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The proportion of frozen local polarization in relaxor ferroelectrics

Zhi-Rong Liu[1], **Yong Zhang**[2], **Bing-Lin Gu**[3] **and Xiao-Wen Zhang**[4]

[1] Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China
[2] Beijing Fine Ceramics Laboratory, Institute of Nuclear Energy Technology, Tsinghua University, Beijing 100084, People's Republic of China
[3] Centre for Advanced Study, Tsinghua University, Beijing 100084, People's Republic of China
[4] State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

E-mail: zrliu@phys.tsinghua.edu.cn (Zhi-Rong Liu)

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Abstract

A Landau-type phenomenological cluster theory for modelling the freezing process of the local polarization in relaxors is presented. On the basis of the theory, the proportion of frozen polarization in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMNT) is calculated from the experimental dielectric non-linearity. The local polarization is shown to freeze continuously in a cooling process. The amount of frozen polarization increases with increasing measuring frequency.

Relaxor ferroelectrics (relaxors) have taken on great importance both as regards fundamental solid-state science and applications to advanced technology [1–3]. Relaxors experience no macroscopic phase transition at zero electric field until very low temperatures are reached. However, local polarization exists at much higher temperatures; this is widely believed to be responsible for the special characteristics of relaxors. The concept of a 'polar microregion' in relaxors was first presented by Smolenskii within chemical inhomogeneity theory [4]. The presence of polar microregions was later confirmed by experiments on the non-linear variation of the optical refractive index, the thermal strain, and the thermal expansion coefficient [1,5–7]. The deviation from paraelectric Curie–Weiss behaviour of the dielectric permittivity also suggested the presence of polar regions. Cross [1] showed, within a superparaelectric model, that the polar microregions (represented by independent dipoles) are able to switch between equivalent orientation states and gave a reasonable picture of the nature of the micropolarization at high temperatures. When the temperature decreases, the coupling between the polar microregions controls the kinetics of the fluctuations and the system is frozen into a polar–glassy state [8, 9]. Gui *et al* used the Monte Carlo method to simulate the freezing process in relaxors and showed that some dipoles are slowed down or frozen due to the interactions [10]. A special phase transition consisting of successive ergodic space-shrinking episodes was also proposed on the basis of the freezing process [11]. Kleemann and co-workers, however, proposed that the polarization is frozen due to the quenched random electric fields [12, 13].

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Some work has been done with the aim of quantitatively analysing the freezing process of local polarization. Qian and Bursill developed a phenomenological theory to describe the interaction of polar domains and to simulate the dielectric relaxation and phase transition of relaxors [14]. Nambu and Sugimoto proposed a Landau-type mean-field theory based on consideration of a gradual condensation of local polarization, and confirmed a picture of diffuse phase transition in relaxors [15]. In this paper, we propose a Landau-type phenomenological cluster theory of relaxors and calculate the proportion of frozen polarization from the experimental dielectric non-linearity.

The phenomenological free energy is defined as

$$F = 2^{-1}N\alpha(T)P^2 + 4^{-1}N\alpha_{11}P^4 + 2^{-1}\gamma P^2\sum_i n_i P_i^2 + 2^{-1}\sum_i n_i\alpha_i(T)P_i^2 + 4^{-1}\alpha'_{11}\sum_i n_i P_i^4 \tag{1}$$

where P is the uniform polarization, and P_i is the ith frozen local polarization. N is the total number of lattice sites, and n_i is the lattice-site number for the ith local polarization. α and α_i are written as

$$\alpha(T) = (T - T_0)/\varepsilon_0 C \tag{2}$$

$$\alpha_i(T) = (T - T_i)/\varepsilon_0 C_i \tag{3}$$

and α_{11} and α'_{11} are constants as in the conventional Landau theory. The couplings between the global polarization and the local ones are written as $\gamma P^2 P_i^2$ from symmetry considerations.

The equilibrium values of the frozen polarizations $\{P_i\}$ are determined by minimizing the free energy F in equation (1). Minimizing F with respect to $\{P_i\}$ gives

$$\partial F/\partial P_i = 0. \tag{4}$$

That is,

$$\gamma P^2 n_i P_i + n_i\alpha_i(T)P_i + \alpha'_{11}n_i P_i^3 = 0. \tag{5}$$

Thus P_i is solved from equation (5) as

$$P_i^2 = -\alpha_i(T)/\alpha'_{11} - \gamma P^2/\alpha'_{11}. \tag{6}$$

We define P_{i0} as

$$P_{i0}^2 = -\alpha_i(T)/\alpha'_{11} = (T_i - T)/\varepsilon_0 C_i\alpha'_{11} \tag{7}$$

and then P_i can be rewritten as

$$P_i^2 = P_{i0}^2 - \gamma P^2/\alpha'_{11}. \tag{8}$$

When relaxors stay in the non-polar state ($P = 0$), the frozen polarization P_i is equal to P_{i0}. Substituting equations (7) and (8) into equation (1) yields the free energy

$$\overline{F} = 2^{-1}NP^2\left[\alpha(T) + \gamma\frac{1}{N}\sum_i n_i P_{i0}^2\right] + 4^{-1}NP^4\left[\alpha_{11} - \frac{\gamma^2}{\alpha'_{11}}\frac{1}{N}\sum_i n_i\right] + \text{constant}. \tag{9}$$

We introduce

$$q(T) = \frac{1}{N}\sum_i n_i P_{i0}^2 \tag{10}$$

and

$$n(T) = \frac{1}{N}\sum_i n_i \tag{11}$$

and now equation (9) can be expressed as

$$\overline{F} = 2^{-1}Na(T)P^2 + 4^{-1}Nb(T)P^4 + \text{constant} \tag{12}$$

where

$$a(T) = \alpha(T) + \gamma q(T) \tag{13}$$

$$b(T) = \alpha_{11} - \frac{\gamma^2}{\alpha'_{11}}n(T). \tag{14}$$

For relaxors, the sum of local polarizations is equal to zero, while the sum of the squares of local polarizations is not zero as can be observed from the non-linear behaviours of the optical refractive index and the thermal strain, etc [1, 5–7]. So $q(T)$ is the order parameter that we use to represent the appearance of local polarizations. $n(T)$ is the proportion of the lattice sites showing frozen polarization. It should be noted that equation (7) is valid only for $T < T_i$ (for $T > T_i$, $P_{i0} = 0$; i.e. the ith local polarization is not frozen), so the summations in equations (9)–(11) can be carried out only over the non-zero local polarizations ($P_{i0}^2 > 0$), and $n(T)$ and $q(T)$ vary with the temperature.

The dielectric susceptibility is easily calculated from the thermodynamic relation between the dielectric field

$$E = \frac{1}{N}\frac{\partial \overline{F}}{\partial P} = a(T)P + b(T)P^3 \tag{15}$$

and the uniform polarization P; i.e.,

$$\frac{1}{\varepsilon(T)} = \left.\frac{\varepsilon_0 E}{P}\right|_{E=0} = \varepsilon_0 a(T) = \frac{T - T_0}{C} + \varepsilon_0\gamma q(T). \tag{16}$$

It can be seen that the dielectric susceptibility deviates from Curie–Weiss behaviour due to the existence of the local order parameter $q(T)$. Schmitt and Kirsch obtained a relation similar to equation (16) from simple phenomenology for the (Pb, La)(Zr, Ti)O_3 (PLZT) system [16]. Nambu and Sugimoto derived the same relation on the basis of a more general mean-field theory and explained the difference between the phase transitions in PMN and Pb($Sc_{1/2}Ta_{1/2}$)O_3 (PST) [15]. The purpose of this work was to investigate $n(T)$, and not $q(T)$. So we consider the dielectric non-linearity, i.e. the susceptibility corresponding to a non-zero electric field E:

$$\begin{aligned}\varepsilon_E(T) = \frac{P}{\varepsilon_0 E} &= \frac{1}{\varepsilon_0}\frac{1}{a(T) + b(T)P^2} \\ &\approx \frac{1}{\varepsilon_0 a(T)} - \frac{b(T)}{\varepsilon_0 a^2(T)}P^2 = \varepsilon(T) - \varepsilon_0^3 E^2 \varepsilon^2(T)\varepsilon_E^2(T)b(T).\end{aligned} \tag{17}$$

According to equations (17) and (14), $n(T)$ can be obtained as

$$n(T) = \frac{\alpha'_{11}}{\gamma^2}\left[\alpha_{11} + \frac{1}{\varepsilon_0^3 E^2}\frac{\varepsilon_E(T) - \varepsilon(T)}{\varepsilon^2(T)\varepsilon_E^2(T)}\right]. \tag{18}$$

The value of α_{11} can be obtained from the experimental data at high temperatures by setting $n(T) = 0$ in equation (18) since there is no frozen polarization at high temperatures. So, by using equation (18), the proportion of frozen polarization, $n(T)$, can be determined, except a constant coefficient α'_{11}/γ^2, from the experimental dielectric non-linearity.

We take a typical and well-known relaxor, Pb($Mg_{1/3}Nb_{2/3}$)O_3–$PbTiO_3$ (PMNT), as an example to analyse the proportion of frozen polarization. The samples were prepared by a two-stage calcination method. The magnesium niobate is synthesized by calcining $MgCO_3{\cdot}Mg(OH)_2{\cdot}6H_2O$ and Nb_2O_5 at 1000 °C for 6 h. The columbite phase was then mixed with lead oxide and titanium oxide to form the composition 0.96PMN–0.04PT. Excess PbO

(0.3 wt%) was added to compensate for PbO loss during heat treatment. The mixture was ball milled and calcined again at 800 °C for 2 h. A 10 mm uniaxial steel die was employed to produce green pellets from the calcined powder, using a pressure of 100 MPa. The pressed pellets were subsequently sintered in a covered alumina crucible at 1200 °C for 1 h. After sintering, the pellets were polished to a thickness of 0.6 mm and silver paste was applied and fired at 600 °C to achieve a conductive and adherent coating. The dielectric susceptibility was measured at various frequencies with an LCR precision meter (Model HP 4284A, Hewlett-Packard, Palo Alto, CA) remotely controlled through a desktop computer. A temperature chamber (Model 2300, Delta Design, San Diego, CA) was interfaced to the computer to allow measurement of dielectric properties at various temperatures. The amplitudes of the ac measurement fields were 0.05 and 0.25 kV cm^{-1}.

An illustration of the temperature dependence of the dielectric response at a low frequency, 100 Hz, is shown in figure 1(a), and the corresponding calculated proportion of frozen polarization is given in figure 1(b). The curves in figure 1(a) demonstrate typical dielectric

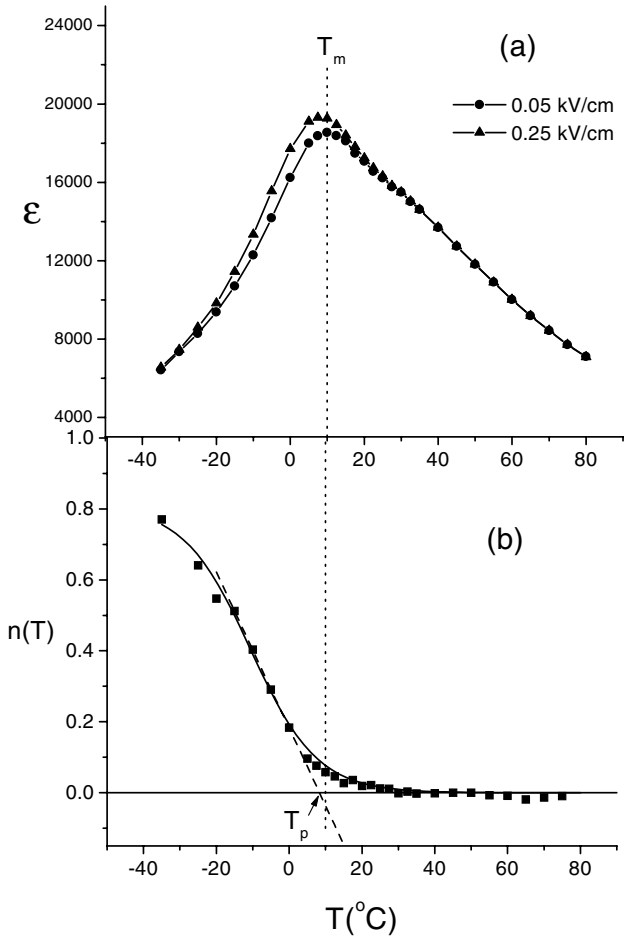

Figure 1. (a) The dielectric permittivity of PMNT as functions of temperature at various drive amplitudes when the frequency is fixed as 100 Hz. (b) The proportion of frozen polarization (arbitrary units) in PMNT calculated from the data in (a) using equation (18).

non-linear behaviour with the magnitude of the susceptibility increasing with increasing field amplitude and the maximum shifting to lower temperatures, which is consistent with the previous observations [17]. The curve of the proportion of frozen polarization, $n(T)$, is determined with an arbitrary factor. It can be seen that $n(T)$ is equal to zero at high temperatures, which means that the local polarization is all dynamic [1, 14]. When the temperature decreases to approach the temperature of the susceptibility maximum (T_m), $n(T)$ starts to increase; i.e. some local polarization is frozen. After crossing T_m, $n(T)$ increases rapidly with decreasing temperature, and an extrapolation of the slope at the inflection point to zero yielded a critical temperature $T_p = 8.3\ ^\circ$C. The monotonic increase of $n(T)$ with decreasing temperature in figure 1(b) shows that the calculation is physically realistic.

In the works of other researchers [9,16], the calculated quantity is the local order parameter $q(T)$ which is determined from the temperature dependence of the zero-field susceptibility (see equation (16)). The increase of $q(T)$ with decreasing temperature is ensured by the decrease of the susceptibility at low temperatures. However, the quantity investigated here, $n(T)$, is calculated from the non-linear effect (see equation (18)). It should be noted that the dielectric non-linearity is strongest when the temperature is near T_m, while the proportion of frozen polarization is not large in that temperature range. This seems to be in conflict with the notion that the frozen polarization is the origin of the dielectric non-linearity. The key to dealing with this problem is that the non-linearity is approximately proportional to the fourth power of the susceptibility (see equation (17)). The susceptibility reaches its maximum at T_m, so the non-linearity is strong near T_m. This can also explain the weakening of the non-linearity when the proportion of frozen polarization increases on further decreasing the temperature.

Another feature of figure 1 is that the frozen polarization, i.e. the local polarization which experiences a phase transition and loses ergodicity, does not appear suddenly, but increases continuously, this increase being accompanied by a decreasing of the susceptibility. This is a kind of phase transition where the ergodic space shrinks in successive episodes [11].

A few sentences can be included here exploring the origin of the effect of the dielectric amplitude on the susceptibility. From equation (8) one knows that the magnitude of the frozen polarization decreases with increasing external field. In other words, the driving force on the polarization is enhanced when the ac-field amplitude increases, so the frozen polarization is forced to flip faster, and some frozen polarization is unfrozen and gives a contribution to the polarization process. Thus the susceptibility increases with increasing field amplitude.

Figure 2 shows the curves of frozen polarization proportion at different measuring frequencies. When the frequency increases, the curve of the proportion shifts slightly towards higher temperatures. This implies that the timescale of polarization flipping is shortened when the frequency increases, so more polarization cannot reach the equilibrium state within the observation time, i.e. more polarization is frozen. The slight increase of frozen polarization would result in the decreasing of the susceptibility at higher frequency, which is known as the frequency dispersion in relaxors. The curve for T_p (T_p is defined in figure 1(b)) is depicted in figure 3 together with the curve for T_m for comparison. It clearly demonstrates the increase of T_p with increasing frequency. And we can see that T_m increases more rapidly than T_p does.

There are several points that should be discussed here. Firstly, the couplings between local polarization are not included in equation (1). However, if the couplings between polarization are considered, through a solution procedure similar to that in reference [15], the results presented in this paper remain valid on redefining the parameters. Secondly, we only consider the fourth-power terms in the free energy and ignore the influence of the higher terms in this work. And the coefficients α_{11}, α'_{11}, and γ are considered as temperature independent. All of these defects restrict the application of the theory. Finally, in this paper the local properties are included within the Landau expansion by introducing the locally changing quantities n_i.

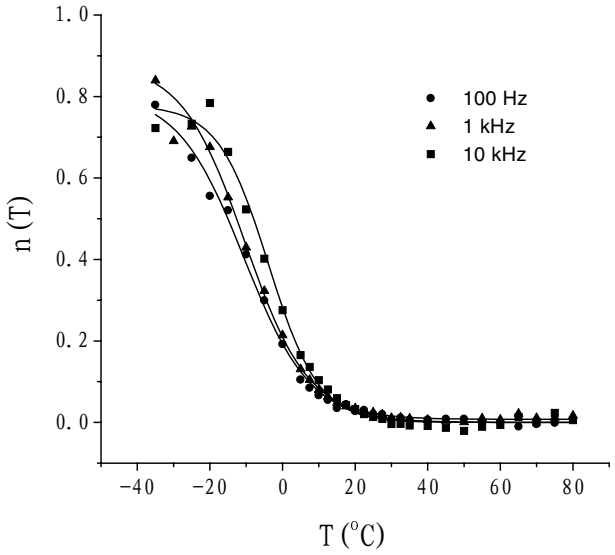

Figure 2. The proportion of frozen polarization in PMNT for different measurement frequencies.

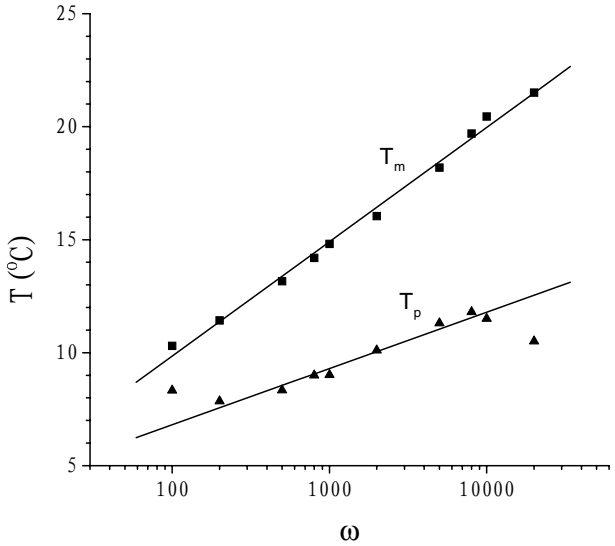

Figure 3. The curves for T_m (temperature of the susceptibility maximum) and T_p (defined in figure 1) as functions of measurement frequency.

Consequently, one expects the appearance of a distribution for n_i which is lacking in the model. As a result, all quantities should be averaged over such a distribution.

In summary, a Landau-type phenomenological cluster theory of relaxors is proposed in this paper for evaluating the influence of frozen polarization. The proportion of frozen polarization in PMNT is calculated from experimental data on dielectric non-linearity. It is shown that the frozen polarization starts to appear when the temperature decreases near to T_m, and increases rapidly after T_m is crossed. When the ac-field frequency increases, the amount of frozen polarization rises too.

Acknowledgments

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