

**Structure factor of a relaxor ferroelectric**G. G. Guzmán-Verri<sup>1,2,3</sup> and C. M. Varma<sup>1</sup><sup>1</sup>*Department of Physics and Astronomy, University of California, Riverside, California 92521, USA*<sup>2</sup>*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*<sup>3</sup>*Centro de Investigación en Ciencia e Ingeniería de Materiales and Escuela de Física, Universidad de Costa Rica, San José, Costa Rica 2060*

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We study a minimal model for a relaxor ferroelectric including dipolar interactions and short-range harmonic and anharmonic forces for the critical modes as in the theory of pure ferroelectrics together with quenched disorder coupled linearly to the critical modes. We present the simplest approximate solution of the model necessary to obtain the principal features of the correlation functions. Specifically, we calculate and compare the structure factor measured by neutron scattering in different characteristic regimes of temperature in the relaxor  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ .

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**I. INTRODUCTION**

Relaxor ferroelectrics, a typical example of which is  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN), a perovskite in which the  $\text{Mg}^{2+}$  and  $\text{Nb}^{5+}$  randomly occupy the octahedrally coordinated site, have a very high dielectric constant for a very wide region in temperature and have no ferroelectric transition except in applied electric fields. Cowley *et al.* [1], in a detailed review of relaxor ferroelectrics, have commented that although they were first synthesized over 50 years ago and their properties have been well explored, a satisfactory theory explaining their properties has not yet been formulated. Here we present a minimal model for the canonical relaxor PMN and its simplest necessary approximate solution based on Onsager's results on models with dipolar interactions, the displacive transition model of pure ferroelectrics, and quenched random fields.

The properties of the relaxors such as PMN may be summarized as follows [1–5]: In zero external electric field they have a region of collective dielectric fluctuations which is bounded at the upper end by a temperature  $T_B$ , the Burns temperature [6], above which the susceptibility has a Curie-Weiss form [7]. A broad region extending down to  $T = 0$  below  $T_B$  is marked by a temperature  $T_{\max}$  where the susceptibility is maximum and has a width in temperature  $\Delta T_{\max}$ . Both  $T_{\max}$  and  $\Delta T_{\max}$  depend on the frequency  $\omega$  at which the dielectric susceptibility is measured [8–12]. Very significantly, neutron scattering experiments have revealed that the structure factor  $S_q$  has unusual temperature [13–15], power-law [13] forms and anisotropies [16], which are unlike those in the random field or the random bond disorder models with short-range interactions [17–19].

Typically only such interaction models with quenched disorder have been used to describe relaxor ferroelectrics. These models in three dimensions for weak disorder also have long-range order at a finite temperature [17], which is not observed in the canonical relaxor PMN [1]. Several other models have been proposed for relaxors [20–25], including those of Burton *et al.* [21] and of Tinte *et al.* [22], which, just as is done in the present paper, considers well-known effective Hamiltonians for conventional ferroelectrics with quenched disorder; however, they have almost exclusively been solved by numerical methods, which makes it difficult to determine general aspects of the solution of such models.

Recently, it has been proposed that the ground state of relaxors is that of a cluster glass in which polar domains generated by random fields cluster at low temperatures due to frustrating nature of the dipolar force [26]. The mechanism by which such a glassy state is formed is described by the subsequent formation of polar domains due to random electric fields and the clustering of mesoscopic domains due to frustrated random dipolar interactions. While we do not study this problem here, we cannot rule out that such freezing mechanisms may be out of reach of the theoretical treatment that is presented here, as nucleation of polar domains within the disordered matrix may occur as there are stable ordered states in the free energy of our model [27]. Such domains would then interact through the dipolar force, which is in itself frustrating due to its anisotropy.

In a previous paper [27], we developed a variational method which allowed us to study the temperature evolution of the free energy with compositional disorder, which is essential to understand the dielectric properties of solid solutions of relaxors with conventional ferroelectrics such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PMN-PT). We found that there are disordered states with a region of metastability that extends to zero temperature for moderate disorder and that field-induced transitions to stable ferroelectric states can occur only for applied electric fields sufficiently large to overcome the energy barriers that result from disorder. Here we present a different solution of the model based on Onsager's results on systems with dipolar interactions [28] that provides an important physical insight that is not obvious from the variational solution.

In formulating the minimum necessary model for PMN, it is important to recall Onsager's result [28] that, unlike in the Clausius-Mossotti or Lorentz approximation, dipole interactions alone do not lead to ferroelectric order except at  $T = 0$ . Moreover, pure ferroelectric transitions were understood with the realization [29] that they are soft transverse optic mode transitions due to dipoles induced by structural transitions so the low-temperature phase does not have a center of symmetry. The first point is not in practice important for pure ferroelectrics which are well described by a mean-field theory for the dielectric constant and is often a first-order transition only below which the dipoles are produced [30]. But, as we show below, in the relaxor PMN the random

location of defects acts in concert with the dipole interactions to extend the region of fluctuations to zero temperatures. Therefore dipole interactions must be a necessary part of the model. The essential physical points in the simplest necessary solution is to formulate a theory which considers thermal and quantum fluctuations at least at the level of the Onsager approximation [28] and random field fluctuations at least at the level of a replica theory [31].

## II. MODEL HAMILTONIAN

We consider the model Hamiltonian presented in Ref. [27], which we present here for the sake of completeness. We focus on the relevant transverse optic mode configuration coordinate  $u_i$  of the ions in the unit cell  $i$  along the polar axis (chosen to be the  $z$  axis);  $u_i$  experiences a local random field  $h_i$  with probability  $P(\{h_i\})$  due to the compositional disorder introduced by the different ionic radii and different valencies of  $\text{Mg}^{+2}$ ,  $\text{Nb}^{+5}$ , in PMN. The model Hamiltonian is

$$H = \sum_i \left[ \frac{\Pi_i^2}{2M} + V(u_i) \right] - \frac{1}{2} \sum_{i,j} v_{ij} u_i u_j - \sum_i E_i^{\text{ext}} u_i - \sum_i h_i u_i, \quad (1)$$

where  $\Pi_i$  is the momentum conjugate to  $u_i$  and  $M$  is an effective mass and we have included an external electric field  $E_i^{\text{ext}} = E_0^{\text{ext}} + E_i^{\text{ext}}(t)$ , with a static and uniform component  $E_0^{\text{ext}}$  and an infinitesimally small time-dependent component,  $E_i^{\text{ext}}(t)$ . We assume the  $h_i$ 's are independent random variables with zero mean and variance  $\Delta^2$ .  $V(u_i)$  is an anharmonic potential,

$$V(u_i) = \frac{\kappa}{2} u_i^2 + \frac{\gamma}{4} u_i^4, \quad (2)$$

where  $\kappa, \gamma$  are positive constants.  $v_{ij}$  is the dipole interaction,

$$v_{ij}/e^{*2} = \begin{cases} 3 \frac{(Z_i - Z_j)^2}{|\mathbf{R}_i - \mathbf{R}_j|^5} - \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|^3}, & \mathbf{R}_i \neq \mathbf{R}_j \\ 0, & \mathbf{R}_i = \mathbf{R}_j, \end{cases} \quad (3)$$

where  $e^*$  is the Born effective charge and  $Z_i$  is the  $z$  component of  $\mathbf{R}_i$ . The Fourier transform of the dipole interaction  $v_{\mathbf{q}}/(ne^{*2}) = 1/(ne^{*2}) \sum_{i,j} v_{ij} e^{i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} = \frac{4\pi}{3} (1 - 3 \frac{q_z^2}{q^2}) - \zeta |q\mathbf{a}|^2 + 3\zeta (q_z a)^2$  is nonanalytic for  $\mathbf{q} \rightarrow 0$ . For future use, we denote  $v_0^\perp = 4\pi ne^{*2}/3$  as the  $\mathbf{q} \rightarrow 0$  component of  $v_{\mathbf{q}}$  in the direction transverse to the polar axis ( $\mathbf{q} \perp \hat{z}$ ),  $n$  as the number of unit cells per unit volume, and  $a$  as the lattice constant.  $\zeta$  is a dimensionless coefficient that depends on the structure of the lattice [32].

The Hamiltonian of Eq. (1) presents (i) long-ranged (anisotropic) dipolar interactions, (ii) compositional disorder, and (iii) anharmonicity. We now present the procedure used to find the correlation functions for (1). We use the quasiharmonic approximation, similar to that used for pure displacive ferroelectrics to treat anharmonicity [30]. This reduces the problem to that of harmonic oscillators with a renormalized stiffness which is determined self-consistently. Disorder is treated by an approach which may be termed the ‘‘poor man’s replica method’’ and has been used to study two- and three-dimensional magnets with quenched random fields [33]. The

Onsager approximation, which may be considered the leading fluctuation correction over the mean-field approximation [34], is used for the dipolar interactions as well as for the general statistical-mechanical treatment of the problem.

## III. SOLUTION BY ONSAGER CAVITY METHOD

In this approximation,

$$H \approx \sum_i H_i = \sum_i (H_i^0 - h_i u_i - E_i^{\text{cavity}} u_i), \quad (4)$$

with  $H_i^0 = \Pi_i^2/(2M) + V(u_i) - (\lambda/2)u_i^2$ .  $E_i^{\text{cavity}}$  is the Onsager cavity field,

$$E_i^{\text{cavity}} = \sum_j v_{ij} \langle u_j \rangle - \lambda \langle u_i \rangle + E_i^{\text{ext}}. \quad (5)$$

$\langle X \rangle$  denotes the thermal average of any quantity  $X$ ; similarly, we will denote by  $\overline{\langle X \rangle}$  the configurational average over the quenched random fields  $h_i$  taken *after* the thermal average is taken.

Onsager calculated the parameter  $\lambda$  for the simpler problem of dipolar forces alone using continuum electrostatics. More generally, one may determine  $\lambda$  by use of a self-consistent procedure such that the response functions obey the fluctuation dissipation theorem [35]. To find the self-consistent response functions, we consider the thermal average of  $u_i$  made up of a static and uniform order parameter  $p = \overline{\langle u_i \rangle}$  and a linear response part  $\delta \langle u_i \rangle$ , i.e.,  $\langle u_i \rangle = p + \delta \langle u_i \rangle$ . The linear response is determined from the cavity field  $E_i^{\text{cavity}}$  [30],

$$\delta \langle u_i \rangle = \phi_{h_i}(\omega) \delta E_i^{\text{cavity}}, \quad (6)$$

where  $\phi_{h_i}(\omega)$  is the dielectric susceptibility for the problem with Hamiltonian,  $H_i^0 - u_i h_i - u_i p (v_0^\perp - \lambda) - u_i E_0$  and  $\delta E_i^{\text{cavity}} = \sum_j v_{ij} \delta \langle u_j \rangle - \lambda \delta \langle u_i \rangle + \delta E_i^{\text{ext}}(t)$ . To take the average over configurations, we assume that the effects of the random fields  $h_i$  decouple in  $\phi_{h_i}(\omega)$  and  $\langle u_i \rangle$ . For our model, as will be shown below,  $\overline{\phi_{h_i}(\omega)}$  is independent of  $i$  and therefore has only a  $\mathbf{q} = 0$  component denoted simply by  $\overline{\phi_h(\omega)}$ . Then, taking a Fourier transform, we get the formal expression for the susceptibility function,

$$\chi_{\mathbf{q}}(\omega) = \frac{\overline{\delta \langle u_{\mathbf{q}} \rangle}}{\delta E_{\mathbf{q}}^{\text{ext}}} = \frac{\overline{\phi_h(\omega)}}{1 + \overline{\phi_h(\omega)}(v_{\mathbf{q}} - \lambda)}. \quad (7)$$

Next we determine  $\phi_h(\omega)$ . The equation of motion for  $u_i$  due to  $H_0 - h_i u_i - u_i p (v_0^\perp - \lambda) - u_i E_0^{\text{ext}}$  and including a damping force characterized by  $\Gamma$  are

$$M \ddot{u}_i = - \frac{dV(u_i)}{du_i} + \lambda u_i + h_i + p (v_0^\perp - \lambda) + E_0^{\text{ext}} - \Gamma \dot{u}_i. \quad (8)$$

We now linearize (8) by considering fluctuations  $\delta u_i$  around the static and uniform expectation value of  $u_i$ , i.e.,  $u_i = p + \delta u_i$ , to get that

$$\overline{\phi_h(\omega)} = \frac{1}{M\Omega^2 - \omega^2 + i\omega\Gamma}, \quad (9)$$

$$E_0 = [M\Omega^2 - (v_0^\perp - \lambda) - 2\gamma p^2]p, \quad (10)$$

where  $M\Omega^2 \equiv \kappa - \lambda + 3\gamma \overline{(\langle \delta u_i \rangle^2)} + p^2$ .

The fluctuations  $\overline{\langle(\delta u_i)^2\rangle}$  of the  $H_0 - h_i u_i$  problem are easily shown to be

$$\overline{\langle(\delta u_i)^2\rangle} = \frac{\hbar}{2M\Omega'} \coth\left(\frac{\beta\hbar\Omega'}{2}\right) + \overline{\langle u_i \rangle^2} - p^2. \quad (11)$$

We finally find the susceptibility (7),

$$\chi_q(\omega) = \frac{1}{M\Omega_q^2 - M\omega^2 + i\omega\Gamma}, \quad (12)$$

where  $\Omega_q$  is the vibration frequency of  $u_i$  for the full problem,

$$M\Omega_q^2 = M(\Omega_0^\perp)^2 + (v_0^\perp - v_q), \quad (13)$$

and  $\Omega_0^\perp$  is the  $\mathbf{q} = 0$  component of the phonon frequency in the direction perpendicular to the polar axis,

$$M(\Omega_0^\perp)^2 = M\Omega^2 - (v_0^\perp - \lambda). \quad (14)$$

We now determine the parameter  $\lambda$  by enforcing the fluctuation dissipation theorem,

$$\overline{\langle u_i^2 \rangle} - \overline{\langle u_i \rangle^2} = \frac{1}{N} \sum_q \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth\left(\frac{\beta\hbar\omega}{2}\right) \text{Im}[\chi_q(\omega)]. \quad (15)$$

The summation over  $\mathbf{q}$  extends over the first Brillouin zone. To close the system of equations the polarization  $\langle u_i \rangle_T^0$  must itself be related to the random fields through the susceptibility (12). For a fixed realization of disorder [33],

$$\langle u_i \rangle = p + \sum_j \bar{\chi}_{ij} h_j, \quad (16)$$

where  $\bar{\chi}_{ij}(0)$  is the zero-frequency susceptibility averaged over compositional disorder with the Fourier transform  $\chi_q(0) = \sum_{ij} \bar{\chi}_{ij}(0) e^{iq \cdot (\mathbf{R}_i - \mathbf{R}_j)}$ .

Using  $\bar{h}_j = 0$  and  $\overline{h_i h_j} = \Delta^2 \delta_{ij}$ ,

$$\overline{\langle u_i \rangle} = p, \quad \overline{\langle u_i \rangle^2} = p^2 + \frac{\Delta^2}{N} \sum_q \chi_q^2(0). \quad (17)$$

Given the above solution, the temperature and disorder dependence of the the dielectric susceptibility  $\chi_q(\omega)$  given by Eq. (12), the phonon frequency  $\Omega_q$  of Eq. (13), and the static polarization  $p$  of Eq. (17) can be determined self-consistently together with the parameter  $\lambda$  in Eq. (15). It is easy to show that by eliminating  $\Omega'$  and  $\lambda$  from Eqs. (10), (11), and (14) one recovers the results of Ref. [27].

The static structure factor  $S_q$  is derivable from  $\chi_q(\omega)$  by use of the standard procedure [36]. We obtain the following result:

$$S_q = p^2 \delta_q + \frac{\hbar}{2M\Omega_q} \coth\left(\frac{\beta\hbar\Omega_q}{2}\right) + \frac{\Delta^2}{(M\Omega_q^2)^2}, \quad (18)$$

where the transverse optic phonon frequency  $\Omega_q$  is given in Eq. (13) and it is calculated self-consistently as described above. In the absence of disorder and in the classical limit ( $\hbar \rightarrow 0$ ), we recover the standard results for conventional ferroelectrics [30]. The line shape of the structure factor (13) resembles that of the well-known Lorentzian plus Lorentzian squared for disordered magnetic systems [37] with the

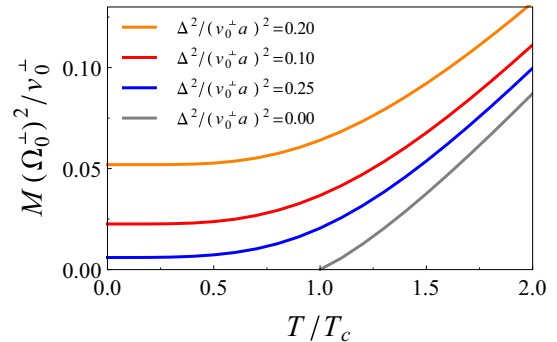


FIG. 1. (Color online) Temperature dependence of the zone center optic phonon frequencies  $\Omega_0^\perp$  for dipole interactions and compositional disorder. The frequencies remain finite down to  $T = 0$  for finite disorder, thus excluding long-range ferroelectric order.

important distinction that the relevant interactions in our problem are long-ranged and anisotropic dipolar forces rather than short-ranged isotropic exchange interactions.

#### IV. RESULTS

We now present results of the calculations to illustrate the physical principles. We focus on the disordered states ( $p = 0$ ) as the experiments we will compare have been performed in such a phase. The model parameters are obtained from fits to the experimental structure factor of PMN (see Fig. 4).

Figure 1 presents the calculated temperature dependence of the (mean) transverse optical model frequency at  $\mathbf{q} = 0$  suitably normalized to show its different regimes. The frequency remains finite at all temperatures, even for weak disorder, thus excluding long-range order in the model which includes dipolar interactions and weak disorder (long-range order would be present for the model with short-range interactions alone) [17]. This state is metastable at low temperatures [27]. As expected, these results are similar to those found previously [27] and are shown here for the sake of completeness.

Associated with the phonon frequency is the dielectric response  $\chi_0(\omega)$ , shown in Fig. 2, where  $T_{CW}$  and  $T_B$  are also identified (see the inset in Fig. 2). Figures 3(a)–3(b) give the variation of  $T_{CW}$ ,  $T_B$ , and  $T_{max}$  with the parameters of the model. We see that the characteristic temperatures are understood by the ratio of the disorder distribution to the transverse dipole interaction with the damping  $\Gamma$  playing a major role for  $T_{max}$ . Clearly, our model is too simple to give the dynamics observed in the relaxor susceptibility such as the Vogel-Fulcher behavior [12]. Nonetheless, it can capture several of the temperature scales. To get detailed dynamics, one must add the full landscape of potentials and relaxation processes, which have already been considered in the literature [21,24]. This is not the aim of the present paper which is concerned with the simpler question of static structure factor. We may add, however, that it is necessary to have the theory of static structure factor well in hand before one can reliably consider the more complicated dynamical problems.

We now compare the static structure factor  $S_q$  with that measured by neutron scattering experiments [13,14]. Without

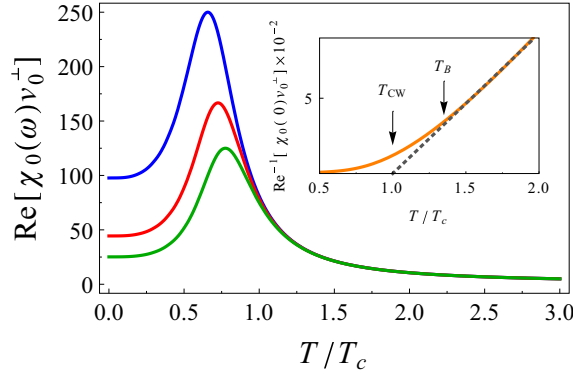


FIG. 2. (Color online) Temperature and frequency dependence of the real part of the dynamic susceptibility  $\chi_0(\omega)$ . Inset: Inverse of the real part of the static susceptibility with compositional disorder  $[\Delta^2/(v_0^\perp a)^2 = 0.03]$ . Deviations from Curie-Weiss law are indicated by the gray dashed line. Blue (top), red (middle), and green (bottom) lines correspond to  $\omega\Gamma/v_0^\perp = 2.0 \times 10^{-2}$ ,  $3.0 \times 10^{-2}$ ,  $4.0 \times 10^{-2}$ .

compositional disorder ( $\Delta = 0$ ), simple inspection shows that  $S_{q=0}$  diverges as the mode frequency softens in the vicinity of the critical point  $T_c$  where long-range ferroelectric order sets in. For finite compositional disorder ( $\Delta > 0$ ),  $S_{q=0}$  remains finite at all temperatures and there is no long-range ferroelectric order. We find this temperature behavior is in agreement with that observed by neutrons in PMN, as shown in Fig. 4(a). The flat behavior of  $S_q$  at low temperatures ( $T \rightarrow 0$ ) is due to zero-point fluctuations: In the classical limit ( $\hbar \rightarrow 0$ ),

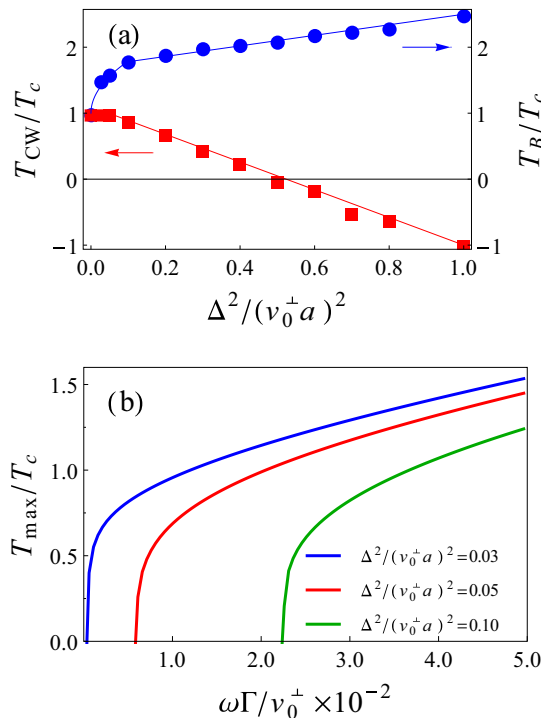


FIG. 3. (Color online) (a) Curie-Weiss ( $T_{CW}$ ) and Burns ( $T_B$ ) temperature dependence on compositional disorder. (b) Frequency and disorder dependence of the temperature  $T_{\max}$  at which the dielectric constant is maximum.

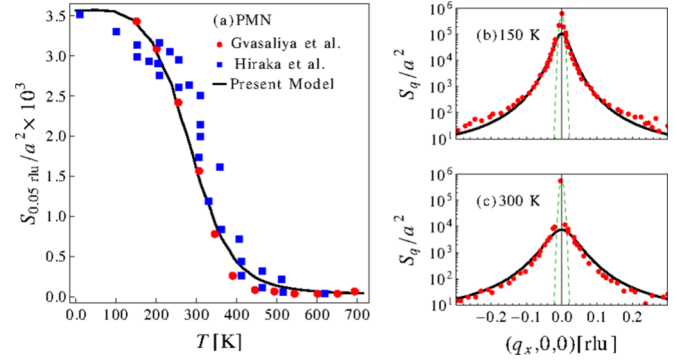


FIG. 4. (Color online) (a) Temperature and [(b) and (c)] wave-vector dependence of the structure factor  $S_q$ . Red dots and blue squares correspond to neutron scattering data from Refs. [13,14] in the vicinity of the (110) and (100) Bragg peaks in PMN. Black solid line corresponds to the calculated  $S_q$  with  $(v_0^\perp - \kappa)/v_0^\perp = 0.85$ ,  $\gamma a^2/v_0^\perp = 0.09$ ,  $\hbar/(Mv_0^\perp a^4)^{1/2} = 5.0$ ,  $\Delta^2/(v_0^\perp a)^2 = 0.03$ , and  $k_B T_c/(v_0^\perp a^2) = 1.0$  with  $T_c = 465$  K. The green dashed line is a Gaussian Bragg peak of width given by the experimental resolution used in Ref. [13] ( $\simeq 0.01$  rlu).

$S_q$  of Eq. (18) increases with decreasing temperature and is finite at  $T = 0$ .

Figures 4(b) and 4(c) compare the calculated wave-vector distribution of  $S_q$  with that observed for the relaxor PMN at  $T = 150$  K and  $T = 300$  K. We use the same value of the model parameters as those of Fig. 4(a). The observed line shape cannot be described by a simple Lorentzian seen for conventional perovskite ferroelectrics or the “squared Lorentzian” expected for random field models.

We now compute the spatial dependence and anisotropy of the correlation functions of polarization at various characteristic temperatures and various normalized disorder strengths. These spatial correlations have been Fourier transformed to give the static structure factor  $S_q$ . One of the purposes of this section is to contrast the correlations of our model to those expected from hypothetical polar nanoregions (PNRs) on which we will comment at the end.

We first consider the correlation functions of polarization at large distances ( $|\mathbf{R}_{ij}| \rightarrow \infty$ ). For low temperatures ( $T \rightarrow 0$ ) and arbitrarily small but finite disorder ( $0 < \Delta/(v_0^\perp a) \ll 1$ ), the correlations are anisotropic and slowly decaying functions,

$$\overline{\langle u_i u_j \rangle} = \begin{cases} \left(\frac{4\pi}{3}\right)^2 \frac{\Delta^2}{(v_0^\perp)^2} \times \frac{32\pi^3 (\bar{\chi}_0^\perp)^3}{v_{BZ} |\mathbf{R}_{ij}|^3}, & \mathbf{R}_{ij} \parallel \hat{\mathbf{z}}, \\ -\left(\frac{4\pi}{3}\right)^2 \frac{\Delta^2}{(v_0^\perp)^2} \times \frac{1}{2} \frac{\pi^{3/2} (\bar{\chi}_0^\perp)^{3/2}}{v_{BZ} |\mathbf{R}_{ij}|^3}, & \mathbf{R}_{ij} \perp \hat{\mathbf{z}}, \end{cases} \quad (19)$$

where  $(\bar{\chi}_0^\perp)^{-1} = (4\pi/3)(\chi_0^\perp)^{-1}/v_0^\perp$  is a small but finite dimensionless inverse susceptibility and  $v_{BZ}$  is the volume of the Brillouin zone. The ratio of the longitudinal to transverse components is proportional (in absolute value) to  $(\bar{\chi}_0^\perp)^{3/2}$ , indicating that the positive longitudinal correlations are stronger than the negative transverse components. This behavior is similar to that of ferroelectrics without random fields. For a uniaxial ferroelectric without compositional disorder and above the critical temperature  $T_c$ , the correlation functions exhibit the same anisotropy, power-law decay,

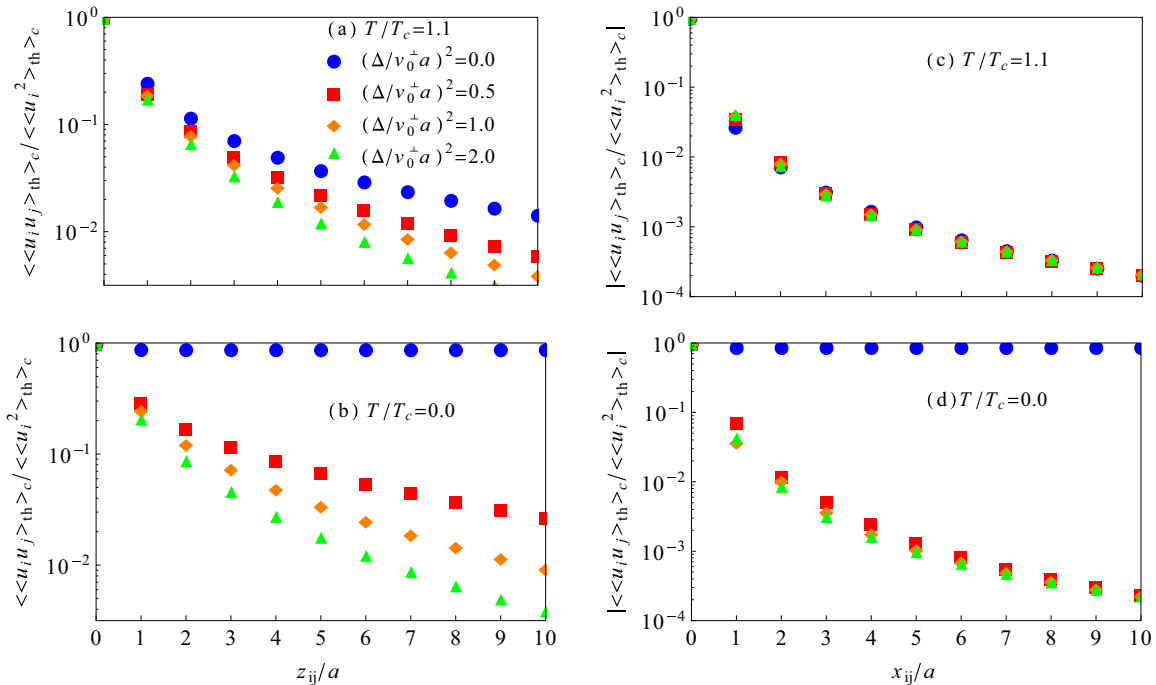


FIG. 5. (Color online) Log-linear plot of near-neighbor correlation functions of polarization for several temperatures and disorder strengths. Here  $(v_0^+ - \kappa)/v_0^+ = 0.40$ ,  $\gamma a^2/v_0^+ = 0.10$ , and  $\hbar/(Mv_0^+ a^4)^{1/2} = 1.0$ .

and longitudinal-to-transverse ratio [38]. The correlations of Eq. (19) are, however, in sharp contrast with those of short-range interactions with quenched random fields in three dimensions where the correlation functions decay exponentially [39].

We now discuss the nearest-neighbor correlations with compositional disorder. For temperatures slightly above  $T_c$ , the nearest-neighbor longitudinal correlations with and without disorder show similar decay with an overall strength that decreases with increasing compositional disorder [Fig. 5(a)]. This behavior persists down to  $T = 0$  for finite compositional disorder [Fig. 5(b)]. For no disorder, the correlations exhibit the long-range order expected at  $T = 0$ . The correlations in the transverse direction follow similar decay as that of the longitudinal components except that they are negative and significantly weaker [Figs. 5(c) and 5(d)].

To compare with the idea of PNRs invoked to rationalize the behavior of relaxors, we note that we find that significant correlations develop below the Burns temperature  $T_B$ . However, we do not find a difference in the characteristic behavior at short distances compared to that at long distances, which might have been expected for PNRs. We find that the correlations have a power-law behavior which joins smoothly to a short-range part where they must saturate to near the on-site correlations. This is characteristic of the fluctuation regime of any cooperative problem. We have emphasized that relaxors may be looked on as materials in which the fluctuation regime extends from the Burns temperature all the way to  $T = 0$ . We therefore conclude that the diffuse scattering observed by neutrons does not support the qualitative picture of PNRs. Recently, other works have arrived at similar conclusions [24,40,41]. We point out, however, that nucleation of local polar domains within the

nonpolar phase may occur as there are stable ferroelectric states in the free energy [27].

## V. CONCLUSIONS

We have used the insight that the frustrating nature of the dipolar interactions (due to their anisotropy) introduced in a perovskite due to a putative displacive transition together with quenched disorder impedes a ferroelectric transition at all temperatures and leads instead to a region of extended ferroelectric fluctuations in PMN. The nature of the dipolar interactions is such that the physics cannot be captured in a mean-field-like or two-body correlation approximations to the problem. Using a minimal approximation scheme which is able to handle the special nature of the problem, we are able to derive the observed structure factor of the relaxor PMN and relate it to their static and dynamic microscopic properties.

In addition to the difficulties posed to our current theoretical treatment by the complex dynamic processes of relaxors (see Sec. IV), there are several other challenges which should be addressed in future extensions of this work such as the effects of cubic symmetry, of disorder in the bonds (e.g., lattice stiffness and dipole interactions), and of electrostriction. These are all important ingredients of any model that aims to describe the universality class [1], glassiness [26], and ultrahigh piezoelectricity [42] of typical relaxors such as PMN and its solid solutions with conventional ferroelectrics such as PMN-PT.

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- [1] R. A. Cowley, S. N. Gvasaliya, S. G. Lushnikov, B. Roessli, and G. M. Rotaru, *Adv. Phys.* **60**, 229 (2011).
- [2] A. A. Bokov and Z.-G. Ye, *J. Mater. Sci.* **41**, 31 (2006).
- [3] W. Kleemann, *J. Mater. Sci.* **41**, 129 (2006).
- [4] G. A. Samara, *J. Phys.: Condens. Matter* **15**, R367 (2003).
- [5] L. E. Cross, *Ferroelectrics* **151**, 305 (1994); **76**, 241 (1987).
- [6] G. Burns and B. A. Scott, *Solid State Commun.* **13**, 423 (1973); G. Burns and F. H. Dacol, *ibid.* **48**, 853 (1983); *Phys. Rev. B* **28**, 2527 (1983).
- [7] D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, *Phys. Rev. B* **46**, 8003 (1992).
- [8] G. A. Smolenskii, *J. Phys. Soc. Jpn.* **28**(Suppl.), 26 (1970).
- [9] V. Bovtun, S. Kamba, A. Pashkin, M. Savinov, P. Samoukhina, J. Petzelt, I. P. Bykov, and M. D. Glinchuk, *Ferroelectrics* **298**, 23 (2004).
- [10] J. Hlinka, J. Petzelt, S. Kamba, D. Noujni, and T. Ostapchuk, *Phase Transit.* **79**, 41 (2006).
- [11] A. A. Bokov and Z.-G. Ye, *J. Adv. Dielec.* **2**, 1241010 (2012).
- [12] A. E. Glazounov and A. K. Tagantsev, *Appl. Phys. Lett.* **73**, 856 (1998).
- [13] S. N. Gvasaliya, B. Roessli, R. A. Cowley, P. Huber, and S. G. Lushnikov, *J. Phys.: Condens. Matter* **17**, 4343 (2005); R. A. Cowley, S. N. Gvasaliya, and B. Roessli, *Ferroelectrics* **378**, 53 (2009).
- [14] H. Hiraka, S.-H. Lee, P. M. Gehring, Guangyong Xu and G. Shirane, *Phys. Rev. B* **70**, 184105 (2004).
- [15] P. M. Gehring, H. Hiraka, C. Stock, S.-H. Lee, W. Chen, Z.-G. Ye, S. B. Vakhrušev, and Z. Chowdhuri, *Phys. Rev. B* **79**, 224109 (2009).
- [16] For reviews, see G. Xu, *J. Phys. Conf. Ser.* **320**, 012081 (2011); and P. M. Gehring, *J. Adv. Dielec.* **02**, 1241005 (2012).
- [17] Y. Imry and S. Ma, *Phys. Rev. Lett.* **35**, 1399 (1975).
- [18] R. Pirc and R. Blinc, *Phys. Rev. B* **60**, 13470 (1999); R. Blinc, J. Dolinsek, A. Gregorovic, B. Zalar, C. Filipic, Z. Kutnjak, A. Levstik, and R. Pirc, *Phys. Rev. Lett.* **83**, 424 (1999).
- [19] V. Westphal, W. Kleemann, and M. D. Glinchuk, *Phys. Rev. Lett.* **68**, 847 (1992).
- [20] M. D. Glinchuk, *Br. Ceram. Trans.* **103**, 76 (2004).
- [21] B. P. Burton, E. Cockayne, S. Tinte, and U. V. Waghmare, *Phase Transit.* **79**, 91 (2006).
- [22] S. Tinte, B. P. Burton, E. Cockayne, and U. V. Waghmare, *Phys. Rev. Lett.* **97**, 137601 (2006).
- [23] A. R. Akbarzadeh, S. Prosandeev, E. J. Walter, A. Al-Barakaty, and L. Bellaiche, *Phys. Rev. Lett.* **108**, 257601 (2012).
- [24] H. Takenaka, I. Grinberg, and A. M. Rappe, *Phys. Rev. Lett.* **110**, 147602 (2013).
- [25] D. Sherrington, *Phys. Rev. B* **89**, 064105 (2014).
- [26] W. Kleemann, in *Mesoscopic Phenomena in Multifunctional Materials*, Springer Series in Materials Science, Vol. 198, edited by A. Saxena and A. Planes (Springer, Berlin, 2014), p. 249; *Phys. Stat. Solidi B* **251**, 1993 (2014).
- [27] G. G. Guzmán-Verri, P. B. Littlewood, and C. M. Varma, *Phys. Rev. B* **88**, 134106 (2013).
- [28] L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).
- [29] W. Cochran, *Phys. Rev. Lett.* **3**, 412 (1959); *Adv. Phys.* **9**, 387 (1960); P. W. Anderson, *Fizika Dielektrikov*, edited by G. I. Skanavi (Akad. Nauk SSSR Fizicheskii Inst., im P. N. Levedeva, Moscow, 1960); P. W. Anderson, *A Career in Theoretical Physics* (World Scientific, Hackensack, NJ, 1994).
- [30] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).
- [31] C. De Dominicis and I. Giardina, *Random Fields and Spin Glasses: A Field Theory Approach* (Cambridge University Press, Cambridge, UK, 2010).
- [32] A. Aharony and M. E. Fisher, *Phys. Rev. B* **8**, 3323 (1973).
- [33] I. Vilfan and R. A. Cowley, *J. Phys. C: Solid State Phys.* **18**, 5055 (1985).
- [34] J. H. Van Vleck, *J. Chem. Phys.* **5**, 320 (1937).
- [35] R. Brout and H. Thomas, *Phys.* **3**, 317 (1967); H. Thomas and R. Brout, *J. Appl. Phys.* **39**, 624 (1968).
- [36] B. I. Halperin and C. M. Varma, *Phys. Rev. B* **14**, 4030 (1976).
- [37] D. P. Belanger and A. P. Young, *J. Magn. Magn. Mater.* **100**, 272 (1992).
- [38] M. Lines, *Phys. Rev. B* **9**, 950 (1974).
- [39] R. J. Birgeneau, H. Yoshizawa, R. A. Cowley, G. Shirane, and H. Ikeda, *Phys. Rev. B* **28**, 1438 (1983).
- [40] J. Hlinka, *J. Adv. Dielec.* **2**, 1241006 (2012).
- [41] A. Bosak, D. Chernyshov, S. Vakhrušev, and M. Krischa, *Acta Cryst. A* **68**, 117 (2012).
- [42] S.-E. Park and T. R. ShROUT, *J. Appl. Phys.* **82**, 1804 (1997).