Orientational Contribution to the Giant Electrostriction Effect and Dielectric Permittivity in Relaxors

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Abstract

A microscopic model is developed considering randomly oriented polar regions stuck to the directions of random fields or stresses. The application of an external field (stress) in this model results in a dielectric and acoustic reply connected with a polarization (strain) rotation. Polarization (strain) fluctuation contributions are also studied.

1 Introduction

Relaxors like PMN posses very high values of the electrostriction constant and dielectric permittivity; the addition of PbTiO$_3$ (PT) results in a large piezoelectric coefficient, which is important for applications [1]. In the last decade these properties have attracted the attention of theorists because of fundamental reasons: first-principle computations revealed the fact that, under the action of field, the polarization in the steady state can rotate and the system can go through a series of metastable states that results in a dramatic change of strains [2, 3].

The polarization rotation mechanism seems to be general for systems close to frustrations and, in relaxors, we have additional facts supporting this mechanism. In particular this is the finding of the monoclinic phase in PZT and PMN[4, 5]. This phase can be obtained by a continuous rotation of the polarization vector between the tetragonal and rombohedral phases.

It is remarkable that the description of this finding within a 3-order-parameter scheme requires using a Landau expansion up to the 12th-order [6, 7] although from the point of view of the polarization rotation mechanism this phase is natural when going through a continuous path of the rotated polarization vector.

The polarization rotation in relaxors is facilitated by the fact that the local polarization can rotate only in comparatively small volumes, which were called polar regions [8]. The existence of such regions was recently convincingly established by neutron scattering experiments, which showed the so called ”waterfall”
phenomenon \[9, 10\], the essence of which is the limited size of the polar regions leading to the existence of the neutron scattering at large wave vectors only.

At high temperatures the polar regions are absent and the neutron scattering shows the normal behavior; the dielectric permittivity obeys the Curie-Weiss law. Obviously at these temperatures the radius of the ferroelectric polarization fluctuations is small compared to the heterogeneity radius but it increases with the temperature decrease and at some temperature, known as the Burns temperature, it reaches the heterogeneity radius.

At lower temperatures the correlation radius is unable to increase further, because of the limitations imposed on the size of the ferroelectric fluctuation in a disordered media, and a deviation from the Curie-Weiss law is evidenced. At the same time the neutron scattering at small wave vectors becomes flat and, correspondingly, the optic modes can not be separated from the acoustic ones; the central peak, which is usually attributed to the elastic scattering, is growing. These features exactly correspond to the idea of the polarization rotation but in this case local polarization fluctuations of the rotational kind (they can be also called the hydrodynamic polarization fluctuations in order to distinguish them from the ordinary ferroelectric fluctuations) in the finite-size polar regions become important as the correlation radius of the ordinary ferroelectric fluctuations had been already saturated. Just these fluctuations, in our opinion, are responsible for the central peak, waterfall phenomenon dielectric losses and, as we will see, also for the strong electrostriction and piezo-effects.

If one imagined for a moment that the polarization vector direction is fully frustrated in the space then such a system would be unstable due to the degeneracy of the energies of the states with different polarization vector directions; the transverse dielectric susceptibility of such a system would diverge. However this system can be stabilized by fields or stresses.

In relaxors there are special conditions for such fields (stresses) but they are local and random \[11\]. The origin of these fields (stresses) is in the random distribution of the ions with different charges (sizes) over the similar sites. The stabilization of the nanoscale polar regions by the random fields and stresses proves to be one of the most important features of the relaxors, in our opinion.

In fact one can consider the polarization vector directions frustrated but stuck to the local random fields, which can have different magnitudes in different crystallographic directions. It implies that, from the first glance, the polarization vector conserves its magnitude when turning aside but the energy of this dipole is different in different directions due to the interaction of the polarization with the internal local fields (stresses).

Thus the idea of the polarization rotation \[3\] supplemented by the idea of the random fields (stresses) \[11\] seems to be rather promising and further studies in this direction are necessary. As this idea is general for all systems close to frustrations the main features and consequences stemming from this mechanism should be described within a clear and simple (possibly analytical) model in order to use it for qualitative explanations of new experimental facts and predictions.

The present study is kind of an endeavor to develop such a model within a
random field approach and based on the results of first-principle computations \[2,3\]. Some preliminary results applied to KTa$_{1-x}$Nb$_x$O$_3$ as an example were published in Ref. [12]. At the first stage the polarization rotation contribution to the dielectric reply will be considered. Then this approach will be extended to the case of the acoustic reply.

2 Orientable Polar Regions

Consider random fields $\mathbf{e}$ and merged to their directions local dipole moments $\mu$. In the field $\mathbf{E} = \mathbf{E}_0 + \eta \mathbf{P}$, where $\mathbf{E}_0$ is the external field and $\mathbf{P}$ being the polarization, the dipole moments are directed along $\mathbf{E} + \mathbf{e}$.

We assume further that the local polarization has been already appeared in the polar regions and, due to this fact, the action of the field results in the redirection of the dipole moments without changing their magnitudes. It is true if $k_B T \ll \mu e$. Thus this is a purely geometrical problem: one should find the new directions of the local fields at each of the points in space and redirect the local dipole moments from the previous directions determined by only the random fields to the new directions, which are the vector sums of the random and external fields. The final result should be averaged over the points in the space.

It is obvious that in the presence of the external field the average polarization is not longer zero. It can be found from the following analytical expression

$$\langle \mathbf{P} \rangle = \frac{n \mu}{2} \int_0^\pi p(\theta, E) \sin \theta d\theta$$  \hspace{1cm} (1)

where

$$p(\theta, E) = \frac{E + \epsilon \cos \theta}{\sqrt{E^2 + \epsilon^2 + 2 \epsilon E \cos \theta}}$$  \hspace{1cm} (2)

The integration gives

$$\langle \mathbf{P} \rangle = \begin{cases} n \mu (1 - \epsilon^2 / 3E^2) & E > e \\ 2n \mu E / 3e & E < e \end{cases}$$  \hspace{1cm} (3)

It follows from this result that the susceptibility of noninteracting polar regions can be found from the expression:

$$\chi_0 = \frac{1}{\varepsilon_0} \left. \frac{d\mathbf{P}}{dE} \right|_{E=0} = \begin{cases} 2n \mu / 3e \varepsilon_0 & E < e \\ 2n \mu e^2 / 3e_0 E^3 & E > e \end{cases}$$  \hspace{1cm} (4)

where $n$ is the dipole (heterogeneity) concentration. The temperature dependence of the dipole moment is determined by: $\mu = \mu_0 \tanh [(\mu_0 e) / k_B T]$ where $\mu_0$ is the dipole moment magnitude. The Free energy of the noninteracting dipoles can be found by the integration of the dielectric susceptibility:
\[ F = \begin{cases} \frac{3e}{4n\mu} (P - P_0)^2 - EP & E < e \\ \frac{8n\mu^2}{3\sqrt{r_1 - r}} - EP & E > e \end{cases} \]  
where \( P_0 \) and \( P_1 \) are the lowest and highest values of the polarization in the field correspondingly. The \( P \) value is the polarization magnitude as the direction of the field coincides with the direction of the polarization.

The Hamiltonian, which takes into account the local field effects and interactions among the polar regions, can be written in the form

\[ H = \frac{1}{2} \left( \frac{3e}{2n\mu} - \eta \right) \delta P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\xi P^6 + v (\nabla P)^2 - EP \]  

where \( \beta = \beta - 4q/c \), \( q \) is the electrostriction constant and \( c \) being the elastic constant. A large value of the electrostriction constant leads to negative values of the nonlinearity constant \( \beta \) and, consequently, to the phase transition of the first order. Hence the orientable polarization in relaxors results in an additional contribution to the dielectric permittivity, which can be rather large at small random field values.

To take into account the scattering of the random field magnitude we used the following distribution function for a reorientable part of the random fields

\[ f(e) = \frac{1}{(\sqrt{\pi}a)} e^{-|e-\eta P|^2/a^2} \]  

By integrating the expression for the dielectric susceptibility (4) with this function we obtained at \( E < e \)

\[ \chi_0 = \frac{4\eta\mu}{3\varepsilon_0\eta P} \text{erf} (\eta P/a) \approx \frac{4\eta\mu}{3\sqrt{\pi}\varepsilon_0 a} \left[ 1 - \frac{\eta^2 P^2}{3a^3} + ... \right] \]  

It is seen that the bare susceptibility decreases with the width of the distribution function (5) and with polarization \( P \).

We regard the frequency dependence of the dielectric permittivity to potential barriers separating different positions of the random fields. One can consider the random fields coupled to the soft vibrations and these random fields can be polarized by external field according to the distribution function (6).

Consider the case when the polar regions are embedded in an \( ac \) field. Polarization can be found as

\[ P_z = n\mu^2 F(T) E_z \]  

4
where $F(\omega) = \left[4k_B T \left(1 - i (\omega \tau)^{1-\alpha}\right)\right]^{-1}$; $\tilde{E}_z = E_z + \lambda P_{TO}$ is the local field, $E_z$ is an external field and $P_{TO}$ is the polarization connected with the soft mode and $\lambda$ is a coupling constant. The corresponding contribution to the dielectric susceptibility can be written as

$$\chi = \frac{1}{\varepsilon_0} \frac{dP_z}{dE_z} = \frac{n\mu^2}{\varepsilon_0} F(T) (1 + \lambda\varepsilon_0\chi_{TO}) \quad (10)$$

Now one can obtain

$$\chi_{TO} = \frac{1}{\varepsilon_0} \frac{1 + \lambda n\mu^2 F(T)}{A(T) - \lambda^2 n\mu^2 F(T)} \quad (11)$$

$$A(T) = \alpha + 3\beta P_{TO}^2 + 5\gamma P_{TO}^4 - qe \quad (12)$$

Here $q$ is an electrostriction constant and $e$ is strain. It is seen that the dielectric susceptibility connected with ferroelectric fluctuations and polar regions is enhanced due to their mutual coupling; the critical temperature is shifted to higher temperatures; the frequency dispersion is also enhanced at the phase transition point.

3 The dependence of strain on the field

The strained samples become softer in the direction of the elongated axis due to the decrease of the short-range forces. This effect leads to the ordinary electrostriction coupling $-qP^2 e$. The electrostriction coupling can trigger even a phase transition if the stress is large enough. Besides this, ordinary, effect, which has been already well known, we consider here another effect, the alignment of the polar regions due to the stress. The polar regions can be aligned due to the enhancement of the indirect dipole-dipole interaction over the soft mode and because of the enlargement of the probability to occupy the wells at the elongated axis. At first we consider the former possibility and then the latter.

To take a look at the former effect one can use expression (11), from which it is seen that the Debye reply $F(T)$ in the denominator is enhanced by the factor $\lambda^2/A(T)$. Hence the decrease of $A(T)$ due to electrostriction coupling increases the polar region contribution to the dielectric susceptibility and can result in the alignment of the dipoles.

Further we analyze the latter mechanism in the same manner as in the previous section. One can imagine that each polar region produces a stress along the axis of the local polarization and this stress is proportional to the square of the local dipole moment. In the paraelectric phase, on average, the sample is cubic but, nevertheless, the local stress does exist due to the existence of the local dipole moments. When the sample is poled the average stress is not longer zero because of the "alignment" of the strained polar regions in the poling field (this mechanism could be called the "strain rotation" mechanism, which resembles the "polarization rotation mechanism").
The average strain in the field $E$ can be found from

$$s \sim \langle P^2 \rangle = n\mu^2 \int_{-\pi}^{\pi} d^2(\theta, E) \sin \theta d\theta =$$

$$= \frac{n\mu^2}{16eE_3^3} \left[ 12eE^3 - 4e^3E + (E^2 - e^2)^2 \ln \left( \frac{e + E}{e - E} \right) \right]$$

(13)

At small fields this average behaves quadratically with the field

$$\langle P^2 \rangle = \frac{n\mu^2}{3} \left( 1 + \frac{E^2}{10e^2} + \ldots \right)$$

(14)

In the case of the poled sample one should replace $E$ in Exp. (14) with $E + E_p$ where $E_p$ being the internal field arising due to poling the sample. At small poling fields it results in

$$\langle P^2 \rangle = \frac{n\mu^2}{3} \left( 1 + \frac{E_pE}{5e^2} + \ldots \right)$$

(15)

Hence, in ferroelectrics one has

$$s \sim \frac{n\mu^2 E_pE}{3} + \ldots$$

(16)

It is seen that this contribution to the strain is especially large in the case of small magnitudes of the random fields (which, nevertheless, should satisfy the inequality: $\mu e \gg k_B T$).

The piezoeffect coefficient, $ds/dE$, increases with the poling field $E_p$ but at large poling fields the stain saturates. If one takes into account the interaction among the dipoles then an abrupt change of the polarization at some field is possible and this change can cause an abrupt change of the stress.

Thus the orientational polarization and strain can contribute much to the average macroscopic dielectric susceptibility, electrostriction constants and piezo-effect in the case if the sample contains orientable polar regions stuck to small random fields (stresses).

Notice that the question about the conditions for the appearance of the polar regions is a hard question because of the depolarization field. However in the presence of movable charge carriers or due to a cooperative appearance of self-compensated polar regions these conditions become easier.

## 4 Polarization fluctuations

Here we study longitudinal polarization fluctuations caused by the polarization rotations. We will see that the polarization fluctuations in the polar regions can
provide a large additional contribution to the dielectric permittivity. We consider the polarization field \( \mathbf{P}(\mathbf{r}) \) directed along the local field \( \mathbf{E}_l \). In a weak transverse field \( \delta \mathbf{E}_{\perp} \) the transverse polarization has the form:

\[
\delta \mathbf{P}_{\perp} = \mathbf{P}_1 \frac{\delta \mathbf{E}_{\perp}}{\mathbf{E}_l}
\]

where \( \mathbf{P}_1 \) is the polarization magnitude inside the polar region. Hence the transverse susceptibility is \( \chi_{\perp\perp} = \mathbf{P}_1 / \varepsilon_0 \mathbf{E}_l \).

The transverse polarization appeared at one of the space points causes the appearance of a transverse polarization at nearest space points. In order to describe the profile of the polarization field fluctuation one can write the Hamiltonian with taking into account the gradient term

\[
\mathcal{F}_{\perp\perp} = \int \left( \chi_{\perp\perp}^{-1} \mathbf{P}_{\perp\perp}^2 + c (\nabla \mathbf{P}_{\perp\perp})^2 - \mathbf{E}_{\perp\perp} \mathbf{P}_{\perp\perp} \right) dV.
\]

The corresponding correlation function is the Ornstein-Cernike function

\[
< \delta \mathbf{P}_{\perp\perp}(0) \delta \mathbf{P}_{\perp\perp}(\mathbf{r}) > = \frac{k_B T}{4\pi \kappa r} \exp(-\kappa r) \tag{18}
\]

where \( \kappa^2 = (c\chi_{\perp\perp})^{-1} = \varepsilon_0 \mathbf{E}_l / e \mathbf{P}_1 \).

In order to find the longitudinal susceptibility we use the mathematical trick suggested in (14): we employ the condition of the polarization magnitude conservation \( \delta \mathbf{P}_{\parallel} = (\delta \mathbf{P}_{\perp\perp})^2 / 2 \mathbf{P}_1 \) and find that

\[
\chi_{||} = \frac{d}{dE_l} \mathbf{P}_{||} = \frac{1}{2 \mathbf{P}_1} \frac{d}{dE_l} \mathbf{P}_{\perp\perp}^2 = \frac{1}{2 \mathbf{P}_1} \frac{d}{dE_l} \langle \mathbf{P}_{\perp\perp}(0) \mathbf{P}_{\perp\perp}(\mathbf{r}) \rangle \bigg|_{\mathbf{r}=0} \tag{19}
\]

This leads to

\[
\delta \mathbf{P}_{\parallel} = \frac{k_B T}{8\pi (c\mathbf{P}_1)^{3/2} (\varepsilon_0 \mathbf{E}_l)^{1/2}} \delta \mathbf{E}_l = \frac{a}{\sqrt{\mathbf{E}_l}} \delta \mathbf{E}_l \tag{20}
\]

Now, by averaging the result over the random field directions and projecting the result onto the \( z \) axis we have

\[
\chi_{||} = \frac{2a}{7eE_3} \left\{ |E + e|^{7/2} - |E - e|^{7/2} - \frac{7}{6} (E^2 + 2e^2) \left[ |E + e|^{3/2} - |E - e|^{3/2} \right] \right\} \tag{21}
\]

where \( \chi_{||} = d\mathbf{P} / dE \) and \( \mathbf{P} \) is the projection of the polarization on the direction of the external field. The longitudinal contribution has a finite value at zero external field (4\( a/3\sqrt{e} \), which increases with the random field magnitude decrease), increases in small fields quadratically, then reaches a maximum and then decreases as \( E^{-1/2} \). Thus the polarization rotation mechanism results in a large fluctuation contribution to the dielectric permittivity.
In similar way one can consider an acoustic reply. In this case the strain fluctuation should be considered instead of the transverse polarization fluctuation. The physics of these fluctuations is similar as the stress like the field can provide a polar region reorientation. This reorientation appears because in a tetragonally distorted crystal the probability of the occupation of the wells lying at the elongated axis differs from the probability to occupy the wells at the other axes.

5 Easy domain wall movement

The polarization rotation mechanism can result in facilitating the domain wall movements [17] in multidomain ferroelectric samples. Indeed consider domain walls at random directions stabilized by the electrostatic potential produced by the surrounding domains. Let \( \mathbf{n} \) be a unit vector perpendicular to the wall. If one shifts the wall along \( \mathbf{n} \) by a small distance then a force appears returning the wall to the previous place: \( F = -kx \) where \( k \) is a spring constant. Consider \( \theta \) be an angle between the external field \( E \) and \( \mathbf{n} \). In this case the average polarization in the field \( E \) is:

\[
P = \frac{Z^* E}{k} \int_{0}^{\pi} \cos^2 \theta \sin \theta d\theta = \frac{Z^* E}{3k} \tag{22}
\]

where \( Z^* = PS \), \( P \) is polarization magnitude and \( S \) being the domain width. It is seen that the dielectric susceptibility here is determined mainly by the small spring constant value, which is governed by small potential barriers between the dipoles oriented in different possible directions. By employing the same assumptions as above regarding the average strain one can obtain

\[
s \sim \frac{Z^* E^2}{2k^2} \int_{0}^{\pi} \cos^4 \theta \sin \theta d\theta = \frac{Z^* E^2}{5k^2} \tag{23}
\]

which for poled samples results in

\[
s \sim \frac{Z^* E_p E}{5k^2} \tag{24}
\]

Again one can see that a large strain can appear because of the fact that the system is nearly frustrated at the equilibrium position and it is stabilized by only weak random fields and stresses. Such a description is rather similar to the orientational mechanism, which we considered above. In both cases we have the result, which increases with the random field (stress) constants decrease. However the fact that these constants have finite values is significant as just these fields (stresses) stabilize the considered state of the system where we have the system at the frustration point.

This consideration can hold only at comparatively small deviations from the equilibrium state. In the case if the fields are large then the domains can change
their stable configuration abruptly, which can be considered as the relaxation of the random fields (stresses) to new positions with a new distribution function (see Section 3). Coupling between this relaxation and polarization fluctuations can produce a cooperative dynamics.

6 Discussion

The present study has shown that the existence of the nanoscale orientable polar regions in relaxors can provide an additional to the ordinary ferroelectric fluctuations contribution to the dielectric permittivity, electrostriction and piezo effects. Besides this a fluctuation contribution was shown to be also large. These data shed light to the experimental fact found that the relaxors have extremely large electrostriction and piezo- coefficients.

A support of these data was given also by the study of solid solutions of quantum paraelectrics like KTN \[15\], which showed a softening of the elastic constants of KTN in the paraelectric phase well above of the ferroelectric phase transition due to the impurity cluster formation. A rotational mechanism employed in Ref. \[16\] gave a good explanation of the nonlinear electrostriction behaviour in this solid solution.

Thus the nanoscale formations in the disordered materials can play an important role in determining the physical properties of these materials that can be used in practice.

Notice that the Ising model misses these effects as it considers usually two states while in the explanation shown above the 3-dimensional structure of the polar regions is significant as just this structure allows the orientational polarization and fluctuations. The superparaelectric model is also very different as it considers the thermally fluctuating dipoles with the average dipole magnitude dependent on temperature and this is the main point in this model. We showed above that such a model is unstable with respect to the transverse polarization fluctuation and one must to consider fields or stresses stabilizing the polar regions and their fluctuations.

The present model considers the polar region dipoles stuck to the random directions of internal electric fields (stresses), which is significant for the final result. We have shown that being close to the instability at small random field values one can have a rather large contribution to the dielectric permittivity, electrostriction and piezo- effects due to the polarization and stress rotations.

The rotational mechanism is not the only possible mechanism for the large polarization fluctuations in relaxors. Another possibility is the dynamics of the domain walls separating the nanoscale domains \[17\]. This mechanism is similar to the one discussed in the present paper in the point that we have a system close to frustration and actions of small fields or stresses shift the equilibrium coordinates sufficiently. In the orientational mechanism these coordinates are the angles but in the domain walls case these are the positions of the walls.

In any case we have to have random fields or stresses in order to stabilize such a system. If these fields are small then the dielectric and acoustic replies
will be large. The presence of nonlinearities can provoke a phase transition in the field or under the stress.

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