Mesoscopic model of a system possessing both relaxor ferroelectric and relaxor ferromagnetic properties

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A pseudospin model of a multiferroic system which exhibits both relaxor ferroelectric and relaxor ferromagnetic behavior is presented. The electric and magnetic degrees of freedom associated with the simultaneous presence of polar nanoregions and magnetic nanoregions are described by two sets of pseudospin variables, which satisfy separate spherical conditions. The spin-glass-like random interactions within each subset are assumed to be infinitely ranged. In addition, the polar nanoregions are subject to random electric fields. By introducing strain modulation of the corresponding random interaction parameters, a fourth-order interaction between polar and magnetic degrees of freedom is derived whose strength can be estimated from the phenomenological electrostriction and magnetostriction coefficients. Dynamic dielectric susceptibility in the presence of a static magnetic field H is calculated from the Langevin equations of motion. The value of the critical magnetic field at which long-range ferroelectric order appears is determined. By considering the corresponding free-energy density functional, the local electric field inside the polar nanoregions is derived and it is shown that the mechanism of growth and percolation of polar nanoregions is also affected by the magnetic field. Thus the Vogel-Fulcher relaxation time is predicted to diverge on a line of percolation critical points in the H,T plane, in agreement with recent experiments.

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I. INTRODUCTION

In recent years, there has been a resurging interest in multiferroic and magnetoelectric (ME) materials[1–4] mainly because of their potential applicability in memory devices. Much of the work has focused on ferromagnetic-ferroelectric multiferroics, especially the ones known or expected to exhibit the ME effect. Symmetry requirements severely limit the occurrence of the linear ME effect.[5] However, composite systems with ME properties can be prepared as solid solutions of ferroelectric and (anti)ferromagnetic materials. Actually, the ME effect in composites is often stronger than in single-phase systems.[6]

The multiferroic concept should, in principle, also be applicable to compositionally disordered systems, such as dipolar glasses and relaxor ferroelectrics on one hand and spin glasses or relaxor ferromagnets on the other. Several examples of disordered systems of the above type have so far been described, for example, ME relaxors,[7,8] multiferroic relaxors,[9] and ME multiglasses.[10] In the present work we will introduce a theoretical model of a system, which possesses both relaxor ferroelectric and relaxor ferromagnetic properties, to be referred to as *birelaxor*. In analogy to relaxor ferroelectrics,[11] a relaxor ferromagnet[12,13] is expected to have no long-range magnetic order but exhibit a high value of the quasistatic magnetic response in a broad temperature range, strong frequency dispersion, as well as a Vogel-Fulcher (VF)-type freezing of the dynamic magnetic response. Therefore, in birelaxors these magnetic properties should coexist with the corresponding dielectric features. From a mesosopic point of view, birelaxors are characterized by the existence of polar nanoregions (PNRs) and magnetic nanoregions (MNRs), which appear as a result of strong compositional fluctuations. In principle, the above description applies to both single phase and composite systems.

The possibility of direct magnetoelectric coupling between the PNRs and MNRs in birelaxors will not be discussed here. Since long-range order (LRO) is absent in a normal relaxor state by definition, the average spatial-inversion and time-reversal symmetries are not broken and the occurrence of a linear ME effect is not allowed. Strain modulation of the PNR-PNR and MNR-MNR interactions may, however, give rise to indirect higher-order coupling between electric and magnetic degrees of freedom.[4] In the absence of piezoelectric and piezomagnetic coupling, the strain-mediated PNR-MNR interactions will be dominated by the electrostriction and magnetostriction coefficients, which are related to the strain (stress) derivatives of the PNR-PNR and MNR-MNR interaction parameters. The resulting PNR-MNR interaction term in the Hamiltonian is bilinear in the pseudospin coordinates of both the PNRs and MNRs, and its sign depends on the relative signs of the electrostriction and magnetostriction coefficients. A positive sign will result in positive fourth-order ME effect, i.e., the dielectric constant will increase upon application of a static magnetic field. This then opens the possibility of a magnetic-field-induced phase transition from a relaxor state to a LRO ferroelectric state. The value of the critical magnetic field H_c can be estimated from the values of the striction coefficients. On the other hand, a negative sign means that the value of the dielectric constant should decrease with the magnetic field. This implies, for example, that if the system is originally in a long-range-ordered ferroelectric state, the field $H > H_c$ will tend to destroy this order, leading to a normal birelaxor state.

A similar reasoning can be applied to the free-energy density of birelaxors. The local electric field inside a PNR, which determines its correlation radius r_c and volume v_c,[14] in a birelaxor acquires an extra contribution due to the magnetic field H, which either enhances or reduces v_c, depending on the coupling sign. The percolation temperature T_p, at which an infinite cluster of PNRs is formed, is also shifted by the field H. Thus the VF temperature $T_0(H)=T_p$ becomes a function of the field, and the VF relaxation time diverges on a line of percolation critical points $T=T_0(H)$ in the H,T plane. This effect agrees quantitatively with a recent observation of magnetic-field-controlled relaxation of dielectric polarization in the solid solution of $PbFe_{2/3}W_{1/3}O_3$ (PFW) and $PbZr_{0.54}Ti_{0.46}O_3$ (PZT) thin films.[15]

II. SPHERICAL MODEL OF BIRELAXORS

Following the spherical random bond–random field (SRBRF) model of relaxor ferroelectrics,[16,17] we assume that the PNRs are coupled through infinitely ranged Gaussian random interactions in the presence of random local electric fields, and an analogous assumption is made for the MNRs. As a straightforward generalization of the SRBRF model we introduce two sets of pseudospins, S_{ri}, $r=1,2,\ldots,N_e$ and $i=x,y,z$ for PNRs, and σ_{sj}, $s=1,2,\ldots,N_m$ for the MNRs. The spherical conditions for the pseudospins are chosen as

$$\sum_{r=1}^{N_e}(\vec{S}_r)^2=N_e, \quad \sum_{s=1}^{N_m}(\vec{\sigma}_s)^2=N_m. \tag{1}$$

The Hamiltonian can be symbolically written as the sum

$$\mathcal{H}_0=\mathcal{H}_e+\mathcal{H}_m, \tag{2}$$

where $\mathcal{H}_e$ and $\mathcal{H}_m$ are the electric and the magnetic terms

$$\mathcal{H}_e=-\tfrac{1}{2}\sum_{r\neq r'}J_{rr'}\vec{S}_r\cdot\vec{S}_{r'}-\sum_r\vec{f}_r\cdot\vec{S}_r-g_e\sum_r\vec{E}\cdot\vec{S}_r, \tag{3a}$$

$$\mathcal{H}_m=-\tfrac{1}{2}\sum_{s\neq s'}K_{ss'}\vec{\sigma}_s\cdot\vec{\sigma}_{s'}-\sum_s\vec{h}_s\cdot\vec{\sigma}_s-g_m\sum_s\vec{B}\cdot\vec{\sigma}_s, \tag{3b}$$

respectively. In these expressions, $J_{rr'}$ and $K_{ss'}$ are the PNR-PNR and MNR-MNR coupling parameters, respectively, and $\vec{f}_r$ and $\vec{h}_s$ are the corresponding random fields, while $\vec{E}$ and $\vec{B}=\mu_0\vec{H}$ are the external fields. Finally, g_e and g_m represent the average dipole moments of the PNRs and MNRs, respectively.

The random variables $J_{rr'}$ and $K_{ss'}$ obey two independent Gaussian distributions with mean values $[J_{rr'}]_{av}=J_0/N_e$ and $[K_{ss'}]_{av}=K_0/N_m$, and with variances $[J^2_{rr'}]^c_{av}=J^2/N_e$ and $[K^2_{ss'}]^c_{av}=K^2/N_m$, respectively. The random fields have zero mean and respective variances $[f_{ri}f_{r'j}]_{av}=\delta_{rr'}\delta_{ij}\Delta_e$ and $[h_{si}h_{s'j}]_{av}=\delta_{ss'}\delta_{ij}\Delta_m$. We choose $\Delta_m=0$ and write $\Delta_e\equiv\Delta$.

Next we assume that the PNR-PNR and MNR-MNR interactions depend on the components of the lattice strain (or stress) tensor u_{ij} (or X_{ij}). Expanding $J_{rr'}(\mathbf{X})$ to linear order in stresses we obtain

$$J_{rr'}(X)=J_{rr'}(0)+\sum_{ij}J^{(1)}_{rr',ij}X_{ij}+\cdots, \tag{4}$$

with $J^{(1)}_{rr',ij}=\partial J_{rr'}(\mathbf{X})/\partial X_{ij}$, and similarly for $K_{ss'}(\mathbf{X})$. Since by assumption $J_{rr'}$ in Eq. (3) is isotropic, we will limit ourselves to the isotropic part of the second term in Eq. (4). The random average of $J^{(1)}_{rr',ii}$ is parametrized by first introducing the stress derivatives of the average coupling parameter J_0, namely, $J^{(1)}_{0,ii}=\partial J_0/\partial X_{ii}$. Thus, the derivative of J_0 is simply related to the derivative of the field-cooled static dielectric susceptibility, which according to the SRBRF model is given by

$$(\chi_e^{-1})_{ij}=\frac{1}{k\theta_e}\left(\frac{kT}{1-q_e}-J_0\right)\delta_{ij}. \tag{5}$$

This result has been derived earlier by use of the replica formalism[16,17] and contains the spherical glass order parameter q_e of the PNR subsystem, which depends on the parameters J, J_0, and Δ. The parameter $\theta_e=g_e^2/(v_ek\epsilon_0)$ plays the role of an effective Curie constant; however, it should be noted that in relaxors a Curie-Weiss-type behavior holds only approximately in the asymptotic regime $T\gg J/k$. An analogous expression is obtained for the magnetic case.

We can then apply the thermodynamic Maxwell relations between the electro(magneto)striction constants $Q_{e,ijkl}$ and $Q_{m,ijkl}$, and the stress derivatives of χ_e^{-1} (Refs. 17–19) and χ_m^{-1}, respectively,

$$Q_{e,ijkl}=-\frac{1}{2\epsilon_0}\left(\frac{\partial(\chi_e^{-1})_{kl}}{\partial X_{ij}}\right)_T, \quad Q_{m,ijkl}=-\frac{\mu_0}{2}\left(\frac{\partial(\chi_m^{-1})_{kl}}{\partial X_{ij}}\right)_T, \tag{6}$$

where the limit $\vec{P}\to 0$, $\vec{M}\to 0$ is understood. The average of $J^{(1)}_{rr',ij}$ in Eq. (4) and similarly of $K^{(1)}_{rr',ij}$ then leads to the relations

$$J_{0,k}\cong 2\epsilon_0k\theta_eQ_{e,ki}, \quad K_{0,k}\cong 2\mu_0^{-1}k\theta_mQ_{m,ki}, \tag{7}$$

with $k,i=1,2,3$ using the Voigt notation. In view of the presumed isotropy of J_0 the above expressions must be i independent. Thus, we can perform the averages over i and introduce hydrostatic electro(magneto)striction coefficients $Q_{e,h}$ and $Q_{m,h}$ defined by $Q_h=Q_{k1}+Q_{k2}+Q_{k3}$, which are k independent. It follows that $J_{0,k}$ and $K_{0,k}$ are both k independent.

In deriving relations (7) we have ignored the effects of stress deformations on the random distribution widths J and K since they are $O(1/N_e^2)$ and $O(1/N_m^2)$, respectively, and the stress derivatives of θ_e,θ_m have been neglected assuming rigid PNRs and MNRs. Also, it should be noted that q_e,q_m do not depend on J_0,K_0 and hence on $\mathbf{X}$ for $\vec{P}=0$, $\vec{M}=0$.[16]

After adding the elastic energy $\mathcal{H}_{\text{elastic}}=(V/2)\Sigma_{ij=1}^3C_{ij}^{-1}X_iX_j$, where C_{ij}^{-1} is the elastic compliance tensor, the total Hamiltonian is minimized, thus eliminating terms linear in $\mathbf{X}$. This generates a fourth-order PNR-MNR coupling term of the following structure:

$$\mathcal{H}_{me} = -\frac{\Lambda_h}{2VN_eN_m}\sum_{r\neq r'}\sum_{s\neq s'}(\vec{S}_r\cdot\vec{S}_{r'})(\vec{\sigma}_s\cdot\vec{\sigma}_{s'}). \quad (8)$$

The coupling parameter Λ_h is given by

$$\Lambda_h = 2\epsilon_0\mu_0^{-1}k\theta_e k\theta_m C_h Q_{e,h}Q_{m,h}, \quad (9)$$

where $C_h=(1/9)\Sigma_{ij=1}^3 C_{ij}$ is the bulk modulus.

The prefactor $(VN_eN_m)^{-1}$ in Eq. (8) ensures proper scaling of $\mathcal{H}_{\rm me}$ with the system size, Λ_h (Ref. 20) being intensive. Stress-mediated fourth-order PNR-PNR and MNR-MNR coupling terms are not given here since they represent a correction of the anharmonic part of $\mathcal{H}_0$, which has been ignored from the outset.

III. STATIC DIELECTRIC PROPERTIES UNDER CONSTANT MAGNETIC FIELD

In the following we consider a system where the relaxor ferroelectric peak is well separated from the magnetic one and lies at a higher temperature and no LRO is present. This corresponds to the case $J>K$ and $J_0>K_0$, as well as $K_0<K$ and $J_0<J$. Furthermore, we assume that a constant magnetic field $\vec{B}=\mu_0\vec{H}$ has been applied to the system. In discussing the effects of $\mathcal{H}_{me}$ on the time evolution of PNR pseudospins $\vec{S}_i$, we can effectively replace the magnetic part of the coupling by its average value $\Sigma_{s\neq s'}[\langle\vec{\sigma}_s\cdot\vec{\sigma}_{s'}\rangle]_{av}$. In the spirit of perturbation theory, the averages can be evaluated with respect to the initial Hamiltonian $\mathcal{H}_0$. This can be done exactly using the eigenstates and eigenvalues of the random matrix $K_{ss'}$.[21] The result to order $\mathcal{O}(1/V)$ is

$$\frac{1}{VN_m}\sum_{s\neq s'}[\langle\vec{\sigma}_s\cdot\vec{\sigma}_{s'}\rangle]_{av} = (v_m/g_m^2)\sum_i \chi_{m,ii}^2 B_i^2. \quad (10)$$

The dimensionless magnetic susceptibility $\chi_{m,ij}$ is defined through the phenomenological relation $M_i=\Sigma_j\chi_{m,ij}H_j$ and can be explicitly obtained from the magnetic version of Eq. (5). Since all averages have the same value, namely, $[\langle\sigma_{s,i}\rangle]_{av}\equiv\langle\sigma\rangle$, we can write $M_i=(g_m/v_m)\langle\sigma\rangle$, where $v_m\equiv V/N_m$ represents the effective average MNR volume, which is essentially a measure of the MNR concentration $c_m=1/v_m$. The corresponding quantities for the PNRs are $v_e\equiv V/N_e$ and $c_e=1/v_e$.

In the isotropic case the magnetic susceptibility tensor is isotropic, i.e., $\chi_{m,ij}=\delta_{ij}\chi_m$, where $\chi_m=\mu-1$. Similarly the dielectric susceptibility is $\chi_{e,ij}=\delta_{ij}\chi_e$ with $\chi_e=\epsilon-1$.

Finally, the coupling term (8) can be rewritten as

$$\mathcal{H}_{me}(H) = -J_1(H)\frac{1}{2N_e}\sum_{r\neq r'}\vec{S}_r\cdot\vec{S}_{r'}, \quad (11)$$

where $J_1(H)$ represents the shift of the mean PNR interaction J_0, i.e.,

$$J_0(H) = J_0 + J_1(H), \quad (12)$$

for which we obtain, with the use of Eq. (9),

$$J_1(H) = \frac{\mu_0(\mu-1)^2}{k\theta_m}\Lambda_h H^2. \quad (13)$$

The sign of $J_1(H)$ depends on the signs of $Q_{e,h}$ and $Q_{em,h}$ and can be either positive or negative. Thus if both signs are equal, $J_1(H)$ will be positive, implying that the magnetic field enhances the average PNR interaction. In this case there is a possibility of a magnetic-field-induced phase transition from a relaxor state into a long-range-ordered ferroelectric state. In general LRO exists if $J_0(H)\geq J_{0c}\equiv\sqrt{J^2+\Delta}$ and $T\leq T_c(H)$, where

$$T_c(H) = J_0(H)\frac{J_0(H)^2 - J_{0c}^2}{J_0(H)^2 - J^2}. \quad (14)$$

For $J_0<J_{0c}$, a critical value of the magnetic field H_c exists such that for $H>H_c$ LRO is possible. Introducing $\delta J_0\equiv J_{0c}-J_0$ and assuming $\delta J_0>0$ (i.e., no LRO in zero field), we find

$$H_c^2 = \frac{|\delta J_0|}{2\epsilon_0(\mu-1)^2 k\theta_e C_h|Q_{e,h}Q_{m,h}|}. \quad (15)$$

If, however, the system in zero magnetic field is in a ferroelectric state corresponding to the case $\delta J_0<0$ and the sign of $J_1(H)$ is negative then $J_0(H)$ will decrease with H until the critical field H_c is reached. At that point a phase transition from a long-range-ordered ferroelectric into a relaxor ferroelectric state occurs, and LRO is not possible for all $H>H_c$.

To estimate the possible value of H_c from Eq. (15) we use the following representative parameter values: $\mu=5$, $C_h=10^{11}$ J m^{-3}, $\theta_e=10^5$ K, and $\delta J_0/k=33$ K. Then, for $Q_{e,h}$ in the range $10^{-3}-10^{-2}$ m^4 A^{-2} s^{-2} and $Q_{m,h}$ between 10^{-15} and 10^{-14} m^2 A^{-2}, we find

$$0.43 < \mu_0 H_c < 4.3 \text{ T}. \quad (16)$$

Thus H_c lies in the experimentally accessible regime. In Fig. 1 the static zero-field-cooled dielectric susceptibility $\chi_{e,s}$, Eq. (5) is plotted as a function of temperature for several values of magnetic field H. The parameter values are $J_0=0.9J$ or $\delta J_0/J=0.1$, $\Delta/J^2=0.001$, $k\theta_e/J=12.5$, and $J_1(H)/J=0.1(H/h)^2$, where $h^2=0.9H_c^2$. As expected, for $H>H_c$, i.e., $(H/h)^2>10/9$, the system develops LRO and $\chi_{e,s}$ shows a Curie-Weiss-type divergence at $T_c(H)$. The inset shows the magnetic field-cooled susceptibility $\chi_{m,s}$, which monotonically decreases with H at fixed temperature. The cusp for $H=0$ is due to the absence of magnetic random fields ($\Delta_m=0$). The remaining parameters are $K/J=K_0/J_0=0.5$ and $\theta_m=\theta_e/4$.

IV. DYNAMIC DIELECTRIC RESPONSE

We focus on the dynamic dielectric response of the birelaxor in the presence of a static magnetic field under the conditions specified in Sec. III. The Langevin equations of motion for the PNR pseudospins are[21]

$$\tau_e\frac{\partial S_{ri}}{\partial t} = -\frac{\partial(\beta\mathcal{H}_S)}{\partial S_{ri}} - z_e(t)S_{ri}(t) + \xi_{ri}(t), \quad (17)$$

where $\mathcal{H}_S=\mathcal{H}_e+\mathcal{H}_{me}(H)$ and $z_e(t)$ is a Lagrange multiplier enforcing the spherical condition (1) for PNRs. The Lange-

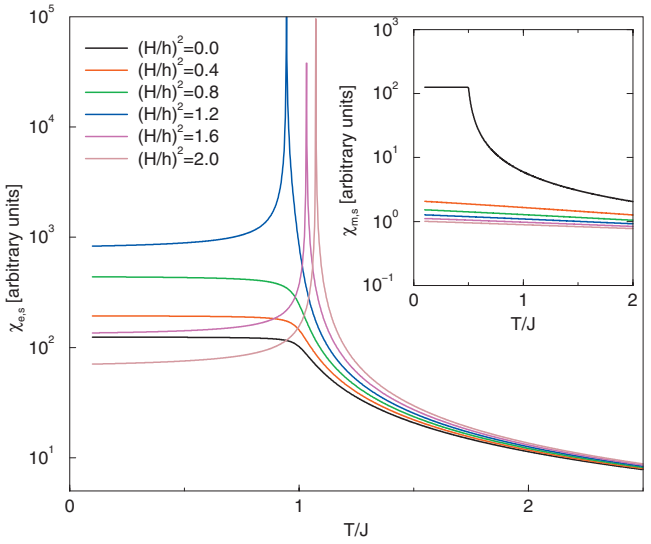

FIG. 1. (Color) Temperature dependence of the static field-cooled dielectric susceptibility of a birelaxor for several values of magnetic field H/h, as indicated, where $h^2=0.9H_c^2$. Inset: field-cooled static magnetic susceptibility for the same values of H/h.

vin forces $\xi_{ri}(t)$ formally obey the Einstein relations $\langle \xi_{ri}(t)\xi_{r'j}(t')\rangle_{av}=2\tau_e\delta_{rr'}\delta_{ij}\delta(t-t')$. To solve Eq. (17) we introduce as usual the eigenvalues J_λ and eigenstates ψ_λ of the random matrix $J_{rr'}$, and replace the original set S_{ri} by the normal modes $S_{\lambda i}$, which decouple the above equations. Assuming an oscillating external electric field $E_i(t)=E_0\exp(-i\omega t)$ and solving for $S_{\lambda i}(t)$ in the asymptotic regime $t\gg\tau_e$,[21] we obtain the following result for the complex linear dynamic dielectric susceptibility:

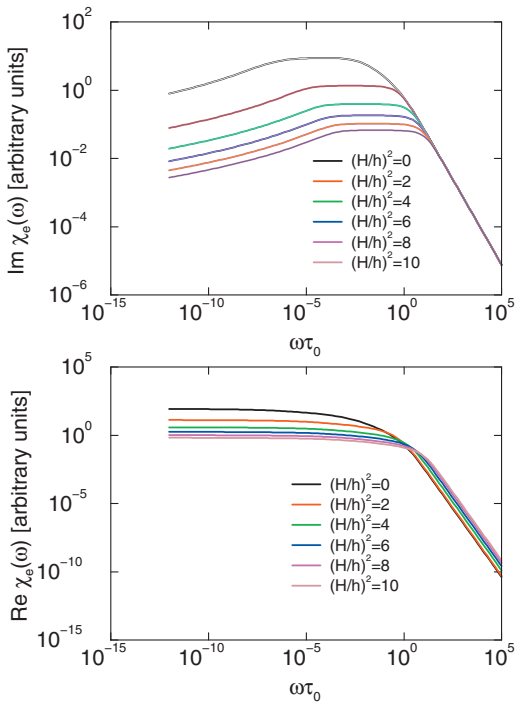

FIG. 2. (Color) Frequency dependence of the real (lower) and imaginary (upper) parts of dynamic dielectric susceptibility for several values of magnetic field H/h, as indicated, calculated at a fixed temperature $T/J=1.025$.

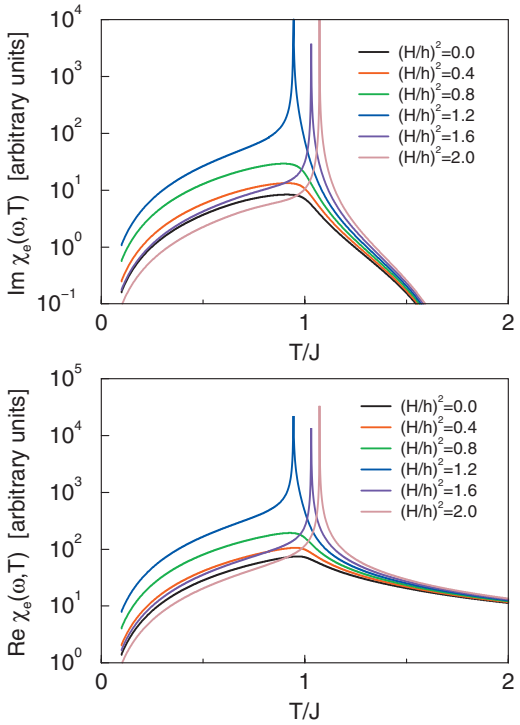

FIG. 3. (Color) Real (lower) and imaginary (upper) parts of the quasistatic zero-field-cooled dielectric susceptibility for the same values of H/h as in Fig. 1, evaluated at a low frequency $\omega\tau_0=10^{-8}$.

$$\chi_e(\omega)=k\theta_e\frac{z(\omega)-r(\omega)-\beta J_0(H)}{\beta[J^2+J_0(H)^2]-2z(\omega)J_0(H)}, \tag{18}$$

where $\chi_e(\omega)_{ij}=\chi_e(\omega)\delta_{ij}$ and we use the notation $z\equiv z_e$, etc., with $z(\omega)=z-i\omega\tau/2$ and $r(\omega)=\sqrt{z(\omega)^2-\beta^2J^2}$.

In principle the parameter z can be calculated from the static spherical condition (1).[21] Alternatively one can determine z from the static susceptibility $\chi_{e,s}=\chi_e(0)$, which is known from the replica theory,[16,17] by inverting Eq. (18).

The relaxation time $\tau\equiv\tau_e$ is not determined by the model and is regarded as a phenomenological parameter. A major simplification in Eq. (17) is the assumption that all modes $S_{\lambda i}$ decay with the same relaxation time τ. However one may introduce a statistical distribution of $\ln\tau$ by writing

$$\langle\chi_e(\omega)\rangle_{av}=\int_0^\infty d(\ln\tau)f(\ln\tau)\chi_e(\omega). \tag{19}$$

Empirically the response of relaxors and dipolar glasses is characterized by a broad probability distribution of relaxation times. An approximate numerical scheme has been developed[22] to extract $f(\ln\tau)$ from the experimentally known response $\langle\chi_e(\omega)\rangle_{av}$. The longest relaxation time appearing in $f(\ln\tau)$ has been found to diverge according to the VF law

$$\tau = \tau_0 \exp[U/(T - T_0)] \quad \text{for} \quad T > T_0, \tag{20}$$

and $\tau=\infty$ for $T \leq T_0$, where T_0 is the VF or freezing temperature. The function $f(\ln \tau)$ can be expressed in terms of two probability distributions, i.e., $g(U)$ and $w(T_f)$ describing the distributions of barrier heights and freezing temperatures T_f, respectively. The result is

$$f(\ln \tau) = \int_0^\infty dT_f w(T_f)(T - T_f) g[(T - T_f)\ln \tau]. \tag{21}$$

For the purpose of illustration we choose $g(U)$ as a Fröhlich box, $g(x)=1/U_{\max}$ for $0<U<U_{\max}$, and a triangular distribution $w(T_f)=(2/T_0)(1-T_f/T_0)$ for $0<T_f<T_0$ with parameter values $U_{\max}/J=11.0$, and $T_0/J=1.0$. The calculated frequency dependence of the real and imaginary parts of $\langle \chi_e(\omega) \rangle_{av}$ is plotted in Fig. 2 at a fixed temperature $kT/J=1.025$ for the same set of parameter values as in Fig. 1; however, the magnetic field H is now varied in a broader range. For $\delta J_0>0$ the maxima of the imaginary part of permittivity move toward higher frequencies on increasing H but this effect seems rather weak.

We can also calculate the temperature dependence of the quasistatic zero-field-cooled susceptibility by choosing a very small value for the frequency. This is shown in Fig. 3 for $\omega\tau_0=10^{-8}$ and the same set of parameters and fields as in Fig. 1. At high temperatures the real part of the response agrees with the field-cooled response in Fig. 1 but for $T \to 0$ the zero-field-cooled response tends to zero, as required.

V. RELAXATION OF DIELECTRIC POLARIZATION IN MAGNETIC FIELD

We now discuss the effects of magnetic field on the relaxation of PNRs due to the presence of fourth-order magnetoelectric coupling between the PNRs and MNRs in a birelaxor. Our aim is to find a general expression for the internal electric field inside a PNR, which is modified by the presence of a magnetic field. We can then apply the mechanism of growth and percolation of PNRs (Ref. 14) to derive a modified Vogel-Fulcher relaxation time.

Rather than follow the Hamiltonian approach used in the preceding sections, we start by writing down the phenomenological Landau-type free-energy density functional of a birelaxor in the absence of stress coupling,

$$\mathcal{F}_0 = \frac{1}{2\epsilon_0}(\chi_e^{-1})_{ij}P_iP_j + \frac{\mu_0}{2}(\chi_m^{-1})_{ij}M_iM_j + \frac{1}{4}b_eP^4 + \frac{1}{4}b_mM^4 + \cdots - E_iP_i - B_jM_j. \tag{22}$$

The inverse susceptibility tensors are explicitly given by Eq. (5). The anharmonic P^4 and M^4 terms have been added to formally ensure thermodynamic stability. Note that there are no direct ME terms in the above free energy.

Following the approach used in Sec. III, we assume that χ_e^{-1} and χ_m^{-1} are functions of the stress field $\mathbf{X}$ and expand them both to linear order in $\mathbf{X}$. We can again apply the Maxwell relations (6) and after including the elastic energy density $(1/2)\Sigma_{ij=1}^3(C^{-1})_{ij}X_iX_j$ and minimizing $\mathcal{F}_0$ with respect to $\mathbf{X}$, we generate a new $\sim P^2M^2$ term, namely,

$$\mathcal{F}_1 = -\frac{1}{2}\lambda_{ij}P_i^2M_j^2, \tag{23}$$

where the indirect fourth-order ME coupling constant is

$$\lambda_{ij} = 2C_{kl}Q_{e,ki}Q_{m,lj}. \tag{24}$$

By averaging λ_{ij} over all i,j we obtain its average value $\lambda_h=2C_hQ_{e,h}Q_{m,h}$, and by comparing with Eq. (9) we see that $\lambda_h=\Lambda_h\mu_0/(\epsilon_0 k\theta_e k\theta_m)$. This establishes a connection between the fourth-order coupling in the Hamiltonian and the corresponding coefficient in the free-energy density. The value of λ_h can be estimated by using the same parameter values as in Eq. (16), yielding $|\lambda_h|$ roughly between 2×10^{-7} and 2×10^{-5} $\mathrm{m^3\ s^{-1}\ V\ A^{-3}}$.

The macroscopic electric field is obtained from the equilibrium condition $\partial(\mathcal{F}_0+\mathcal{F}_1)/\partial P_i=0$ and is given by

$$E_i = \frac{1}{\epsilon_0}\chi_e^{-1}P_i(1 - \epsilon_0\chi_e\lambda_{ij}M_j^2). \tag{25}$$

Since PNRs are mesoscopic objects, we expect that this relation is also valid inside the polarization cloud of a PNR. Following the example of relaxor ferroelectrics,[14] we assume that the polarization inside an isolated PNR falls off with distance as $\vec{P}(r)=\vec{P}_0(r_0/r)^3$ and that the local field $\vec{E}(r)$ is proportional to $\vec{P}(r)$. In the present case, $\vec{P}(r)$ acquires an additional contribution due to ME coupling and $\vec{E}(r)$ becomes

$$E_{loc,i} = \frac{\phi}{3\epsilon_0}P_i(1 - \epsilon_0\chi_e\lambda_{ij}M_j^2), \tag{26}$$

where ϕ is the local field correction factor. The extra term in parentheses can be interpreted as the contribution due to stress field fluctuations, which are induced by the magnetic field via magnetostriction. Since magnetic LRO is absent and the temperature is far above the magnetic relaxor peak, the system is effectively in a (super)paramagnetic regime. Thus we can write $M_j^2=\chi_m^2H_j^2$ and for an isotropic case we also have $\lambda_{ij}=\lambda_h\delta_{ij}$.

From this point on we can follow the reasoning used in Ref. 14 and consider the electrostatic energy $U_{\mathrm{dip}}=-\vec{\mu}\cdot\vec{E}_{\mathrm{loc}}$ of a virtual electric dipole $\vec{\mu}$ at distance r from the PNR center. The correlation radius r_c is determined by the condition that $|U_{\mathrm{dip}}|$ should be balanced against the thermal fluctuation energy $\sim kT$. Thus the correlation volume behaves as $v_c=v_0T_d^*(H)/T$, where v_0 is the "core" volume of PNR at some reference temperature $T_d^*(H)$. In the present case, we can write $T_d^*(H)=T_d^*(0)[1-\epsilon_0\chi_e\lambda_h(\chi_m)^2H^2]$. As the temperature is lowered, v_c increases and so does the volume fraction η occupied by PNRs. As η reaches the percolation threshold η_p an infinite cluster of PNRs is formed. This occurs at the percolation temperature $T_p=4\pi nT_d^*(H)/3\eta_p$, where n is the volume concentration of PNRs and η_p is around ~0.3 in $d=3$ dimensions and $\eta_p\sim0.6$ for $d=2$.[23] The dielectric relaxation time τ then behaves as

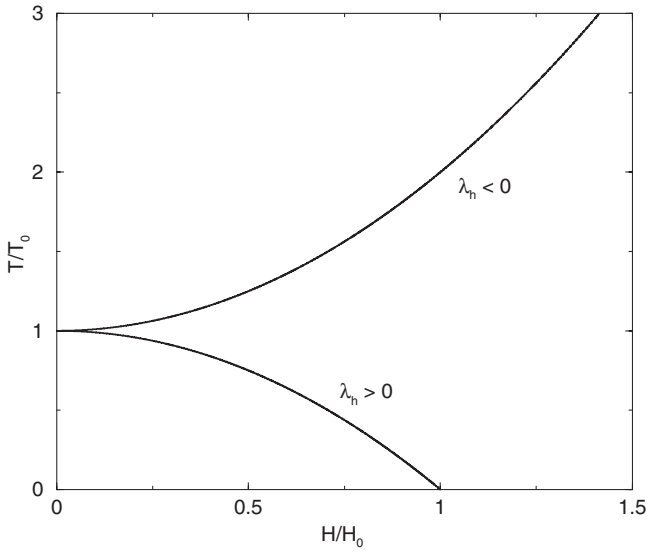

FIG. 4. Lines of percolation critical points in the H,T plane corresponding to positive and negative values of coupling parameter λ_h. The Vogel-Fulcher relaxation time diverges on approaching the corresponding line from above.

$$\tau = \tau_0 \exp\left(\frac{U}{T - T_p(H)}\right), \tag{27}$$

which has the same general form as the VF Eq. (20) with $T_0 = T_p(H)$. It follows that the relaxation time diverges on a line of percolation critical points $T = T_p(H)$ in the H,T plane, where

$$T_p(H) = T_0[1 - \mathrm{sgn}(\lambda_h)(H/H_0)^2], \tag{28}$$

with $H_0^2 = 1/(|\lambda_h|(\chi_m)^2)$, or explicitly,

$$H_0^2 = \frac{1}{2\epsilon_0 \chi_e \chi_m^2 C_h |Q_{e,h} Q_{m,h}|}. \tag{29}$$

The sign of λ_h in Eq. (28) depends on the signs of $Q_{e,h}$ and $Q_{m,h}$, i.e., $\mathrm{sgn}(\lambda_h) = +1$ if the two signs are equal, and -1 if they are opposite. The two cases are illustrated schematically in Fig. 4.

Equation (29) is consistent with the approximate relation (15) since in view of Eq. (5) one can write $\chi_e \simeq k\theta_e/|J - J_0|$. It should be noted, however, that Eq. (29) is based on the phenomenological relations (6) and (22) and is thus model independent.

Let us consider the case $\mathrm{sgn}(\lambda_h) = -1$. The percolation temperature then increases with magnetic field, and at fixed temperature the relaxation time diverges according to

$$\tau = \tau_0 \exp\left(\frac{U_1}{H_p^2 - H^2}\right), \tag{30}$$

where $U_1 = UH_0^2/T_0$ and the critical field H_p is given by

$$H_p(T)^2 = \frac{T - T_0}{T_0} H_0^2. \tag{31}$$

We can estimate the value of H_0 by assuming $\chi_e \sim 3 \times 10^3$ near $T \approx J/k$ and $\chi_m \simeq 4$, and by using the same values of C_h, $Q_{e,h}$, and $Q_{m,h}$ as in Eq. (16). We find $0.43 < \mu_0 H_0 < 4.3$ T, in agreement with Eq. (16). The value of the critical field H_p at any temperature can then be obtained from Eq. (31) if the zero field value of the VF temperature T_0 is known.

The effects of magnetic field on the dielectric relaxation spectra at room temperature have been observed recently by Kumar *et al.*[15] in thin films $(PZT)_{0.8}(PFW)_{0.2}$, where PZT and PFW mean $PbZr_{0.54}Ti_{0.46}O_3$ and $PbFe_{2/3}W_{1/3}O_3$, respectively. The relaxation rate $f = 1/\tau$ corresponding to the temperature peaks in the spectra was found to obey the Vogel-Fulcher law and was extrapolated to zero at a critical field H_c according to the empirical relation

$$f = f_0 \exp\left(-\frac{U_1}{H_c^2 - H^2}\right). \tag{32}$$

This expression is equivalent to the above Eq. (30) with $H_c = H_p$. The experimental value of the critical field at room temperature is $\mu_0 H_c = 0.92$ T, which lies within the range of H_0 estimated above. Smaller values of H_c could be obtained by either going to temperatures closer to T_0 as implied by Eq. (31) or shifting T_0 by changing the iron concentration. The experimental temperature dependence of H_c is not available at present, and similarly the values of the parameters $Q_{e,ij}$, $Q_{m,ij}$, and C_{ij} are not yet known.

VI. DISCUSSION AND CONCLUSIONS

We have formulated a mesoscopic spherical random bond–random field model of a birelaxor which shows both relaxor ferroelectric and relaxor ferromagnetic properties. The underlying physical scenario is based on the simultaneous presence of polar nanoregions (PNRs) and magnetic nanoregions (MNRs). The PNR-PNR and MNR-MNR random interactions are modulated by the lattice stress tensor, thus giving rise to fourth-order PNR-MNR coupling terms. Using thermodynamic Maxwell relations the strength of the PNR-MNR interaction can be expressed in terms of the electrostriction and magnetostriction coefficients and elastic constants. Depending on the relative signs of these coefficients, a long-range-ordered ferroelectric state can be induced by the magnetic field larger than a critical field H_c. Estimates for the possible range of values of H_c are given.

The probability distribution of the dipole moments of PNRs and MNRs for real systems is at present unknown. As shown earlier for a relaxor ferroelectric,[17] the choice of an asymmetric Gaussian distribution leads to the spherical condition for the associated pseudospin variables. The same approach can be applied to the corresponding magnetic degrees of freedom. In fact, the spherical condition has been originally introduced for uniaxial spin glasses, mainly because it leads to an exactly solvable model. The infinite range interactions of the Sherrington-Kirckpatrick-type are a reminder of the long-range nature of the PNR-PNR and MNR-MNR interactions. Their principal advantage is that the number of physical parameters is kept at a minimum of two for each subsystem, to which one only adds the strength of the random electric fields. One should, of course, be aware of the possible limitations of this approach and more realistic interaction models will have to be considered in a future work,

however, at the expense of introducing new sets of parameters.

The dynamics of the PNR subsystem has been studied by means of the Langevin equations of motion, which had been used earlier both for Ising and spherical spin glasses, as well as for relaxor ferroelectrics. Quenched randomness is taken into account on two levels, namely, first by performing random averages over the eigenvalues of the random interaction matrix and over random fields, and second by assuming a broad probability distribution of relaxation times in the spirit of dynamic heterogeneity which is assumed to be applicable to relaxors and birelaxors alike.

An alternative approach to relaxor ferroelectrics based on the slow glassy dynamics near the ferroelectric threshold was introduced by Vugmeister and Rabitz.[24] As discussed in detail by Vugmeister,[25] the dynamic behavior of PNRs can be understood within the model of short-range polar clusters inside the PNR induced by off-center ions in highly polarizable materials. An extension of this model to relaxor ferromagnets and hence to birelaxors has not yet been attempted. This is an interesting but nontrivial problem in view of the lack of quenched random magnetic fields in spin glasses and relaxor ferromagnets.

Using a standard phenomenological Landau-type free-energy density functional of a birelaxor the polarization magnetization or magnetoelectric (ME) coupling term of $\sim P^2M^2$ type has been derived. It has been shown that the local internal electric field in a PNR acquires an extra component due to the ME coupling. According to the model of growth and percolation of PNRs in relaxors, the correlation radius r_c and volume v_c of PNRs is reduced (enhanced) by the magnetic field, again depending on the sign of the ME coupling. As the volume fraction of PNRs reaches the percolation threshold η_p, an infinite cluster of PNRs appears and its reorientation time diverges asymptotically according to the Vogel-Fulcher (VF) relation. The VF freezing occurs on a line of percolation critical points $T=T_p(H)$ in the H,T plane, where $T_p(H)$ corresponds to the VF temperature in a magnetic field. The result for $T=T_p(H)$ does not depend on the parameters of the SRBRF model. The predicted H-field effect on the dielectric relaxation time agrees quantitatively with the observed magnetic-field-controlled dielectric relaxation in solid solution PFW/PZT thin films.

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