

## Dielectric properties of relaxor ferroelectric films

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Citation: [Journal of Applied Physics](#) **98**, 094105 (2005); doi: 10.1063/1.1980538

View online: <http://dx.doi.org/10.1063/1.1980538>

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## Dielectric properties of relaxor ferroelectric films

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(Received 6 August 2004; accepted 29 May 2005; published online 7 November 2005)

Dielectric properties of the relaxor films are theoretically investigated with the Monte Carlo simulation. We find that the size effect on the dielectric susceptibility of films is neglectable while the influence of the surface layer of the film is overlooked. On the contrary, while the surface layer is explicitly considered, we observe a systematic increase of  $T_m$  (the temperature at which the dielectric susceptibility reaches the maximum) and a systematic decrease of the maximum dielectric susceptibility as the film thickness decreases. An additional broadening of the transition region around  $T_m$  and the frequency dispersion of the dielectric susceptibility above  $T_m$  are also observed. The mechanism responsible for these phenomena is presented. © 2005 American Institute of Physics. [DOI: 10.1063/1.1980538]

### I. INTRODUCTION

Relaxor ferroelectrics have been extensively studied because of their anomalous dielectric characteristics<sup>1</sup> their excellent dielectric, electromechanical, and electro-optical properties. A number of different models<sup>2-6</sup> have been proposed to account for the unusual physical properties of relaxor ferroelectrics such as the dipolar-glass model, the quenched random-field model, and the random-band-random-field model. However, the origin of the unusual dielectric features of relaxors has remained the subject of some controversy, and no model has been completely accepted. It has been widely suggested that the presence of polar microregions in nanoscale is crucial to the relaxor behaviors.<sup>1-7</sup>

The potential impact of thin-film relaxor ferroelectrics in integrated actuators and sensing applications has stimulated research on thin films. An issue considerably concerned is whether or not the relaxor films display the relaxor behavior and the excellent dielectric properties. Many experiments have shown that thin-film relaxors retain the relaxorlike behaviors, such as a diffused  $\chi \sim T$  response, frequency dispersion of the dielectric susceptibility, and a deviation from the Curie-Weiss law above  $T_m$ .<sup>8-11</sup> However, contrary to the previous expectations, the excellent dielectric and electromechanical properties of the bulk single crystal or ceramic relaxor ferroelectrics have not been achieved in films. The maximum dielectric susceptibility for films of  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN)-type relaxor ferroelectrics was found to be smaller than that in the bulk by almost two orders of magnitude.<sup>12</sup> This may result from the small thickness of the film (size effect), or low permittivity dielectric layer near the electrode surface (surface layer effect). It is still controversial which is the dominating factor. In many studies, the behavior of the relaxor films was modeled by assuming a special surface layer such as the “dead layer” (nonswitching

passive layer).<sup>8,13-15</sup> These works supported the opinion that there are no size effects in relaxor films. However, it should be pointed out that in these works, the size effects have not been directly investigated and the strong assumption of the capacitance of surface layer may not be reasonable. Therefore, the validity of the conclusion that the size effect is trivial is worth further discussing. Furthermore, the reason for the frequency dispersion of permittivity above  $T_m$  is still unclear.

In this work, we investigated the size effect and the surface layer effect on the relaxor films. We found that without considering the surface layer, the behavior of the dielectric response hardly changes with the film thickness. While the effect of the surface layer is included, the film exhibits unique thickness-dependent dielectric properties. Our model, without any strong assumption to the dielectric response of the surface layer, can well describe the peculiar dielectric behavior of the relaxor films such as an additional broadening of the transition region around  $T_m$ , the frequency dispersion of the dielectric susceptibility above  $T_m$ , and a systematic decrease of the maximum dielectric susceptibility  $\chi_m$  with decreasing film thickness. The reason will be discussed in detail. We found that the frequency dispersion of the dielectric susceptibility above  $T_m$  can always be observed as long as the dielectric response of the surface layer is obviously different from those of the internal layer and the volume of the surface layer is comparable with that of the internal layer.

### II. METHOD

Transmission electron microscopy (TEM) investigations have confirmed the existence of 1:1 ordered nanodomains in a disordered matrix in PMN films.<sup>12</sup> The electron diffraction<sup>16</sup> and Raman spectroscopy<sup>17</sup> also indicated that the microstructures of the films are similar to those of the bulks. Therefore the model Hamiltonian previously

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proposed<sup>3</sup> to describe the dielectric response process in relaxor ferroelectrics should be also valid for relaxor ferroelectric thin films. By regarding microregions as dipoles, the model Hamiltonian including the random interactions between microregion is given as<sup>3</sup>

$$H = - \sum_{i \neq j} J_{ij} \sigma_i \sigma_j - E_{\text{ext}} \bar{\mu} \sum_i \frac{|\mu_i \cos \theta_i|}{\bar{\mu}} \sigma_i, \quad (1)$$

where  $\sigma_i$  and  $\sigma_j = \pm 1$  are dipole spins. When the projection of the  $i$ th dipole moment  $\vec{\mu}_i$  on the direction of the external field  $\vec{E}_{\text{ext}}$  is positive,  $\sigma_i$  takes the value of +1; otherwise,  $\sigma_i$  takes the value of -1.  $\theta_i$  is the angle between  $\vec{\mu}_i$  and  $\vec{E}_{\text{ext}}$ , and  $\bar{\mu}$  is the maximal magnitude of the dipole moments.  $J_{ij}$  is the effective interaction energy between the nearest-neighbor dipoles, which has a Gaussian distribution.  $J_{ij}$  reflects the correlation between polar microregions, which is essential to the glassy behaviors,<sup>2,3,18</sup> and is determined by the following random variables: (a) the magnitude of the polar microregion, (b) the polarization directions of the polar microregions, and (c) the distance between the polar microregions. These random variables may be influenced remarkably by many extrinsic factors such as the electrode and the growth strain. If the film is thick, enough the effect of these extrinsic factors can be completely relaxed and then the internal part of the film is hardly influenced by these extrinsic factors. In this case, the film can be roughly divided into two parts: one is the surface layer where  $J_{ij}$  has a Gaussian distribution with a width of  $\Delta J_2$ , and the other is the internal layer where  $J_{ij}$  has a Gaussian distribution with a width of  $\Delta J_1$ . The similar approximation has been adopted by Wang *et al.*<sup>19</sup> and Aguilera-Granja and Moran-Lopez.<sup>20</sup> In consideration of that the capacitance of the surface layer is always comparatively low, we can reasonably assume that  $\Delta J_2 > \Delta J_1$ .

Monte Carlo simulations were performed on a  $32 \times 32 \times h$  simple cubic lattice with periodic boundary conditions in the  $x$ - $y$  plane. The details of simulation process can be found in Ref. 3. The dielectric susceptibility is defined as

$$\chi = \frac{C}{NT} \left\langle \sum_i^N \frac{1}{1 + (\omega \tau_i)^2} \right\rangle, \quad (2)$$

where  $C$  is a temperature-independent constant,  $1/\tau_i$  is the flip time of the  $i$ th dipole during the observation time  $t_{\text{obs}}$ ,  $\omega$  is the measured frequency, and  $\langle \dots \rangle$  denotes the configurational averaging.

During the simulation, the attempt to flip was made for every dipole on the lattice sites in sequence.<sup>3</sup> The time was measured in units of Monte Carlo step per dipole (MCS/dipole), which consists of  $32 \times 32 \times h$  attempted flips. For relaxors, what is observed at low temperatures is the quasi-equilibrium properties of a certain component in the phase space due to the broken ergodicity. As proved in spin glass, the short-time Monte Carlo simulation gave excellent agreement with experiments.<sup>21</sup> Therefore we chose  $t_0 = 1200$  MCS/dipole to eliminate the influence of the initial state and  $t_{\text{obs}} = 2000$  MCS/dipole to be the observation time.

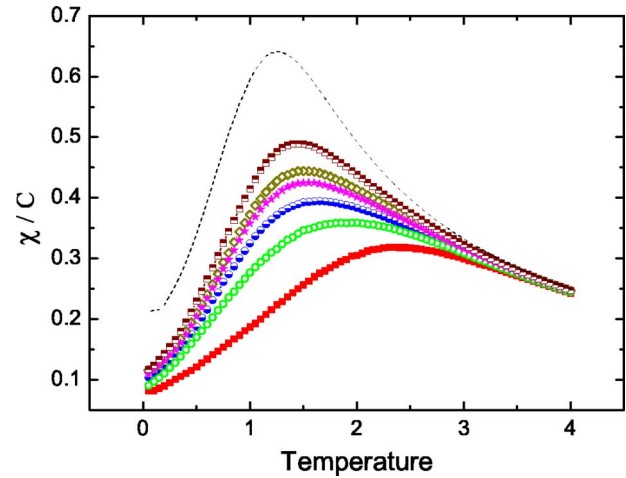


FIG. 1. (Color online) The dielectric susceptibility  $\chi$ , reduced by a temperature-independent constant  $C$  [see Eq. (2)], as a function of temperature  $T$  (in units of  $\Delta J_1/k_B$ ) while  $\Delta J_2/\Delta J_1=2$  and  $h_1=2$ . The film thicknesses  $h$  are, from bottom to top, 5, 7, 9, 11, 13, and 21, respectively. The dashed line corresponds to the case without the surface layer. The measuring frequency is  $70/(2000 \text{ MCS/dipole})$ .

The simulations were performed in many runs with various initial conditions so that the configurational averaging can be done.

### III. RESULTS AND DISCUSSION

First, in order to clarify the size effect, we investigated the effect of the film thickness on the dielectric susceptibility of the film without the surface layer. We found that the curves of  $\chi \sim T$  are almost the same for the films with different thicknesses. This indicates that the size effect is not significant in relaxor ferroelectric films unless the film is too thin to form polar nanodomains.

Then, we investigated the influence of the surface layer on the dielectric susceptibility. In our simulation, we assume that the effect of many extrinsic factors such as the electrode and the growth strain can be fully relaxed in the films, which is valid for thick films. Correspondingly, the surface layer thickness  $h_1$  can be viewed as independent of the film thickness. Figure 1 shows the dielectric susceptibility as a function of the temperature for films with different thicknesses while  $\Delta J_2/\Delta J_1=2$  and  $h_1=2$ . We can see that the dielectric susceptibility  $\chi$  reaches its maximum at a certain temperature ( $T_m$ ) and varies gradually around  $T_m$ , which is known as the diffuse phase transition (DPT) in relaxors. The curve of  $\chi \sim T$  varies with the film thickness. The dielectric susceptibility decreases with decreasing film thickness. For the sake of comparison, the result without the surface layer is also shown in Fig. 1. An additional broadening of the transition region around  $T_m$  can be observed for the film with the surface layer. The thinner the film, the more obvious the broadening. Figure 2 shows the dielectric maximum as a function of the film thickness. We can see that with decreasing film thickness, the dielectric maximum  $\chi_m$  decreases and the corresponding  $T_m$  moves to higher temperature. This is consistent with the experimental observation.<sup>22</sup> The above phenomenon, that the decrease of  $\chi_m$  always goes with the increase of  $T_m$ , has also been observed in many other cases such as

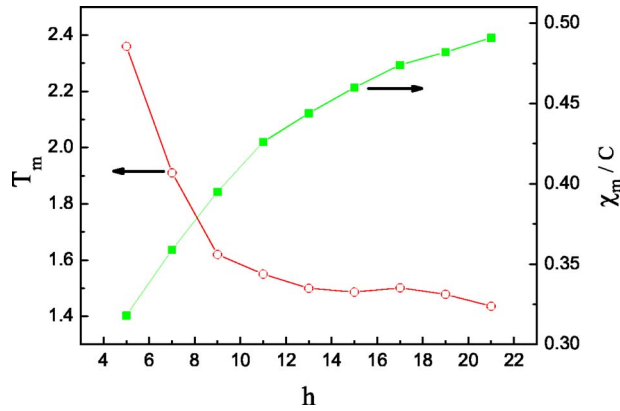


FIG. 2. (Color online) The dependence of  $T_m$  (in units of  $\Delta J_1/k_B$ ) and  $\chi_m$  on the film thickness  $h$  while  $\Delta J_2/\Delta J_1=2$  and  $h_1=2$ . The measuring frequency is  $70/(2000 \text{ MCS/dipole})$ .

applying an external field,<sup>3</sup> enhancing the acceptor doping concentration,<sup>23,24</sup> or increasing the measuring frequency. In all these cases, the overall effect is equivalent to increasing the measuring frequency and the same mechanism works, as suggested in Ref. 3.

In Fig. 3, the dielectric susceptibility is shown as a function of the temperature for different frequencies while  $h=9$ ,  $h_1=2$ , and  $\Delta J_2/\Delta J_1=2$ .  $T_m$  increases with increasing frequency  $\omega$  (as shown in Fig. 4) and  $T_m$  can be well fitted with the Vogel-Fulcher relation (the dashed line in Fig. 4),<sup>2,25,26</sup> which indicates a relaxorlike behavior in the film. The obvious frequency dispersion above  $T_m$  is also observed. The concepts of “slow dipole” and “fast dipole”<sup>3</sup> can help us understand such a frequency dispersion. Fast dipoles are those dipoles which flip fast enough to keep up with the changing of the measuring field and contribute to the dielectric susceptibility. But the slow dipoles do not contribute to the dielectric susceptibility due to their too slow flipping. For a certain measuring frequency, there exists a temperature (denoted by  $T_s$ ) below which the slow dipole appears.<sup>27</sup> At this temperature, the proportion of slow dipole in dipoles increases with increasing measuring frequency, which leads

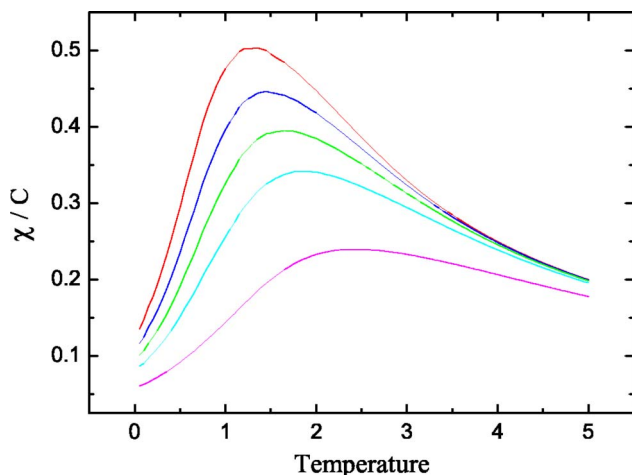


FIG. 3. (Color online) The dielectric susceptibility  $\chi$ , reduced by a temperature-independent constant  $C$  [see Eq. (2)], as a function of the temperature (in units of  $\Delta J_1/k_B$ ). The measuring frequencies (in units of 2000 MCS/dipole) are, from bottom to top, 300, 120, 70, 40, and 20, respectively.

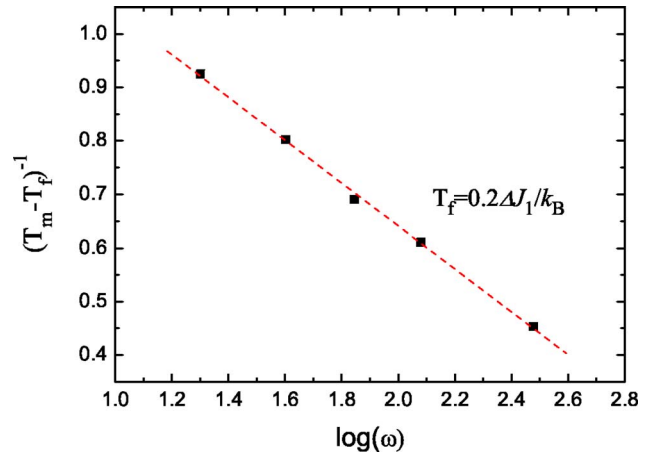


FIG. 4. (Color online) The temperature of the dielectric maxima as a function of the frequency. The dashed line shows the Vogel-Fulcher relationship.

to the frequency dispersion. This temperature is nearby  $T_m$ . Therefore, in general, the frequency dispersion becomes obvious only below  $T_m$ . However, if the materials such as films consist of the components with different Gaussian distribution widths  $\Delta J$ , the situation is different. Each component will have different  $T_s$ . For convenience, we denote  $T_s$  of the surface layer and  $T_s$  of the internal layer as  $T_s^f$  and  $T_s^i$ , respectively. The dipoles in the surface layer are more easily frozen due to a larger Gaussian distribution width. Therefore,  $T_s^f$  is higher than  $T_s^i$ .  $T_m$  is between  $T_s^f$  and  $T_s^i$ , and closer to  $T_s^i$  than to  $T_s^f$  due to a higher dielectric susceptibility in the internal layer. Then the frequency dispersion also appears in the temperature region between  $T_m$  and  $T_s^f$ .

An interesting issue is the dependence of frequency dispersion in relaxor films on the surface layer. Above a certain temperature, denoted as  $T_d$ , the frequency dispersion of the dielectric susceptibility disappears (the dielectric susceptibility is the same for the given two measuring frequencies). We calculated  $T_d - T_m$  (namely, the frequency dispersion temperature scope above  $T_m$ ) as a function of  $\Delta J_2/\Delta J_1$  (the ratio of the Gaussian distribution width of the surface layer to that of the internal layer). We observed a linear dependence, as shown in Fig. 5. Therefore, the frequency dispersion temperature scope above  $T_m$  indeed reflects the extent of the dielectric difference between the surface and internal layers. Whether or not the frequency dispersion is distinct is also determined by the volume ratio of the surface layer to the internal layer. The frequency dispersion above  $T_m$  will disappear when the volume proportion of the surface layer is too large or too small.

#### IV. SUMMARY

In summary, the effect of the electrode and the growth strain in the surface layer is implicitly considered in our model by adopting a different Gaussian distribution width in the surface layer. We do not make any further assumption to the dielectric response of the surface layer. We found that  $T_m$  increases and  $\chi_m$  decreases with decreasing film thickness, which is consistent with the experimental observation. We confirm that the anomalous properties, such as the frequency dispersion above  $T_m$  and low  $\chi_m$ , in relaxor ferroelectric

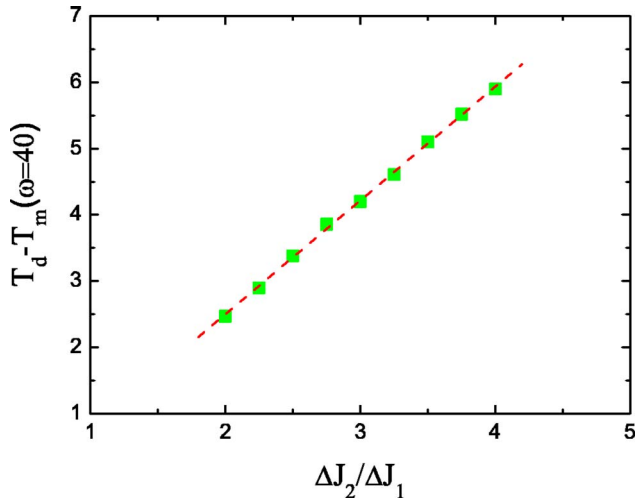


FIG. 5. (Color online) The frequency dispersion temperature scope above  $T_m$  for the given frequency of 20 and 40 (in units of 2000 MCS/dipole) as a function of the ratio,  $\Delta J_2/\Delta J_1$ , of the Gaussian distribution width of the surface layer to that of the internal layer while  $h_1=2$  and  $h=9$ .

films should be attributed to the influence of the surface layer. The obvious frequency dispersion above  $T_m$  can be observed as long as the volume of the surface layer is comparable with that of the internal layer and their dielectric responses (in other words, the Gaussian distribution widths) are markedly different. The frequency dispersion temperature scope above  $T_m$  linearly depends on the ratio of the Gaussian distribution width of the internal layer to that of the surface layer, which indicates that the dielectric difference between the surface and internal layers can be well reflected by the frequency dispersion temperature scope above  $T_m$ .

## ACKNOWLEDGMENTS

This work was supported by the State Key Program of Basic Research Development of China (Grant No. TG2000067108), the National Natural Science Foundation of

China (Grant Nos. 10325415, and 50432030), and the China Postdoctoral Science Foundation.

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