)$ was based on a different relation between $Q(\omega)$ and the permittivity, namely

$$Q(\omega) = \frac{\epsilon(\omega) - \epsilon_0}{\epsilon_{FC} - \epsilon_0}$$

(11)

where we substituted $\epsilon_0$ for $\epsilon_{\infty}$. Equation (11) was introduced earlier in spin glasses, assuming that the relaxation time $\tau$ in Eq. (8) is a characteristic of independent
cluster-relaxators. However this equation has a different meaning when applied to relaxor ferroelectrics. Indeed, Eq. (11) can be obtained from Eq. (10) if we first perform the average over the distribution of the local random fields at a constant value of \( \tau \) and then perform the average over \( \tau \). With such a two-step averaging we arrive at Eq. (11) where \( \tau \) is replaced by \( \tau^* = \tau \epsilon / \epsilon_0 \). Note that \( \tau^* \) is a relaxation time of the collective polar mode with the wave vector \( q \to 0 \), undergoing the critical slowing down of dynamics, rather than the relaxation time of the individual dipoles or clusters. Thus the applicability of Eqs. (11), and (8) to a system with long range or mesoscopic polar order implies that the crystal can be divided into macroregions within which the relaxation time of all dipole moments has the same magnitude, and the average over \( \tau \) means the average of the dielectric response for different macroregions. On the other hand, Eq. (11) is consistent with the formation of the short range clusters in the absence of correlations between the relaxation times of different clusters.

IV. ZERO-FIELD-COOLED SUSCEPTIBILITY AND REMANENT POLARIZATION

The values of \( \epsilon_{ZFC}(t) \) can be obtained by solving Eq. (3) with \( P(0) = 0 \) and \( E_{ex} = \text{const} \). We consider here a particular case when one can approximately neglect the memory effects in Eq. (2) by replacing \( P(t - t') \approx P(t) \) (which implies a fast decay of \( dq/dt \)). Thus, we obtain

\[
\epsilon_{ZFC}(t) = \frac{\epsilon_0}{1 - k(1 - q(t))}
\]

(12)

One can see that \( \epsilon_{ZFC}(t) \) is identical to \( \epsilon(\omega) \) given by Eq. (8), if one substitutes \( \omega \) by \( 1/t \) in Eq. (8).

In order obtain the remanent polarization \( P_r(t) \) we solve Eq. (2) in the same manner as above, but with \( E_{ex} = 0 \) and \( P(0) \neq 0 \). We obtain

\[
\frac{P(t)}{P(0)} = \frac{q(t)}{1 - k(1 - q(t))} = \frac{\epsilon_{FC} - \epsilon_{ZFC}}{\epsilon_{FC} - \epsilon_0}
\]

(13)

The denominator in Eq. (13) reproduces the effect of the critical slowing down of dynamics which is imposed on the effect of glass freezing characterized by the slow decaying function \( q(t) \). For example, when \( k \to 1 \) (i.e., the system is in the vicinity of the second order phase transition temperature) it follows from Eq. (13) that \( P_r(t) = \text{const} \) independently of the value of \( q(t) \).

V. COMPARISON WITH THE EXPERIMENT IN PMN

A. Nonequilibrium spin glass order parameter

The nonequilibrium spin glass order parameter \( q(t, T) \) is a very important quantity determining the dielectric response of relaxors. The dielectric permittivity can be formulated in terms of the parameter \( q(t, T) \) in a way consistent with the description of magnetic susceptibility in magnetic alloys where spin glass and ferromagnetic order coexist. It is convenient to rewrite Eq. (8) in the identical form

\[
\epsilon(\omega, T) = \frac{k \epsilon_0 (1 - q)}{1 - k(1 - q)} + \epsilon_0,
\]

(14)

which separates the contribution to the permittivity from the localized dipole moments and the lattice permittivity \( \epsilon_0 \). The first term in Eq. (14) is very similar to the well known solution for the susceptibility given by the infinite range Sherrington-Kirkpatrick model (mean field theory)

\[
\chi = \frac{C(1 - q)}{T - \theta(1 - q)}
\]

(15)

Equation (15) has been widely used for the description of the experiments on ZFC susceptibility as well as frequency dependent susceptibility in magnetic alloys [17] and relaxors [18] by treating the parameters \( C \) and \( \theta \) as purely phenomenological fitting parameters. In fact, our approach justifies and generalizes Eq. (15) in the case of nonequilibrium spin glass state. The deviation of the parameter \( k(T) \) from \( \theta/T \) indicates the deviation from the mean field picture.

Equations (8) and (14) allow reconstructing the values of the functions \( q(t, T) \) from experiments on the frequency dependent permittivity. We applied them to the recent data on PMN by Levstic et al [13] who obtained the values of the frequency dependent permittivity, as well as field-cooled and zero-field-cooled permittivity.

\[
\text{Temperature, K}
\]

[Graph]

\[
\text{Q}
\]

[Table]
FIG. 1. Reconstructed values of the nonequilibrium spin glass order parameter in PMN as a function of temperature corresponding to the following frequencies of the applied field: 100kHz (1), 1kHz (2), and 20Hz (3). Squares reproduces the data obtained in Ref.[19].

We used $\epsilon_0 \approx 1000$ corresponding to the values of $\epsilon$ in the low temperature limit. The results of the reconstruction are presented in Fig.1 where the temperature dependences of $q(T)$ as shown for three distinct times corresponding to the frequencies of the applied field used in the experiment equal to 20Hz, 1kHz, and 100kHz. One can see that the values of the $q(T)$ are rather small even at $T=200K$ where the values of $\epsilon(\omega)$ are almost 10 times less than the values of $\epsilon_{FC}$. The explanation of this important effect lies in the extremely high dielectric constant of PMN leading to $k \approx 0.98$ at $T=200K$. Thus, the system is extremely close to the ferroelectric instability which results in the significant effect of the critical slowing down, accompanying the glass freezing, upon the system dynamics.

In Fig.1 the reconstructed values of $q$ are compared with the the data obtained from the recent experiments by Blinc at al. [19] on the observation of inhomogeneous broadening of NMR lines of Nb ions. The appearance of inhomogeneous broadening signals the slowing down of the dynamics on the scale of inhomogeneous linewidth (equal to 10-50 kHz). A reasonable correspondence between curve 1 and the data [14] (with the account of comparable time scales in both experiments) allows us to suggest the following scenario for the NMR broadening mechanism in PMN. As known, e.g., from the analysis of nuclear spin lattice relaxation of Li and Nb ions in KTaO$_3$:Li, Nb [20], the appearance of polarization on the mesoscopic length scale in highly polarizable crystals results in a significant modification of the electric field gradient which leads to the modulation of nuclear resonance frequency. Since in disordered PMN crystals all atoms lack a center of symmetry, one can assume the following form of the nuclear frequency shift of Nb atoms

$$\Delta \nu = \alpha P_{cl}$$

where $\Delta \nu$ is the frequency shift of the atoms belong to the given polar cluster. The width $\delta$ of the inhomogeneous line will be proportional to the fraction of polar clusters (given by the nonequilibrium spin glass parameter $q(T)$) whose dynamics is effectively frozen on the time scale of $1/\delta$. The above broadening mechanism gives also a natural explanation of the Gaussian line shape observed in Ref. [19] since the distribution function of cluster polarization is close to Gaussian in highly polarizable crystals [20], and, according to Eq.(16), the shape of inhomogeneous NMR line coincides with the shape of the distribution function of cluster polarization.

**B. Interrelationship between ZFC and frequency dependent permittivity**

Another practical aspect of the proposed model, which helps to clarify the experimental situation in PMN, is the interrelationship between the frequency dependent permittivity and zero-field-cooled permittivity obtained in Sec.4. In order to employ this interrelationship note first that in PMN, at the temperatures nearby the temperature of the permittivity maximum, the characteristic relaxation time satisfies the Vogel-Fulcher (FV) law [3,13]. It allows to replace $\tau$ in Eq.(3) by

$$\tau = \tau_0 e^{\frac{1}{T - T_0}}$$

and introduce the temperature independent distribution function $q(U)$ of potential barriers [17,14]. We obtain

$$q(t) = 1 - \int_0^{(T - T_0) \ln(\frac{T}{T_0})} dU g(U)$$

Thus, $q$ is a function of $(T - T_0) \ln(t/\tau_0)$ which leads to the validity of the scaling relation $q(t,T) = q(t_1,T_1)$ with

$$T_1 = (T - T_0) \ln(\frac{T}{T_0}) + T_0$$

Using Eqs. (19), (8), and (3) one can reconstruct the values of $q(t,T)$ and $Q'(\omega, T)$ and, therefore, the values of $\epsilon(\omega)$ by employing the experimental data on $\epsilon(\omega_1)$ at a given frequency $\omega_1$.

The reconstructed values of $\epsilon(\omega)$ at $\omega = 20Hz$ are presented in Fig.2 (solid line) where the data at $\omega_1 = 1kHz$ have been taken as a reference. The parameters of the fit are $T_0 \approx 223K$ and $\tau_0 \approx 4 \cdot 10^{-11}sec$, which are almost the same as obtained in Ref. [13] $T_0 \approx 224K$ and $\tau_0 \approx 4.3 \cdot 10^{-11}sec$. One can see that at high temperatures ($T > 245K$) the reconstruction reproduces the experimental data with good accuracy. The deviation between the reconstructed and experimental data for lower temperatures is due to violation of the VF law in PMN already discussed in Refs. [3,13]. The self-consistency of the model has been tested also by reconstructing the values of the zero-field cooled permittivity using Eq.(12) and the same reference data as above. In order to find the time $t$ entering Eq.(12) we use the fact that in the experiment [3] the dielectric constant was measured by slowly heating the crystal from 80K at the rate 0.5 K/min. It gives e.g., the estimate $t = 330$ min at $T = 245K$. The result of the reconstruction is shown in Fig.2 by the solid line. As one can see from Fig.2, the position and the height of the maximum of $\epsilon_{ZF C}$ are reproduced with very good accuracy. The deviation between the reconstructed values and experimental data is due to violation of the VF law taking place at low temperatures. Indeed, the
temperature of the maximum of $\epsilon_{ZF C}$ corresponds to $T \approx 245K$, which, as discussed above, is the boundary value for the validity of the VF law. If the VF law would be valid for all temperatures then both $\epsilon_{ZF C}$ and $\epsilon(\omega)$ would approach the value $\epsilon_0$ at $T = T_0$. One can see that this tendency is reproduced by the interpolation of the solid curves in Fig.2 to lower temperatures, thus clarifying the origin of the observed low temperature deviations between the reconstructed and experimental values for $\epsilon_{ZF C}$.

VI. CONCLUSION

The high dielectric constant of relaxor ferroelectrics signals that these materials are close to ferroelectric instability which manifests itself in the critical slowing down of dynamics. In disordered relaxor materials the critical slowing down is accompanied by glass like freezing or cluster dynamics, which could be characterized by the non-equilibrium spin glass order parameter. We have developed a dynamical model of the dielectric response in relaxors which explicitly takes into account the co-existence of critical and cluster dynamics and allows for separating them from the experimental observation.

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