Dynamics of the freezing process in relaxor ferroelectrics

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The dynamics of the freezing process in relaxor ferroelectrics are investigated by Monte Carlo computer simulation. The concepts of "frozen dipole" and "slow dipole" are proposed according to the flipping frequency during the observation time of simulation. The deviation from Curie-Weiss behavior and the frequency dispersion in relaxor ferroelectrics have been proved to be caused by the increasing proportion of slow dipoles. The simulation shows that the external field reduces the dielectric constant and increases the temperature of dielectric maximum, which agrees with the experiment results. The polarization behavior with various electrical and thermal histories and starting from different initial states is also simulated and a systematic explanation based on the bifurcation tree of components in phase space is given. It is proposed that the relaxor characteristics are caused by a gradual freezing process of polar microregions, which arises from the inhomogeneous crystal structure of this kind of material.

I. INTRODUCTION

Relaxor ferroelectrics are characterized by the diffuse phase transition (DPT), a strong frequency dispersion of the dielectric constant, and the absence of macroscopic polarization and anisotropy at temperatures far below T_{max}.[1] The polarization mechanism of relaxors is believed to be different from that of normal ferroelectrics. Smolenski and Agranovskaya[2] originally proposed that the DPT was caused by the chemical inhomogeneity arising from the B-site cation disorder in complex perovskite relaxors. Later, nanoscale ordered microregions were found by transmission electron microscopy (TEM) in these materials.[3-5] The lattice image of nanoscale ordered microregions embedded in the disordered matrix has been revealed by high-resolution TEM recently.[6] It was suggested that the nanoscale ordered microregions act as locations of polar microregions.[1,4,5,7] Cross[1] has proposed that nanoscale dipole clusters thermally fluctuate between equivalent polarization directions, analogous to superparamagnetism.[8] But physically unreasonable values of the activation energy and preexponential factor were obtained when modeling the frequency dispersion of T_{max} by the simple Debye equation.[9] It was then found that the data of (ω, T_{max}) fitted the Vogel-Fulcher relationship better,[10,11] showing that there is a freezing process in relaxors analogous to spin-glass systems.[12] Glassy polarization behavior is also found in relaxors.[13]

The special phase transition in a spin glass is known to be caused by the randomly competing forces between spins due to the oscillating nature of the long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange in-

teractions.[12] It has been proposed in relaxors that the correlations between polar microregions are essential to the glassy behaviors,[10,11,13,14] but how the correlations affect the polarization process remains unclear. In this contribution, a model Hamiltonian is proposed after analyzing the characteristics of interactions between polar microregions. The dynamics of the freezing process is simulated by the Monte Carlo method. The purpose is to study the basis of relaxor characteristics.

II. THEORETICAL MODEL

We base our model on the following hypotheses which are supported by experimental facts or theoretical calculations in relaxors.

(1) There exist large quantities of nanoscale ordered microregions with different volumes distributed in the disordered matrix.[3-6]

(2) Spontaneous polarization occurs in these ordered microregions when the temperature decreases below T_d, which is several hundred degrees above T_{max}. Although such a picture has only been proved in the $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) relaxor,[7] we generalize it to other relaxors, believing that the structural homogeneity of ordered microregions is the cause of cooperative displacement of central ions, which gives rise to the local spontaneous polarization.

(3) The local polarizations are oriented randomly along different easy axes and fluctuating between them at high temperatures since the activation energy of the nanoscale polar microregion can be overcome by the thermal energy.[1,15,16]

A two-dimensional model diagram of relaxors is de-

picted in Fig. 1. The circles with different radii represent the polar microregions with various volumes. The arrow shows the polarization direction on the assumption that the easy polarization axes are $\langle 11 \rangle$. When considering the interaction between polar microregion pairs, we first restrict our discussion on the assumption that the polar microregions can be regarded as point dipoles. Such an assumption may be of dubious validity and we will discuss it later in Sec. III. The interaction between the two dipole moments μ_1 and μ_2 of the corresponding polar microregions is

$$
\begin{aligned}
J_{12} &= -\mu_2 \cdot E_1 \\
&= -\mu_2 \cdot \frac{1}{4\pi\varepsilon_0} \left[\frac{3\mu_1 \cdot r_{12}}{r^3} r_{12} - \frac{\mu_1}{r^3} \right] \\
&= -\frac{1}{4\pi\varepsilon_0} \frac{3\cos\varphi_1\cos\varphi_2 - \cos\phi}{r^3} \mu_1\mu_2 ,
\end{aligned}
\tag{1}
$$

where E_1 is the electrical field of point dipole moment μ_1 at the position of μ_2, r_{12} is the unit vector from μ_1 to μ_2, r is the distance between them, φ_1 and φ_2 are the angles between μ_1, μ_2, and r_{12}, and ϕ is the angle between μ_1 and μ_2. The Hamiltonian of the relaxor system is

$$
H = \frac{1}{2} \sum_{i \neq j} J_{ij} - E \sum_i \mu_i \cos\theta_i ,
\tag{2}
$$

where μ_i is the magnitude of the dipole moment of the ith polar microregion, E represents the external electric field, and θ_i is the angle between the external field and the ith dipole moment. Let

$$
J'_{ij} = \frac{1}{4\pi\varepsilon_0} \frac{3\cos\varphi_1\cos\varphi_2 - \cos\phi}{r^3} ,
\tag{3}
$$

then

$$
H = -\frac{1}{2} \sum_{i \neq j} J'_{ij}\mu_i\mu_j - E \sum_i \mu_i \cos\theta_i .
\tag{4}
$$

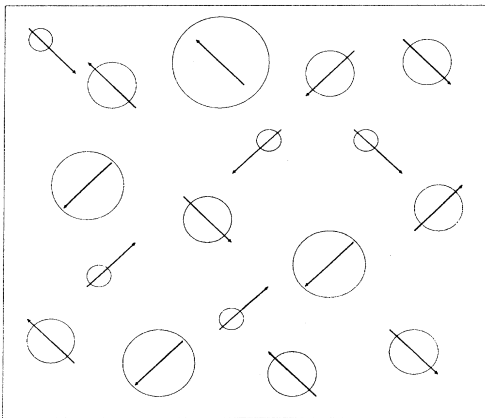Since the dipole moment μ_i is proportional to the volume

FIG. 1. Two-dimensional model diagram of relaxors. The circles with different radii represent the polar microregions with various volumes. The arrow shows the polarization direction on the assumption that the easy polarization axes are $\langle 11 \rangle$.

of the corresponding polar microregion, it has a random distribution due to the inhomogeneous structure of relaxors. In order to make a clear discussion, the magnitude and direction of μ_i are separated by introducing a quantity σ_i, which is defined as the dipole of the ith polar microregion. The value of σ_i is determined as follows. First, a main axis is set for the system. If there is an external field, the main axis is taken along its direction. In the case of zero field, the main axis is chosen along one of the main crystal axes. Then the dipole moment μ_i is projected to the main axis. When the projection is positive, σ_i takes the value $+1$, otherwise, σ_i takes the value -1. Then

$$
\mu_i \cos\theta_i = |\mu_i \cos\theta_i| \sigma_i ,
\tag{5}
$$

with $\sigma_i = \pm 1$. An effective exchange energy parameter $\tilde{J}_{ij}$ is introduced:

$$
\frac{1}{2} J'_{ij}\mu_i\mu_j = \tilde{J}_{ij}\sigma_i\sigma_j .
\tag{6}
$$

It can be seen that the magnitude of μ_i is included in $\tilde{J}_{ij}$, and its direction is expressed explicitly by σ_i in the Hamiltonian for study of the polar microregions' flipping process.

Assuming that there are N polar microregions in the system, we may rearrange them in a regular lattice approximately preserving the original topology, i.e., the ith dipole has the jth dipole as its nearest neighbor. The distribution of the distance between dipole moments is again included in the distribution of $\tilde{J}_{ij}$, i.e., $P(\tilde{J}_{ij})$. Then the relaxor is modeled to be a system consisting of Ising-like dipoles on a regular lattice with randomly distributed interactions:

$$
H_{\text{model}} = - \sum_{i \neq j} \tilde{J}_{ij}\sigma_i\sigma_j - E\bar{\mu} \sum_i \frac{|\mu_i \cos\theta_i|}{\bar{\mu}} \sigma_i ,
\tag{7}
$$

where $\bar{\mu}$ is the maximum projection of the dipole moments on the main axis. It is known from Eqs. (3) and (6) that the effective energy parameter $\tilde{J}_{ij}$ is determined by the following random variables: (a) the volumes, (b) the polarization directions of the polar microregions, and (c) the distance between them. We assume that the distributions of the above random variables remain unchanged in the whole temperature range and upon application of a weak external field. In the case of a strong field, such an assumption is not valid since the polar microregions will grow to larger volumes and the randomness of the polarization directions disappears. In this case, however, we suppose the second term in Eq. (7) plays the most important role in determining the relaxors' properties, whereas the first term has relatively little effect. Therefore the change of $P(\tilde{J}_{ij})$ is ignored and a unique distribution is assumed. Generally, a random variable influenced by many uncertain factors will have a Gaussian distribution:

$$
P(\tilde{J}_{ij}) \propto \exp\left[-\frac{\tilde{J}_{ij}^2}{2(\Delta J)^2} \right] ,
\tag{8}
$$

where ΔJ is the width of the distribution. The mean value is chosen to be zero on account of the symmetry of the random system. Equations (7) and (8) suggest that

the interaction in relaxors is analogous to that of a spin glass of the Edwards-Anderson (EA) model.[17] Using the above model Hamiltonian Eq. (7), in which the factor $|\mu_i \cos\theta_i|/\bar{\mu}$ is neglected,[18] the dynamics of the freezing process in relaxors is simulated by the Monte Carlo method.[19]

The simulation is performed on a $16 \times 16 \times 16$ simple cubic lattice with periodic boundary conditions. First, a set of exchange energy parameters $\tilde{J}_{ij}$ is generated according to the distribution of Eq. (8). Then an initial state is chosen for the system. There are two kinds of initial states used in the calculation. One is $\sigma_i(t=0)=+1$; the other is that $\sigma_i(t=0)$ takes values ± 1 randomly $(i=1,\ldots,N)$. They correspond to the poled and unpoled samples in experiments and so are called the poled and unpoled initial state, respectively. When the dielectric response of relaxors is investigated, the unpoled initial state is adopted, whereas when various polarization process are simulated different initial states are chosen. Given the values of temperature T (in units of $\Delta J/k_B$) and external field E (in units of $\Delta J/\bar{\mu}$), the dipoles attempt to flip according to the flipping probability W:

$$W = \frac{1}{\tau} \quad (\delta H < 0), \quad \frac{1}{\tau}\exp\left[-\frac{\delta H}{k_B T}\right] \quad (\delta H \geq 0) , \qquad (9)$$

where τ is an arbitrary rate constant which is chosen to be 1 in this contribution, and δH is the change of energy involved in the flip:

$$\delta H = 2\sum_j \tilde{J}_{ij}\sigma_i\sigma_j + 2E|\mu_i \cos\theta_i|\sigma_i . \qquad (10)$$

For simplicity, the nearest-neighbor approximation is adopted in the simulation. The attempt to flip is made for every dipole on the lattice sites in sequence. One Monte Carlo step per dipole (MCS/ dipole) consists of $16 \times 16 \times 16$ attempted flips. A series of configurations is thus generated. The above Metropolis sampling process[20] ensures that the system develops in favor of lowering its energy and settles down at a thermal equilibrium state for large times (in units of MCS/dipole), so the Monte Carlo calculation can be used to simulate the dynamic process and macroscopic properties in real materials.[19]

In order to study the freezing process in relaxors, a quantity called the local dipole is defined as

$$\langle \sigma_i \rangle = \frac{1}{t_{\text{obs}}} \sum_{\nu=t}^{t+t_{\text{obs}}} \sigma_i(\nu) , \qquad (11)$$

where $\sigma_i(\nu)$ is the value of σ_i at the νth MCS/dipole. We chose $t=1000$ MCS/dipole to eliminate the influence of the initial state and $t_{\text{obs}}=400$ MCS/dipole to be the observation time.[21] $\langle \sigma_i \rangle$ is the time average of σ_i over the observation time and has a close relation with the flipping frequency of the corresponding dipole. We call the dipoles with $|\langle \sigma_i \rangle|=1$ "frozen dipoles" since no flipping occurs over the observation time. Those with $\sigma_l \leq |\langle \sigma_i \rangle| \leq 1$ are called the "slow dipoles" because a low flipping frequency is necessary to maintain a high value of the local dipole. σ_l may take different values.

As is discussed in Sec. III, the magnitude of σ_l has definite physical meaning related to the frequency of the measuring electrical field.

III. RESULTS AND DISCUSSION

The proportions of frozen and slow dipoles ($\sigma_l=0.9$) in the system as functions of temperature are shown in Fig. 2. The data points are averages over several computer runs to smooth the statistical fluctuation. So are the points in the following diagrams. The frozen dipole begins to appear at $T=1.5\Delta J/k_B$. We define it as the freezing temperature T_f, which coincides with the critical temperature determined by the calculation of susceptibility in a three-dimensional spin glass.[22] The slow dipole appears at a higher temperature. Both proportions increase as the temperature decreases. When the temperature is much higher than T_f, all dipoles in the system are fast enough to follow the switching of the measuring field. The exact susceptibility of this system is $\chi_{\text{eq}}=1/T$.[23] When the temperature is lowered, the flipping frequencies of dipoles decrease. When some of them become so slow that they cannot keep up with the external field, the susceptibility no longer has the thermal equilibrium value. If we assume that the slow dipoles do not contribute to the equilibrium susceptibility, while the others are in thermal equilibrium,[21] then

$$\chi = \frac{1-p}{T} , \qquad (12)$$

where p represents the proportion of slow dipoles in the system. Figure 3 shows the susceptibility points ($*$, $+$, and $\triangle$) obtained by Eq. (12) when the lower limit of slow dipoles σ_l equals 0.9, 0.8, and 0.6, respectively. The dashed line represents the equilibrium susceptibility. It can be seen that the deviation from the thermal equilibri-
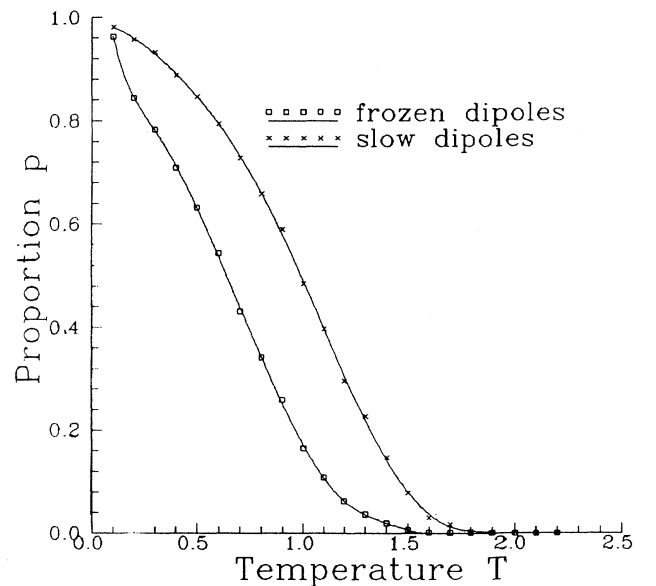

FIG. 2. Proportions of frozen and slow dipoles ($\sigma_l=0.9$) in the system as functions of temperature (in units of $\Delta J/k_B$).
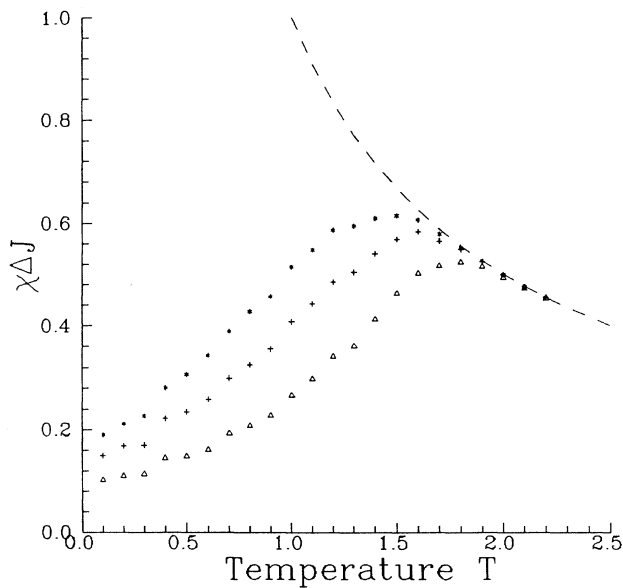
FIG. 3. Zero-field susceptibility as a function of temperature (in units of $\Delta J /k_B$). The dashed line represents the equilibrium susceptibility. The points ($*$, $+$, and $\triangle$) are obtained by Eq. (12) when the lower limit of slow dipoles σ_l equals 0.9, 0.8, and 0.6, respectively.
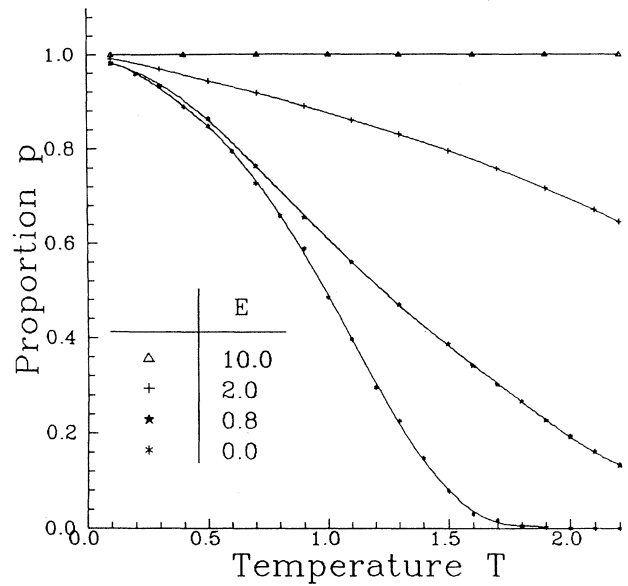

FIG. 4. Proportion of slow dipoles in the system as a function of temperature (in units of $\Delta J /k_B$) at various external fields (in units of $\Delta J /\overline{\mu}$).

um susceptibility is caused by the appearance of slow dipoles, and different susceptibility values result from different σ_l values at low temperatures. When the frequency of the measuring field is low, most dipoles can keep up with it except a small proportion of very slow ones. σ_l corresponding to this case has a relatively high value. As the measuring frequency increases, some dipoles previously in thermal equilibrium become slow because of not being able to follow the switching of the measuring field. This can be simulated by defining the dipoles with higher flipping frequencies to be "slow." So the increase of the measuring frequency may be represented by the decrease of σ_l. When $\sigma_l=0.9$, $T_{\max}=1.5\Delta J /k_B$, which equals T_f. Therefore T_f corresponds to the temperature of the susceptibility maximum under a certain low-frequency measuring field. As σ_l decreases, the slow dipoles appear at higher temperatures and their proportion increases. The susceptibility decreases and the temperature of the susceptibility maximum $T_{\max}$ moves to higher temperatures. Such a gradual freezing process gives a good explanation for the frequency dispersion of relaxors.

When a static external field is applied to the system, the proportion of slow dipoles ($\sigma_l=0.9$ in the following) increases until all dipoles are aligned along the external field (Fig. 4). Again we use Eq. (12) to calculate the susceptibility. The results under three values of external field are shown in Fig. 5. It can be seen that the external field reduces the susceptibility and increases the temperature of the susceptibility maximum. The field dependence of $\chi_{\max}$ and $T_{\max}$ is shown in Figs. 6(a) and 6(b). Both curves have plateaus at small E values. $T_{\max}$ remains at $1.5\Delta J /k_B$ until E is greater than $0.6\Delta J /\overline{\mu}$. Such field

dependences of dielectric responses have been observed in experiments on the PMN relaxor (see Figs. 1 and 2 in Ref. 24). It was reported that the 0.1 kHz $\chi_{\max}$ was approximately 15 000 under zero bias, decreased slowly at lower bias levels, and then decreased quadratically to approximately 1500 under 28 kV/cm. The 0.1 kHz $T_{\max}$ showed a wider plateau at lower bias levels, went through a minimum of approximately 38 °C under 3 kV/cm, and increased to approximately 110 °C under 28 kV/cm. $T_{\max}$ was approximately 60 °C at the bias (designed as
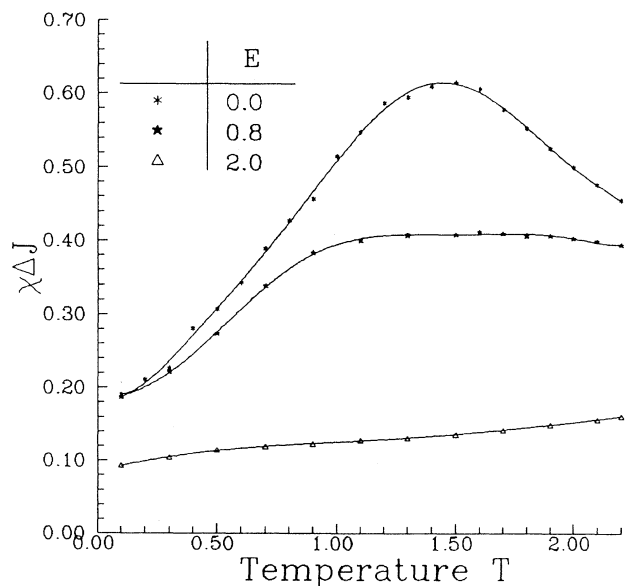

FIG. 5. Susceptibility as a function of temperature (in units of $\Delta J /k_B$) at various external fields (in units of $\Delta J /\overline{\mu}$).

E_h) under which χ_{max} decreases to half of its zero-bias value. The ratio of $T_{max}(E_h)/T_{max}(0)$ is between 1.5 and 1.6. According to our simulation result, $E_h \approx 1.2\Delta J/\bar{\mu}$. The ratio of $T_{max}(E_h)/T_{max}(0) \approx 1.6$. It can be seen that the simulation agrees with the experiment very well.

In addition to the dielectric response investigated above, the Monte Carlo simulation can also help to understand the special polarization behaviors of relaxors. The polarization of the model system is defined as[19]

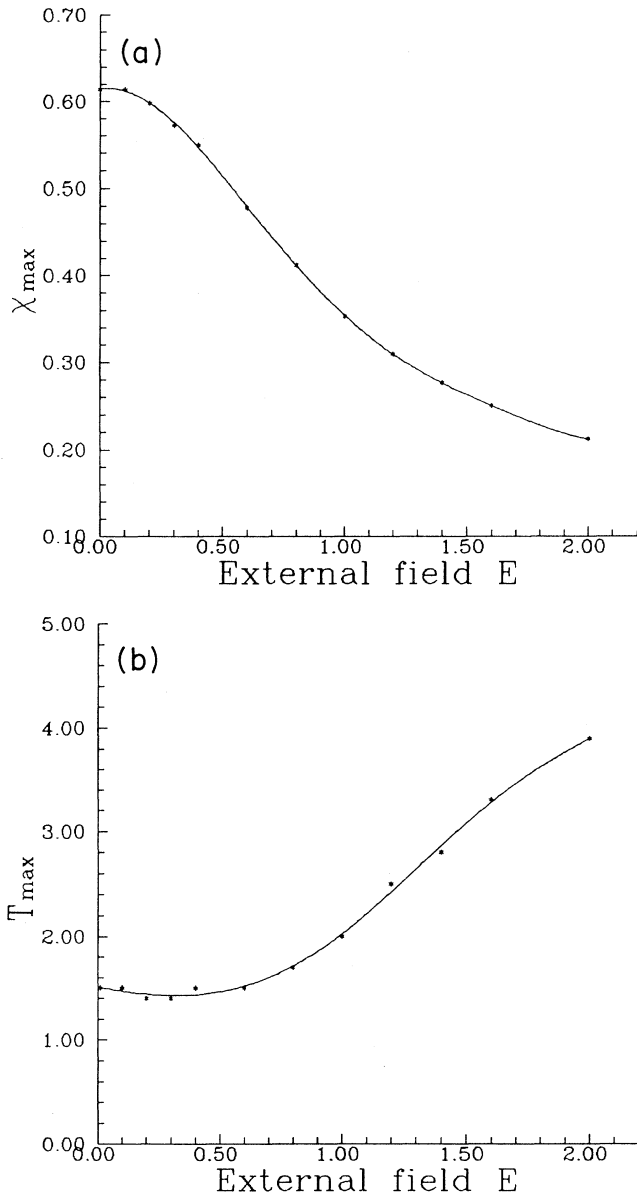$$P = \frac{\int_{t_i}^{t_f} \langle \sigma(t) \rangle dt}{(t_f - t_i)} , \qquad (13)$$

FIG. 6. (a) Susceptibility maximum (χ_{max}) as a function of the external field (in units of $\Delta J/\bar{\mu}$). (b) Temperature of the susceptibility maximum (T_{max}) as a function of the external field (in units of $\Delta J/\bar{\mu}$).

where

$$\langle \sigma(t) \rangle = \frac{1}{N} \sum_{j=1}^{N} \langle \sigma_j(t) \rangle . \qquad (14)$$

The observation time $t_{obs} = t_f - t_i$ is chosen to be 400 MCS/dipole as above and t_i is chosen to be 50 MCS/dipole in order to study the quasiequilibrium polarization behavior at low temperatures. The implication is that the component in which the system is confined at low temperatures has reached internal ergodicity after a short time.[25] The remnant polarization P_r as a function of temperature is shown in Fig. 7. It is simulated by choosing a poled initial state and zero external field. The system stays at each temperature for 450 MCS/dipole; then the temperature is increased. The results show that P_r collapses near the freezing temperature $T_f = 1.5\Delta J/k_B$, which agrees with the experiments.[10,11] It can be seen that P_r is mainly sustained by the frozen dipoles that are aligned along the same direction determined by the initial state. When the simulation is started from an unpoled initial state, the polarizations remain fluctuating around zero at all temperatures. Upon application of an external field, the polarization behaviors of slow heating are shown in Fig. 8. Symbols + and Δ represent the polarizations simulated from the poled and unpoled initial states and Figs. 8(a) and 8(b) correspond to $E = 0.2\Delta J/\bar{\mu}$ and $0.6\Delta J/\bar{\mu}$, respectively. The results show that at low temperatures a macroscopic polarization develops in the unpoled sample. It reaches a maximum close to the polarization of the poled sample at $T < T_f$. Then the two polarizations become equal to each other and decrease monotonically with increasing temperature. The temperature at which the two polarizations meet decreases as the external field increases. It can be seen that the simulation results manifest most of the important features observed in experiments.[14,26,27] Yao, Xi, Chen, Zhili, and Cross[26,27] proposed that a
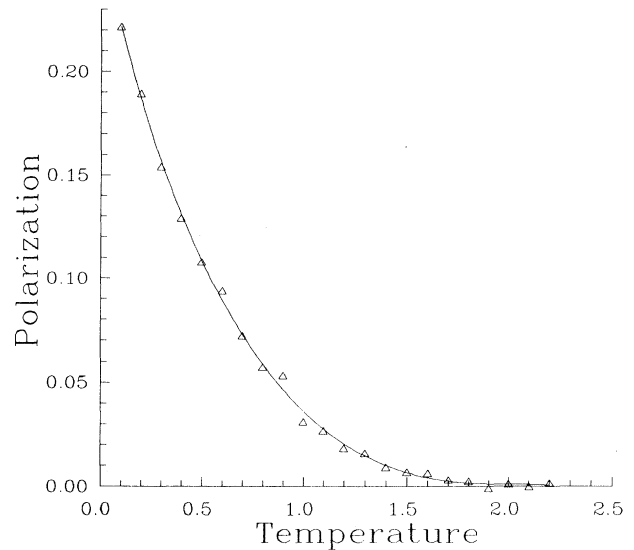
FIG. 7. Remanent polarization as a function of temperature (in units of $\Delta J/k_B$).

microdomain-to-macrodomain transition occurs in the unpoled relaxor under the external field. Viehland et al.[14] suggested that effective nonergodicity sets in the unpoled state due to many degenerate energy minima in the configurational space. The energy degeneracy is partially broken on application of a bias. A global equilibrium is therefore established from the unpoled state. Our explanation for this behavior based on the freezing process of dipoles in relaxors will be given later in this section.

The slow cooling process is simulated for comparison. Figure 9 shows the cooling processes started from $T > T_f$. Symbols $\star$, $\triangle$, and $*$ represent the polarizations under the external field $E=0$, $0.2\Delta J/\mu$, and $0.6\Delta J/\bar{\mu}$ re-

spectively. It can be seen that when the system is cooled under zero field the dipoles are frozen in random directions so that no macroscopic polar order can be established, so x-ray diffraction reveals a pseudocubic structure of relaxors at temperatures far below T_{max}.[1] Some dipoles happen to have the same direction as their neighbors, so a local polar cluster is formed. But the possibility for many layers of dipoles to have the same polarization direction is small, so the correlation length saturates to be nanoscalar at $T < T_f$.[28] When a small external field is applied to the system, the second term in Eq. (9) is of the same order as the first one. It can regarded as a part of the fluctuations of the random interactions between dipole moments. Therefore the flipping frequency is less influenced by the external field than the flipping direction. The flipping probabilities of dipoles parallel to E decrease whereas the probabilities of those antiparallel to E increase, so that the polarization of the whole system increases monotonically with the external field. As the field increases to the extent that the term of interactions between dipole moments can be neglected, the flipping probability is mainly determined by the term caused by the external field. Then the dielectric properties show a strong field dependence [see Figs. 6(a) and 6(b)]. The strong field gives rise to a deep potential well for the "right" flipping (σ_i from -1 to $+1$) and a high potential barrier on the contrary. More and more dipoles are fixed in the external field direction. The alignment of polar microregions may cause a strong internal field under which the paraelectric disordered matrix is polarized along the same direction. The polarization inhomogeneity arising from the structural inhomogeneity in relaxors is removed by the large external field so that a macroscopic polar order can be established. So rhombohedral structure was observed in poled PMN samples.[29] We have noticed that
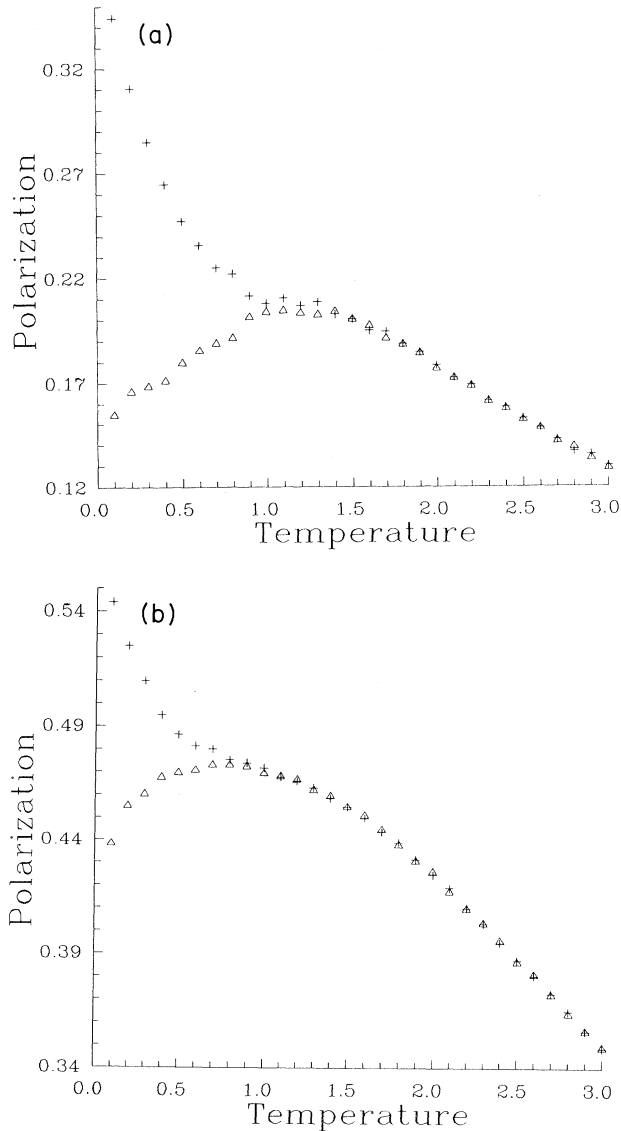

FIG. 8. Polarization as a function of temperature (in units of $\Delta J/k_B$) under different external fields and started from different initial states in the slow heating process. Symbols $+$ and $\triangle$ represent the polarizations simulated from the poled and unpoled initial state, respectively. (a) $E=0.2\Delta J/\bar{\mu}$. (b) $E=0.6\Delta J/\bar{\mu}$.
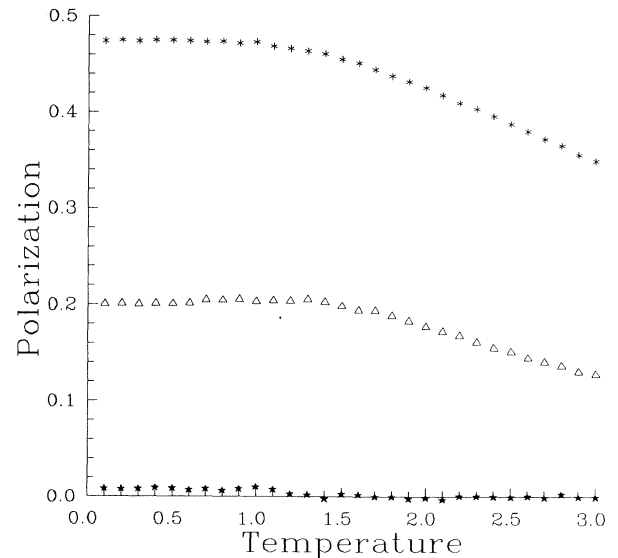

FIG. 9. Polarization as a function of temperature (in units of $\Delta J/k_B$) under different external fields in the slow cooling process started from a temperature far above T_f. Symbols $\star$, $\triangle$, and $*$ represent the polarizations under the external field $E=0$, $0.2\Delta J/\bar{\mu}$, and $0.6\Delta J/\bar{\mu}$, respectively.

when the cooling is started from $T > T_f$ the processes are not influenced by the initial state. When the simulation is started from a temperature below T_f, however, the result is closely related to the initial state. When starting from an unpoled initial state, the polarization remains fluctuating around zero at all temperatures. When starting from a poled initial state, the remanent polarization corresponding to the starting temperature is retained through the cooling process except for a slight decrease (shown in Fig. 10). The decrease is believed to be caused by the dipoles that are frozen in the component corresponding to the initial state, but whose relaxation times are not long enough that a flip occurs when the system continues to develop at lower temperatures. Since the flipping frequencies decrease with decreasing temperature, this kind of "thawing" effect almost disappears when T is much lower than the starting temperature. Similar behavior has been observed in experiments.[14]

The appearance of frozen dipoles shows that the system has not reached thermal equilibrium during t_{obs} at low temperatures. The ergodicity is broken so that the system is confined in a certain component in phase space. As shown in Fig. 2, the proportion of frozen dipoles increases with decreasing temperature so the component in which the system is confined repeatedly bifurcates as the temperature is lowered. Figure 11 shows the bifurcation tree of a model system containing four dipoles $(\sigma_1, \ldots, \sigma_4)$. It is supposed that the four dipoles are frozen in sequence at $T_1 > \cdots > T_4$. At $T \gg T_1$, the relaxation times of all dipoles are much shorter than t_{obs} so the system is in thermal equilibrium. When $T_2 < T < T_1$, σ_1 is frozen while the other dipoles are in thermal equilibrium. The phase space is divided into two components, corresponding to $\sigma_1 = \pm 1$ respectively. Similar-
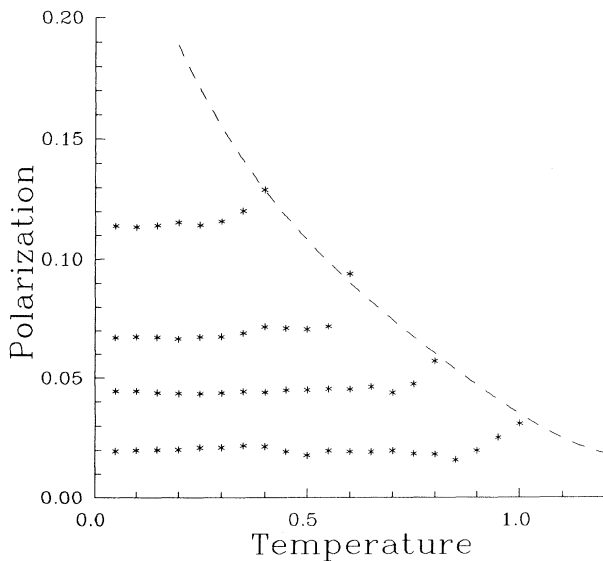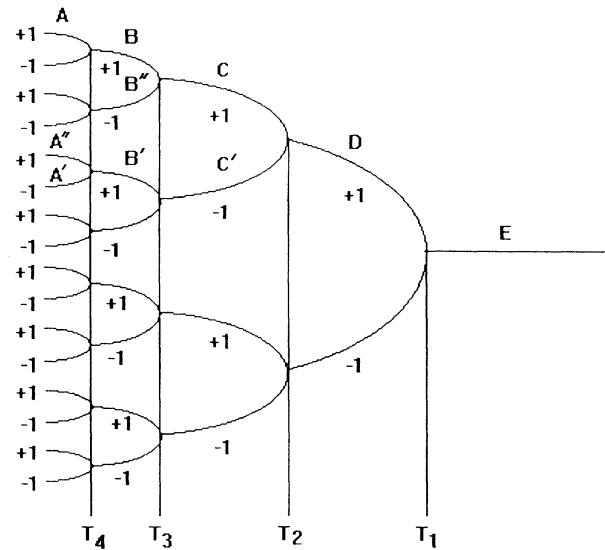

FIG. 11. Component bifurcation tree of phase space of a model system containing four dipoles $(\sigma_1, \ldots, \sigma_4)$. It is supposed that the four dipoles are frozen in sequence at $T_1 > \cdots > T_4$.

ly, each component bifurcates into two when σ_2 is frozen. At $T < T_4$, the four dipoles are all frozen. There are 2^4 components in the phase space. Which component the system is in is determined by (a) the initial state, (b) the thermal, and (c) the electrical history. When the system is slowly heated from a poled initial state at zero bias (the case shown in Fig. 7), it corresponds to the path $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$. Part of the system reaches thermal equilibrium when the transformation from one component to the other takes place. So the polarizations keep on decreasing through the process. The remanent polarization collapses near T_f, above which the system gradually transforms to the thermal equilibrium state. The equilibrium cannot be reached until the temperature is several hundred degrees above T_f because there are still some slow dipoles in the system. The path $A' \rightarrow B' \rightarrow C' \rightarrow D \rightarrow E$ shows a slow heating process from a random initial state. It can be seen that the polarizations fluctuate around zero at all temperatures. When an external field is applied to the system in a slow heating process, a transformation between components at the same temperature takes place. There are large possibilities for frozen dipoles to flip from -1 to $+1$ and then be fixed along the external field. So the path starting from the unpoled initial state changes to $A'' \rightarrow B' \rightarrow C \rightarrow D \rightarrow E$. It coincides with the path of the poled initial state at point C, then develops along the same route. Two competing processes take place in the unpoled sample, i.e., (a) some frozen dipoles are turned and fixed along the external field direction, and (b) some frozen dipoles "thaw" with the increasing temperature. So a maximum polarization results. With the external field increasing, more frozen dipoles flip from -1 to $+1$ at lower temperatures. Therefore the polarization increases, and the temperature at which the two paths coin-

FIG. 10. Polarization as a function of temperature (in units of $\Delta J / k_B$) under zero bias in the slow cooling process started from various temperatures below T_f and the poled initial state. The dashed line represents the remanent polarizations shown in Fig. 7.

cide decreases. Such a picture allows a clear understanding of the polarization behaviors shown in Fig. 8. The slow cooling processes starting from high temperatures are not influenced by the initial state because the system is in thermal equilibrium at $T \gg T_f$. When the cooling starts from a temperature below T_f, part of the dipoles are frozen so the system is confined in a component. For example, let the cooling start from point C. As the temperature decreases, the system has the same probability for taking branch B or B'' at zero bias. The dipoles frozen at lower temperatures are along random directions and make no contribution to the macroscopic polarization. So the polarization almost retains the value of the initial state (Fig. 10).

It is well known that the ergodicity is also broken in normal ferroelectrics as the temperature decreases below the Curie point. Due to the homogeneity of the crystal structure on a macroscopic scale, the breaking of ergodicity takes place at a single temperature, giving rise to a sharp phase transition. The highly inhomogeneous structure of relaxors, however, leads to a broad spectrum of relaxation times. The Monte Carlo simulation results obtained in this contribution show that the polar microregions are frozen in sequence, causing successive bifurcations of components in phase space. The dielectric response and polarization behaviors can be well explained by such a gradual freezing process. The diffuse phase transition in relaxors may be a reflection of the successive transformations from the thermal equilibrium state to a series of quasiequilibrium states at low temperatures.

The simulation results show that the randomly distributed interactions between polar microregions are essential in determining the relaxor characteristics. In our theoretical model, only the interaction between dipoles has been considered and the polar microregions are taken as point dipoles. In fact, the interactions between polar microregions may be more complicated than that between point dipoles, and there exists elastic energy due to local structural distortions. These may lead to some change of the interaction distribution $P(\tilde{J}_{ij})$. However, the randomness of $\tilde{J}_{ij}$ remains. So the theoretical model presented in this contribution may reflect the main features of relaxors. More details of the interaction distribution in relaxors need further research.

IV. CONCLUSION

In this contribution, a theoretical model of relaxor ferroelectrics is proposed where the relaxor is modeled to be a system consisting of Ising-like dipoles on a regular lattice with randomly distributed interactions between them. A Gaussian distribution with zero mean value is assumed for the effective exchange energy parameters and the dynamics of the freezing process in the system is simulated by the Monte Carlo method. The concepts of "frozen dipole" and "slow dipole" are proposed according to the flipping frequency during the observation time of simulation, and the freezing temperature T_f is defined as the temperature at which the frozen dipoles start to appear. It has been proved that the proportions of slow and frozen dipoles increase with decreasing temperature, showing that there is a gradual freezing process in the system, which causes successive bifurcations of components in phase space. Most relaxor characteristics, such as the frequency dispersion, the field dependences of dielectric responses, and various polarization behaviors are explained by the gradual freezing process.

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