Diffusive phase transitions in ferroelectrics and antiferroelectrics

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Abstract. In this paper, we present a microscopic model for heterogeneous ferroelectric and an order parameter for relaxor phase. We write a Landau theory based on this model and its application to ferroelectric PbFe$_{1/2}$Ta$_{1/2}$O$_3$ (PFT) and antiferroelectric NaNbO$_3$:Gd. We later discuss the coupling between soft mode and domain walls, soft mode and quasi-local vibration and resulting susceptibility function.

A simple model ferroelectric thin film with dead layers was recently analyzed by Bratkovsky and Levanyuk [1] resulting in an analytic solution. Based on this study, we proposed a microscopic model for an inhomogeneous ferroelectric consisting of ferroelectric slabs sandwiched between dielectric interfacial layers [2]. Low energy solutions of these models reveal that the ferroelectric slabs break into alternating domains (Fig. 1) with zero total macroscopic polarization. The size of the domains was shown to depend only on the relative total width of the dielectric and ferroelectric regions in the direction of the field [2]. The nanodomain structure appears cooperatively and its origin lies in the reduction of depolarization field [1, 2].

The alternating polarization domains are accompanied by shear strain owing to the electrostrictive coupling. For the case of domains alternating along (110) direction, we obtained atomic displacements corresponding to polarization and strain fields and calculated diffused scattering intensity [2], which agrees well with recent neutron scattering data [3]. We suggest that the relaxor phase corresponds to a finite value of the order parameter describing these alternating domains.

The fluctuations of the order parameter introduced above are conjugated with the field which we will call $H_0$. We will assume the existence of quenched field $H_0$ below Burns temperature. We use the notation $\eta$ for the relaxor order parameter (the magnitude of polarization inside a nanodomain) and write the Landau expansion:

$$F = F_0 + \frac{1}{2} \alpha P^2 + \frac{1}{4} \beta P^4 + \frac{1}{6} \gamma P^6 +$$

$$+ \frac{1}{2} A \eta^2 + \frac{1}{4} B \eta^4 + \frac{1}{6} C \eta^6 - H_0 \eta + \frac{1}{2} \lambda P^2 \eta^2$$

where $\alpha = \alpha_0(T - T_{CW})$ and $A = a(T - T_{\eta})$.

At zero macroscopic polarization, the equilibrium condition with respect to $\eta$ is
FIGURE 1.  A model of inhomogeneous ferroelectrics [2].

\[ A\eta + B\eta^3 + C\eta^5 - H_0 = 0 \]  
(2)

At high temperatures $\eta$ vanishes as $(T - T_\eta)^{-1}$. In this limit, dielectric permittivity

\[ \chi = \frac{1}{v(T - T_{CW}) + \lambda \eta^2}, \]  
(3)

obeys a Curie-Weiss law. At $T = T_\eta$ there is a deviation from this law, and the dielectric permittivity peak is diffused due to the coupling between the new order parameter appearing at the phase transition and frozen conjugated fields.

We used the expression derived in order to describe the diffuseness of the phase transition in relaxor PFT from the para-phase to the relaxor phase with ferroelectric nano-regions. We also took into account a low temperature (glass-type) phase transition which results in a strong decrease of dielectric permittivity below approximately 220 K. We fitted expressions obtained to experimental data (Fig. 2) and got the best fit shown by the solid line. We find that $T_\eta$ is rather close to the extrapolated high-temperature Curie-Weiss temperature. This justifies that the ferroelectric relaxor order parameter, $\eta$, is connected with local polarization, and can be regarded to a wave of polarization described above.

We use the same expression (3) to treat the diffused phase transition in an antiferroelectric NaNbO$_3$ doped with Gd, where the significance of $\eta$ now is an antiferroelectric order parameter. The resulting fit to experimental data is rather good shown in Fig. 3. The critical temperatures are indicated in the figure. We also show in Fig. 3 the difference between the inverse dielectric permittivity and high temperature Curie-Weiss law.
It is seen that this difference, at low temperatures, behaves linearly with temperature while at the dielectric permittivity peak position it is diffused in accord with the theory. Experimental data [4] show that the “waterfall phenomenon” exists in the whole temperature interval between the freezing temperature and Burns temperature, implying that the soft mode is strongly damped in the relaxor phase (note that this soft mode is not the uniform ferroelectric). We believe this mechanism to be connected with the interaction of the soft mode vibrations with domain walls and with local dipoles (a mathematical expression is similar to that obtained for the soft mode coupled with microscopic dipoles [5, 6]).

The acoustic mode can have a dip due to its coupling with optical mode [7] (Fig. 4a). We suggest that, due to disorder, the deviation of the optical and acoustic modes from average is different in different regions of the disordered crystal and one has to introduce a distribution function of these deviations (Fig. 4b). We also consider the case when the optical mode has a dip (Fig. 4c) if the interaction with the acoustic mode is not taken into account (the first row in Fig. 4). In this case the optical mode dispersion curve is: \( \varepsilon = \omega_0^2 - kq^2 + bq^4 + \ldots \). We derived in this case that the correlation function deviates from the Ornstein-Cernike expression by an oscillating factor:

\[
\chi(r) \sim \frac{1}{r} \sin(k_0 r) \exp(-k_c r) \tag{4}
\]

where \( k_c \) is inverse correlation length and \( k_0 \) is the wave vector of the susceptibility oscillations. In the \( k \)-space susceptibility looks as

FIGURE 2. Temperature dependencies of \( \varepsilon' \) (1) and \( 10^3/\varepsilon' \) (2) measured at \( 10^6 \) Hz for PFT crystal. Solid line is the best fit of the theory to experimental data.
FIGURE 3. Temperature dependencies of $\varepsilon'$ (1) and $10^4/\varepsilon'$ (2) measured at $10^5$ Hz for 0.88NaNbO$_3$-0.12Gd$_{1/3}$NbO$_3$ crystal, and the difference between the experimental $1/\varepsilon'$ dependence and the Curie-Weiss fit of $1/\varepsilon'$ (3). Solid lines are the best fits of the theory to experimental data.

$$\chi(q) \sim \frac{a^2}{(q^2 - k_m^2)^2 + a^4}$$ (5)

Here $k_m^2 = k_0^2 - k_c^2$ and $a^2 = 2k_0 k_c$. These constants are expressed in terms of parameters in the optical mode dispersion: $\omega_0^2/b = k_m^4 + a^4$ and $k/b = 2k_m^2$. The inverse correlation length $k_c$ can be obtained from:

$$k_c^2 = \frac{1}{2} \left[ \sqrt{\frac{\omega_0^2}{b} - \frac{k}{2b}} \right]$$ (6)

where, at $\omega_0^2 > k > 0$, $k_c$ is real. Otherwise, it is imaginary, and there appear harmonic beatings.

A general form of the Hamiltonian taking into account the interaction between the acoustic ($u$) and optical ($x$) displacements (and a dip in the optical mode) is:

$$H_{harm}(q) = \frac{1}{2} u_{-q} A(q) u_q + u_{-q} V x_q + x_{-q} V^* u_q + \frac{1}{2} x_{-q} B(k) x_q$$ (7)

where, at small $q$,

$$A(q) = a q^2$$ (8)
FIGURE 4. Model dispersion curves: a) the condensation of the modes is due to mode-mode coupling, b) the same as (a) but with taking into account disorder, c) the condensation of the modes is due to both the polarization instability and mode-mode coupling; The first row is without the mode-mode coupling, the second row is with the mode-mode coupling; The dashed region arises because of disorder.

\[ B(k) = \omega_0^2 - bq^2 + cq^4 \]  \hspace{1cm} (9)

\[ V(q) = v_1 q^2 + iv_2 Pq \]  \hspace{1cm} (10)

Here P is polarization; The imaginary part of the coupling term appears in symmetry broken regions and in the regions where there exists gradient of polarization, that is at the boundaries of the domains or/and polar regions. This coupling leads to a “repulsion” of the acoustic and optical modes as it is shown in Fig. 4.

We also will discuss the correlation of polarization in the case of a finite volume of the polar region. Let us write dielectric permittivity of a finite uniform volume V:

\[ \chi \sim \frac{T}{V^2} \int dV dV' \langle P(r)P(r') \rangle \sim \frac{T_{\text{CW}}}{kV} \min(r^2, r_c^2) \]  \hspace{1cm} (11)

where an Ornstein-Cernike correlator was used, \( \kappa \) being the constant in front of \( (\nabla P)^2 \) in the Landau fluctuation energy, and \( r_c \sim (T - T_{\text{CW}})^{-1/2} \), in the first approximation. It is seen from this expression that, at high temperatures, susceptibility behaves according to the Curie-Weiss law; when the ferroelectric correlation radius reaches the volume V size then susceptibility saturates. The decrease in polarization at the boundary of a polar region would smoothen this crossover.

We finally consider the Hamiltonian consisting of the part describing the long-range ordered polarization \( P_\mathbf{q} \) (with a wave vector \( \mathbf{q} \)) and coupled with it local polar vibrations with local polarization \( P_l \):
\[
H = \frac{1}{2} \alpha_q P_q^2 + \frac{1}{2} \alpha_l P_l^2 - \alpha_q P_q P_l + \frac{1}{4} \beta P_q^4 + \frac{1}{6} \gamma P_q^6 \\
+ \frac{1}{4} B P_l^4 + \frac{1}{2} g P_q^2 P_l^2 - E P_q - E P_l
\] (12)

The susceptibility connected with quasilocal vibrations at zero polarization \(P_q\) can be found by an ordinary procedure [5]:

\[
\chi_l = \frac{\chi_{l0}}{1 - \alpha_{lq}^2 \chi_{q0}}
\] (13)

where

\[
\chi_{l0} = \frac{1}{\alpha_l + 3 \beta P_l^2}
\] (14)

\[
\chi_{q0} = \frac{1}{\alpha_q + g P_l^2}
\] (15)

It is seen that the quasilocal vibrations become unstable when \(\alpha_{lq}^2 \chi_{q0} < 1\). It implies that the local vibrations satisfying this condition will freeze in and will be arranged in space in accordance with the wave vector \(q\). These results are consistent with resent experimental findings [8] that there is a local transformation at Burns temperature.

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