Spherical model of relaxor polymers

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Recent dielectric experiments have revealed a striking analogy between inorganic relaxor ferroelectrics and disordered organic ferroelectric polymers. We propose a model description of these relaxor-like polymers by considering a statistical ensemble of randomly oriented polar nanoregions, embedded in an amorphous matrix. In analogy to the Spherical Random Bond–Random Field (SRBRF) model of inorganic relaxor ferroelectrics, we assume that the polar nanoregions are coupled through infinitely ranged random interactions of a spin-glass type and are subject to random local fields. The second moment of the probability distribution of dipole moments is required to have a fixed value, which is equivalent to a global spherical condition. A general solution of the SRBRF model is presented, and the linear and nonlinear static dielectric susceptibilities are calculated and compared with the experimental data. The phenomenon of giant electrostriction in relaxor polymers is also discussed.

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I. INTRODUCTION

Relaxor ferroelectrics have been the subject of intense experimental and theoretical investigations for many years. Much of this research was focused on compositionally disordered ABO$_3$-type perovskites, such as PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN) and La-substituted PbZr$_{1-x}$Ti$_x$O$_3$ (PLZT). More recently, analogous relaxor phenomena have been observed in disordered organic ferroelectric polymers, for example in electron irradiated copolymer poly(vinylidene fluoride-trifluorochloroethylene) or P(VDF-TrFE), and in its terpolymer with chlorofluoroethylene P(VDF-TrFE-CFE). Similar to their inorganic counterparts, relaxor-like polymer systems are characterized by slow relaxation and a strong frequency dispersion of the dielectric permittivity. In the low-frequency limit, a broad temperature maximum of the dielectric constant is observed, and the longest relaxation time diverges according to the Vogel-Fulcher law, leading to a frozen nonergodic low-temperature state. It was suggested earlier that these relaxor properties of inorganic relaxors are due to the formation of polar clusters, which are analogous to the reorientable magnetic clusters in a superparamagnet. In analogy to dipolar glasses, quenched random interactions between polar clusters together with random electric fields induced by random charges and electric dipoles are responsible for the observed freezing phenomena.

In a simple semi-microscopic model of inorganic relaxor ferroelectrics one assumes a uniform statistical distribution of polar cluster sizes and the associated dipole moments. Thus the local polarization is represented by a 3 dimensional vector field $\vec{S}_i$ subject only to the global constraint $\sum_i (\vec{S}_i)^2 = 3N$, where $N$ is the total number of polar clusters. This so-called Spherical Random Bond–Random Field (SRBRF) model has the advantage of being exactly solvable, and in spite of its simplicity captures a number of physical features of relaxors.

II. SPHERICAL RANDOM BOND–RANDOM FIELD MODEL OF RELAXOR POLYMERS

A. Polar nanoregions

We consider the case of a disordered ferroelectric polymer, characterized by a lamellar crystalline structure surrounded by an amorphous configuration of polymer chains. The chains are assumed to be twisted and broken into nanosized segments of variable lengths by either irradiation as in P(VDF-TrFE) or by compositional disorder as in the case of terpolymer P(VDF-TrFE-CFE). For example, it has been shown that electron irradiation breaks up the all-trans T$_{M-\frac{3}{2}}$G chains in the normal ferroelectric P(VDF-TrFE) polymer, resulting in an irregular structure where the remaining all-trans segments are interrupted by T$_3$G and TG trans-gauche bonds. Similarly, in terpolymers, due to a much larger van der Waals radius of chlorine (1.8 Å) as compared to hydrogen (1.2 Å) and fluorine (1.35 Å) atoms, the addition of CFE or CFTE monomers favors the formation of nonpolar T$_3$GT$_3$G bonds against polar all-trans bonds between the monomers. Thus, in each case the breaking up of the ferroelectric layered structure results in a random network of polar nanoregions embedded in an amorphous matrix, which are responsible for the observed relaxor behavior.

In a simplified description, we will think of a polarized nanoregion as a compact lamellar array of polar nanosegments, with a net dipole moment perpendicular to the segments. The magnitude of the dipole mo-
The first two moments are

\[
\langle S^2 \rangle = 2a \Gamma \left( \frac{2}{a} \right),
\]

where \( a \) is some positive integer, \( p \) is some positive integer, \( \Gamma \) is the Gamma function, and \( S^2 \) is the second moment of the distribution. We can readily evaluate the moments \( \langle S^p \rangle \), where \( p \) is some positive integer,

\[
\langle S^p \rangle = 2^p a \Gamma \left( \frac{m+1}{2} \right) / \Gamma \left( \frac{m}{2} \right). \tag{2}
\]

The first two moments are \( \langle S \rangle = 2^{3/2} a \Gamma \left( \frac{m+1}{2} \right) / \Gamma \left( \frac{m}{2} \right) \) and \( \langle S^2 \rangle = ma^2 \). Returning to the discrete case we find

\[
\sum_{i=1}^{N} (\tilde{S}_i)^2 = ma^2 N.
\]

We can now rescale the fields \( \tilde{S}_i \to \tilde{S}_i/a \) and obtain

\[
\sum_{i=1}^{N} (\tilde{S}_i)^2 = m N. \tag{3}
\]

This is equivalent to a generalized spherical condition for the \( m \)-component order parameter field \( \tilde{S}_i \) with the width of the corresponding distribution \( \rho(S) \) equal to unity. We will, therefore, describe the relaxor polymer by the \( m \)-component SRBRF model in which the order parameter field \( \tilde{S}_i \) satisfies the spherical condition (3).

### B. Free energy

The free energy of a quenched disordered system described by the spherical model can be calculated exactly either by using the eigenvalue spectrum of the random interaction matrix or by applying the replica method. Here it is convenient to apply the second method, which is based on the identity

\[
\beta F = -\lim_{n \to 0} \frac{\partial}{\partial n} \int_{c-i\infty}^{c+i\infty} \frac{dz}{2\pi i} \text{Tr} \left[ \exp \left\{ -\beta \sum_{\alpha=1}^{n} \mathcal{H}_\alpha - z \sum_{\alpha=1}^{n} \left( \sum_{i=1}^{N} (\tilde{S}_{i\alpha})^2 - mN \right) \right\} \right]_{av}, \tag{4}
\]

where \( \mathcal{H}_\alpha \) is the Hamiltonian in replica space, and \( \text{Tr} \) represents the integrals over all \( S_{i\mu\alpha} \) over the entire space. The contour integral over \( z \) enforces the spherical condition (3), and the symbol \( [\cdots]_{av} \) represents the disorder average.

The Hamiltonian of a relaxor polymer is now written as

\[
\mathcal{H} = -\frac{1}{2} \sum_{i,j=1}^{N} \sum_{\mu=1}^{m} J_{ij} S_{i\mu} S_{j\mu} - \sum_{i=1}^{N} \sum_{\mu=1}^{m} (h_{i\mu} + gE_{\mu}) S_{i\mu}. \tag{5}
\]

As usual, \( J_{ij} \) represents the quenched random interaction between the polar nanoregions \( i \) and \( j \), which is infinitely ranged and has a Gaussian probability distribution such that

\[
[J_{ij}]_{av} = J_0 / N; \quad [J_{ij}]_{av} = J^2 / N. \tag{6}
\]

In the last term of Eq. (5), \( h_{i\mu} \) are components of a local random field with zero mean and second cumulant

\[
[h_{i\mu} h_{j\nu}]_{av} = \delta_{ij} \delta_{\mu\nu} \Delta, \tag{7}
\]

\( E_{\mu} \) is the applied field, and \( g \) an effective dipole moment. When \( E = 0 \), the model is characterized by three parameters, namely, \( J_0 \), \( J \), and \( \Delta \).

In inorganic relaxors, compositional fluctuations give rise to so-called chemical clusters, i.e., chemically ordered regions with a net nonzero electric charge, which act as sources of random electric fields. This is to be contrasted with relaxor polymers, where such charged regions are less likely to be created by the random disorder. Therefore, we expect that random electric fields will be weaker in polymers. On the other hand, the breaking up of the layered ferroelectric structure results in large strain fields, which have a different symmetry than the electric fields, but may also affect the polar nanoregions through piezoelectric and electrostrictive coupling. Thus it is not surprising that strong electrostriction is observed in some polymer composites, as discussed Section IV.

In Eq. (4), we perform the standard manipulations from the replica theory of vector spin glasses. After evaluating the integrals over the distributions of \( J_{ij} \) and \( h_{i\mu} \), the mixed terms involving two different sites \( i,j \) are linearized by introducing a set of Gaussian integration variables \( q_{\mu\nu\alpha\beta} \). Interchanging the order of the limits \( n \to 0 \) and \( N \to \infty \), the integrals over \( q_{\mu\nu\alpha\beta} \) are evaluated by the saddle point method, thus reducing the trace
to a product of single-site averages.

For a general direction of the electric field $\vec{E} = (E_1, E_2, ..., E_m)$, where we will choose $E_1 = E$ and $E_2 = ... = E_m = 0$, we obtain three types of thermodynamic averages, namely,

$$
(S_{\mu\alpha}) = P_{\mu\alpha} ;
$$

(8)

$$
q_{\mu
u\alpha\beta} = \langle S_{\mu\alpha}S_{\nu\beta} \rangle \equiv \delta_{\mu\nu}q_{\alpha\beta} ; q_{\mu\alpha} = \langle S_{\mu\alpha}S_{\mu\beta} \rangle ;
$$

(9)

$$
\langle S_{\mu\alpha}S_{\nu\alpha} \rangle = r_{\mu\nu\alpha} \equiv \delta_{\mu\nu}r_{\mu\alpha} ; \quad r_{\mu\alpha} \equiv \langle S_{\mu\alpha}^2 \rangle .
$$

(10)

The $\mu \neq \nu$ averages are zero by symmetry.

It is well known that for a random spherical model the order parameters (8)-(10) as follows:

$$
P_{\alpha 1} = P_L \equiv P , \quad P_{\alpha 2} = \cdots P_{\alpha m} = P_T = 0 ;
$$

(11)

$$
q_{1\alpha\beta} = q_L (1 - \delta_{\alpha\beta}) ; q_{2\alpha\beta} = \cdots = q_{m\alpha\beta} = q_T ;
$$

(12)

$$
r_{1\alpha} = r_L ; \quad r_{2\alpha} = \cdots = r_{m\alpha} = r_T .
$$

(13)

In the limit $n \to 0$ we obtain the following expression for the average free energy per polar nanoregion $f \equiv \mathcal{F}/N$:

$$
\beta f = \frac{1}{2} \beta J_0 P^2 - \frac{1}{4} \beta^2 J^2[q_L^2 - r_L^2 + (m - 1)(q_T^2 - r_T^2)] - mz
$$

$$
- \int_{-\infty}^{+\infty} \prod_{\mu=1}^{m} \left[ \frac{dx_\mu}{\sqrt{2\pi}} \right] \log \int_{-\infty}^{+\infty} \prod_{\mu=1}^{m} dS_\mu \exp \left\{ \beta J \left[ \sqrt{q_L} x_1 S_1 + \sqrt{q_T} \sum_{\mu=2}^{m} x_\mu S_\mu \right] \right. 
$$

$$
- z \sum_{\mu=1}^{m} S_\mu^2 - \frac{1}{2} \beta^2 J^2 \left[ (q_L - r_L) S_L^2 + (q_T - r_T) \sum_{\mu=2}^{m} S_\mu^2 \right] + \beta (J_0 P + gE) S_1 \left. \right\} .
$$

(14)

Here, $\tilde{q}_{L,T} \equiv q_{L,T} + \Delta/J^2$.

C. Order parameters

The equilibrium values of the order parameters $q_{L,T}$, $r_{L,T}$, and $P$ are determined by the saddle point condi-

$$
\beta f = \frac{1}{2} \beta J_0 P^2 - \frac{1}{4} \beta^2 J^2[q_L^2 - r_L^2 + (m - 1)(q_T^2 - r_T^2)] - mz
$$

$$
- \frac{1}{2} \beta^2 \{[J^2 \tilde{q}_L + (J_0 P + gE)^2]B_L + (m - 1)J^2 \tilde{q}_T B_T \} + \frac{1}{2} \log(B_L B_T^{m-1}) ,
$$

(15)

where we have introduced

$$
B_{L,T} = [2z - \beta^2 J^2(r_{L,T} - q_{L,T})]^{-1} .
$$

(16)

The saddle point conditions now lead to the following relations:

$$
q_L = \beta^2 [J^2 \tilde{q}_L + (J_0 P + gE)^2]B_L^2 ,
$$

(17a)

$$
q_T = \beta^2 J^2 \tilde{q}_T B_T^2 ,
$$

(17b)

$$
r_L - q_L = B_L ,
$$

(17c)

$$
r_T - q_T = B_T ;
$$

(17d)
It is convenient to consider the corresponding invariants diagonal elements of point conditions employed in evaluating the free energy. It can be shown that Eqs. (16), (17c), and (17d) imply
\[ r_L - q_L = r_T - q_T, \]
and thus \( B_L = B_T \equiv B \), with \( B \) to be determined below. From Eqs. (17c), (17d), and (18) we find
\[ r_L + (m-1)r_T = m. \]

The field-cooled polarization is given by the equation
\[ P = \beta(J_0P + gE)B, \]
so that Eqs. (17a) and (17b) can be rewritten as
\[
\begin{align*}
q_L &= \beta^2 J^2 \tilde{q}_L B^2 + P^2, \\
q_T &= \beta^2 J^2 \tilde{q}_T B^2.
\end{align*}
\]

The order parameters \( q_{L,T} \) and \( r_{L,T} \) are in general the diagonal elements of \( m \times m \) matrices \( q \) and \( r \), respectively. It is convenient to consider the corresponding invariants
\[
\begin{align*}
q &= \frac{1}{m} \text{Tr} \, q = \frac{1}{m} [q_L + (m-1)q_T]; \\
r &= \frac{1}{m} \text{Tr} \, r = \frac{1}{m} [r_L + (m-1)r_T] = 1,
\end{align*}
\]
where the last relation follows from Eq. (20). The parameter \( q \) plays the role of the Edwards-Anderson (EA) order parameter in dipolar glasses.\(^{14}\)

Eqs. (17)-(20) now yield
\[ B = (1 - q). \]
Thus
\[ q = \beta^2 J^2 \tilde{q}(1-q)^2 + P^2/m \]
and
\[ P = \beta(J_0P + gE)(1-q). \]

Analogous results have been derived earlier using symmetry arguments for inorganic relaxors \((m = 3)\) in a field \( E || [111] \) and for \( P = P(1,1,1). \)^{9}

It should be noted that in analogy to spin and dipolar glasses the quantities \( q \) and \( r \) are not thermodynamic order parameters, and thus cannot be derived by minimizing the free energy, but rather follow from the saddle point conditions employed in evaluating the free energy.

### III. DIELECTRIC SUSCEPTIBILITY

#### A. Longitudinal and transverse susceptibilities

The linear longitudinal static field-cooled susceptibility \( \chi_{1,L} \) of a relaxor polymer is obtained by differentiating the physical polarization \( P = (g/v_0)P \) with respect to the field \( E \), where we introduce \( v_0 = V/N \) as the effective average volume of a polar nanoregion. Eq. (27) yields
\[ \chi_{1,L} = \left( \frac{g^2}{v_0} \right) \frac{\beta(1-q)}{1 - \beta J_0(1-q)}. \]

The corresponding transverse susceptibility \( \chi_{1,T} \) follows from the free energy (4) by differentiating with respect to an infinitesimal field along any of the perpendicular directions \( \mu \neq 1 \), say, \( E_2 \),
\[ \chi_{1,T} = \left( \frac{g^2}{v_0} \right) \beta \left[ \langle S_2^2 \rangle - \langle S_2 \rangle^2 \right]_{av}, \]
where \( \cdots \rvert_{av} \) again represents the random average. It is easily seen that the order parameters \( q_{L,T} \) and \( r_{L,T} \) are given by
\[
\begin{align*}
q_L &= \left[ \langle S_1 \rangle^2 \right]_{av}; \quad q_T = \left[ \langle S_2 \rangle^2 \right]_{av}; \\
r_L &= \left[ \langle S_2 \rangle \right]_{av}; \quad r_T = \left[ \langle S_2^2 \rangle \right]_{av}.
\end{align*}
\]
Thus
\[ \chi_{1,T} = \left( \frac{g^2}{v_0} \right) \beta(1-q), \]
and from Eq. (28) we obtain the relation
\[ \chi_{1,L} = \frac{\chi_{1,T}}{1 - J_0(v_0/g^2)\chi_{1,T}}. \]

In Fig. 1, the calculated temperature dependence of the static field-cooled longitudinal susceptibility \( \chi_1 \equiv \chi_{1,L} \) and the corresponding order parameter \( q \) obtained from Eq. (26) are shown for \( J_0/J = 0.9 \) and three representative values of the random field parameter \( \Delta/J^2 \). Fig. 2 shows a comparison between the experimental and theoretical values of the static field-cooled dielectric constant \( \epsilon_s = 1 + \chi_1/\epsilon_0 \) in electron-irradiated copolymer \( P(\text{VDF-TrFE}) \)\(^7\) and in terpolymer \( \text{P(\text{VDF-TrFE}})\text{-CFE}) \).\(^{15}\) The solid lines were calculated from Eq. (28) and fitted to the data using a set of fit parameters listed in the caption, and by adjusting the amplitude of \( \chi_1 \). The agreement between the experimental and theoretical values is reasonably good. It should also be noted that the fit values \( J/k = 276 \pm 5 \) K and \( 266 \pm 16 \) K are close to the experimental values for the freezing temperature \( T_f = 277 \pm 2 \) K and \( 269 \pm 2 \) K, respectively, determined from the temperature-frequency plots.\(^{7,15}\) The random field strength \( \Delta/J^2 = 0.059 \) in electron irradiated \( P(\text{VDF-TrFE}) \) is much larger than \( \Delta/J^2 = 0.008 \) for
FIG. 1: Calculated temperature dependence of the static linear field-cooled longitudinal dielectric susceptibility of a relaxor polymer in zero field limit, for three values of random field strength $\Delta/J^2$. Inset: Temperature dependence of the Edwards-Anderson order parameter.

P(VDF-TrFE-CFE), suggesting that the degree of local disorder created by electron irradiation may be stronger than the intrinsic compositional disorder occurring in the terpolymer.

In vector spin glasses, the transverse order parameter $q_T$ vanishes above the so-called Gabay-Toulouse (GT) line in the $(E,T)$-plane. In the present case, one has $q_T \neq 0$ at all temperatures and fields due to the presence of random fields, and there can be no GT line. However, even without random fields ($\Delta = 0$) it can be shown that there is no GT line in the spherical model.

To illustrate the above point further, let us consider the simpler case $\Delta = 0$ and $J_0 = 0$, but $E \neq 0$. Let us assume that $q_T \neq 0$. According to Eq. (22b), in which now $q_L.T = q_L.r$, we have $\beta^2J^2B_T^2 = 1$ or

$$r_T - q_T = \frac{1}{\beta J}. \quad (34)$$

Since $r_L - q_L = r_T - q_T$, we see that $r_L - q_L = 1/(\beta J)$ too, and Eq. (22a) cannot be fulfilled unless $P = E = 0$. Thus, for $E \neq 0$ we cannot have $q_T \neq 0$ at any temperature, and there can be no transition from $q_T = 0$ to $q_T \neq 0$, i.e., no GT line.

It should finally be noted that a general feature of classical continuous models—and hence of the SRBRF model—is a negative value of the entropy in the limit $T \to 0$. Thus the model predictions should be treated with some caution on approaching the zero temperature limit.

FIG. 2: Comparison between calculated (solid lines) and experimental (circles) static field cooled dielectric constants for two relaxor polymer systems, as indicated. (a) Data: Ref. [7]. Solid line: Fit with $J/k = 276 \pm 5$ K, $J_0/k = 234$ K, $\Delta/J^2 = 0.059$. (b) Data: Ref. [15]. Solid line: $J/k = 266 \pm 16$ K, $J_0/k = 113$ K, $\Delta/J^2 = 0.008$.

B. Spontaneous polarization

A second illustrative example is the case $E = 0$ with both $\Delta \neq 0$ and $J_0 \neq 0$. For $J_0^2 < J^2 + \Delta$ there is no spontaneous polarization at any temperature. By symmetry, we have $r_T = r_L = 1$ and $q_T = q_L = q$, where $q$ is the solution of

$$q = \beta^2J^2(q + \Delta/J^2)(1 - q)^2. \quad (35)$$

We can show that for $J_0^2 > J^2 + \Delta$ long range order (LRO) exists and the spontaneous polarization $P$ is nonzero at $T < T_c$. This means that the symmetry is broken below some critical temperature $T_c$, i.e., $r_T \neq r_L$ and $q_T \neq q_L$. In general, we can again choose a coordinate system in which $P_1 = P$ and $P_2 = P_3 = \cdots = 0$. Eq. (21) for $E = 0$ yields $r_L - q_L = 1/\beta J_0$, and Eqs.
The derivatives of the EA order parameter at \( T < T_c \) is obtained from Eq. (23) as

\[
q = 1 - \frac{kT}{J_0},
\]

and the spontaneous polarization follows from Eq. (26) as

\[
P^2 = m \left[ \left(1 - \frac{kT}{J_0}\right) \left(1 - \frac{J^2}{J_0^2}\right) - \frac{\Delta}{J_0^2}\right].
\]

The critical temperature \( T_c \) is, therefore, given by

\[
kT_c = J_0 \left(1 - \frac{\Delta}{J_0^2 - J^2}\right).
\]

The spontaneous polarization at \( T = 0 \) is

\[
P(0)^2 = m \left(1 - \frac{J^2 + \Delta}{J_0^2}\right).
\]

This shows that LRO exists only for \( J_0^2 > J^2 + \Delta \).

From Eq. (16) we can obtain the value of the parameter \( z \) below \( T_c \), which is

\[
z = \frac{\beta J_0}{2} \left(1 + \frac{J^2}{J_0^2}\right).
\]

It should be noted that \( q, T_c, \chi_1, L, \) and \( z \) are independent of the effective dimensionality \( m \).

### C. Nonlinear Susceptibility

We introduce the third order nonlinear longitudinal susceptibility \( \chi_3 \) by the usual relation \( \mathcal{P} = \chi_1 E - \chi_3 E^3 \), where the indices \( L \) have been omitted. By performing the derivatives of \( P \) and \( q \) with respect to \( E \) in Eqs. (27) and (26), respectively, we obtain in the limit \( E \to 0 \):

\[
\chi_3 = \frac{kT v_0^3/mq^4}{(1 - q)^2[1 - \beta^2 J^2(1 - q)(1 - 3q - 2\Delta/J^2)]}.
\]

This expression corresponds to the static field-cooled third order nonlinear susceptibility of a relaxor. The temperature dependence of \( \chi_3 \) is shown in Fig. 3a for the same values of the random field strength \( \Delta/J^2 \) as in Fig. 1, and for \( J_0/J = 0.9 \). As known from the theory of dipolar glasses and inorganic relaxors, for small values of \( \Delta/J^2 \), the nonlinear susceptibility has a nearly divergent behavior at the freezing temperature \( T_f \approx J/k \), whereas in spin glasses \( (\Delta = 0) \) \( \chi_3 \) actually diverges as \( \sim |T - T_c|^{-1} \) at the glass transition temperature \( T_g = J/k \). According to the Landau theory for homogeneous ferroelectric systems, \( \chi_3 \) should diverge at the critical temperature \( T_c \) as \( \chi_3 \sim |T - T_c|^{-4} \). This type of behavior is also found in the present model for \( J_0^2 > J^2 + \Delta \). For a trivial paraelectric system with \( J_0^2 = J^2 = \Delta = 0 \), we see from Eq. (42) that \( \chi_3 \sim T \). On the other hand, in the general case of a relaxor polymer with all parameters \( J, J_0, \) and \( \Delta \) nonzero and \( J_0^2 < J^2 + \Delta \), we find for \( T \gg J/k \) that \( q \ll 1 \), and Eq. (42) predicts a linear temperature dependence at high temperatures, similar to the paraelectric case.

It is useful to introduce the scaled third order nonlinear susceptibility \( a_3 = \chi_3/\chi_1^4 \), i.e.,

\[
a_3 = \frac{kT v_0^3/mq^4}{(1 - q)^2[1 - \beta^2 J^2(1 - q)(1 - 3q - 2\Delta/J^2)]}.
\]

By determining \( a_3 \) experimentally, we can simply discriminate between the paraelectric, ferroelectric, and relaxor behavior of a given system. For example, in a mean-field-type ferroelectric \( \chi_3 \) diverges, but \( a_3 \) is finite at \( T_c \), whereas in a relaxor we expect the same type of nearly divergent behavior to occur in both \( \chi_3 \) and \( a_3 \). This is illustrated in the inset of Fig. 3a.

It should be emphasized that the above model of a relaxor must include random bonds — i.e., a non-zero parameter \( J \) — in addition to random fields in order to describe the anomaly in the scaled nonlinear response.

The low-frequency third order nonlinear dielectric response \( \chi_3 \) and the corresponding scaled response \( a_3 \) have been measured in the electron irradiated relaxor copolymer P(VDF-TrFE)\(^7\) and in the terpolymer P(VDF-TrFE-CFE).\(^{15}\) Specifically, in P(VDF-TrFE) the nonlinear susceptibility \( \chi_3 \) shows a peak near \( 300 \) K, whereas the scaled nonlinear response \( a_3 \) shows a crossover between the paraelectric behavior \( a_3 \sim T \) at high temperatures and a relaxor-type behavior \( a_3 \sim (T - J/k)^{-1} \) near \( 300 \) K.\(^7\) In Fig. 3b, the calculated temperature dependence of \( a_3 \) is displayed in the crossover region \( kT/J \gtrsim 1.25 \) for two values of the random field strength \( \Delta/J^2 \). The inset shows the experimental data for \( a_3 \) in electron irradiated P(VDF-TrFE),\(^7\) which is in qualitative agreement with the theoretical predictions.

The static field-cooled nonlinear dielectric constants have so far not been measured in any relaxor polymer. In inorganic relaxors PMN\(^{18}\) and PLZT,\(^{19}\) experiments suggest that an additional nonlinearity mechanism needs to be considered, namely, the field modulation of the cooperative coupling \( J_0 \) between polar nanoregions, i.e., \( J_0 = J_0(E) \). At present, it is not clear whether a similar mechanism is also relevant in organic relaxor polymers.
IV. GIANT ELECTROSTRICITION

It has recently been shown that relaxor polymers and their all-organic composites exhibit a high value of electrostriction, namely, large mechanical strains can be generated by application of an electric field. Typically, the copper-phthalocyanine (CuPc) oligomers have been dispersed in the electrostrictive copolymer P(VDF-TrFE) matrix, leading to a high net dielectric constant while retaining the elastic modulus of the copolymer as well as its flexibility. It has been suggested that the ultra-high strain response in relaxor polymers is due to the expansion of polar nanoregions under an electric field, coupled with a large difference in the lattice strain between the polar and unipolar phases. Alternatively, an exchange coupling between CuPc and the copolymer matrix could lead to a dramatic enhancement of the electrostriction and dielectric constant in the CuPc-P(VDF-TrFE) composite.21

Here we consider a three dimensional system with Cartesian indices \( \mu, \nu, \cdots = 1, 2, 3 \). The electrostrictive coefficients \( Q_{\mu\nu\kappa\lambda} \) are defined by the relation

\[
 u_{\mu\nu} = \sum_{\kappa\lambda} Q_{\mu\nu\kappa\lambda} P_{\kappa} P_{\lambda},
\]

where \( u_{\mu\nu} \) is the strain tensor and \( P_{\kappa} \) are components of the dielectric polarization induced by the applied field, i.e.,

\[
 P_{\mu} = \sum_{\nu} \chi_{\mu\nu} E_{\nu},
\]

with \( \chi_{\mu\nu} \) representing the longitudinal field-cooled dielectric susceptibility tensor.

The electrostrictive coefficients can be calculated from the thermodynamic Maxwell relation

\[
 Q_{\mu\nu\kappa\lambda} = -\frac{1}{2} \left( \frac{\partial \chi_{\mu\nu}^{-1}}{\partial p_{\kappa\lambda}} \right)_{P,T},
\]

where \( \chi_{\mu\nu}^{-1} \) are components of the inverse susceptibility tensor and \( p_{\kappa\lambda} \) of the stress tensor. From Eq. (28) we have

\[
 \chi_{\mu\nu}^{-1} = \frac{\partial u_{\mu\nu}}{\partial \delta} \left( \frac{\nu_0}{g^2} \right) \frac{1 - \beta J_0 (1 - q)}{\beta (1 - q)}.
\]

At constant polarization \( P \), the EA order parameter \( q \) is independent of \( J_0 \) according to Eq. (26). The stress dependence of \( \chi_{\mu\nu} \) is expected to arise from the parameters \( J_0 \) and \( g^2/\nu_0 \). In the following we will limit ourselves to the case of hydrostatic pressure, where \( p_{\mu\nu} = -p \delta_{\mu\nu} \). At high temperatures, the static dielectric constant \( \epsilon_s \) behaves asymptotically as \( \epsilon_s \sim C/(T - T_0) \), where \( T_0 = J_0/k \) plays the role of an effective Curie-Weiss temperature and \( C = g^2/(k \epsilon_0 \nu_0) \) is the corresponding Curie constant. Thus by measuring \( d\epsilon_s/dp \) at high temperatures an estimate for \( dT_0/dp \) and hence for \( dJ_0/dp \) can be obtained.

From Eq. (47) we derive an expression for the hydrostatic electrostriction constant \( Q_h = Q_{33} + 2Q_{13}^{-1} \):

\[
 Q_h = -\frac{1}{2} \left( k \frac{v_0}{g^2} \right) \frac{dT_0}{dp} + \frac{1}{2 \nu_0 \epsilon_0} \left( \frac{dv_0}{dp} - \frac{2 d\nu_0}{d\epsilon_0} \right). \tag{48}
\]

The first term is expected to be dominant in inorganic relaxors of PMN type, where \( dT_0/dp < 0 \) and \( Q_h > 0 \). In electroactive polymers, such as P(VDF-TrFE), however, we have \( Q_h < 0 \), and the pressure dependence of the parameters \( \nu_0 \) and \( g \) must obviously be considered. We assume that \( dv_0/dp < 0 \), i.e., \( \nu_0^{-1} dv_0/dp \approx -1/B \), where \( B \) is the bulk modulus. Adopting the value \( B \approx 0.8 \times 10^9 \text{ N/m}^2 \) as well as \( \epsilon_s \approx 25 \) for 60 Mrad irradiated conventional electrostrictive polymer P(VDF-TrFE) at room temperature, we can estimate the contribution of the second term in Eq. (48) to be of the order
\( Q_h \sim -2.8 \text{ m}^4/\text{C}^2 \). A comparison with the experimental value\(^{23} \) \( Q_h = -6 \text{ m}^4/\text{C}^2 \) suggests that the contribution of the last term in Eq. (48) should also be included, however, there is no estimate of the \( dq/dp \) available at this time. The above value of \( Q_h \) is roughly two orders of magnitude larger than in inorganic relaxors,\(^{25} \) and \( Q_h \) is hence referred to as ”giant electrostriction”.

V. CONCLUSIONS

Using the experimentally established analogy between the dielectric properties of disordered organic ferroelectric polymers and of inorganic relaxor ferroelectrics, a semi-microscopic static Spherical Random Bond–Random Field model of relaxor polymers has been formulated. The main assumption of the model is the existence of polar nanoregions of varying sizes, which are formed by breaking up the ferroelectric layered structure by either electron irradiation of ferroelectric copolymers, as in the case of P(VDF-TrFE), or by introducing compositional disorder as in the terpolymer P(VDF-TrFE-CFE). In the corresponding statistical ensemble, the polarization of a nanoregion is represented by a vector field embedded in a \( m \)-dimensional amorphous medium. The polar nanoregions are coupled through infinitely ranged spin glass-type interactions and are furthermore subject to local random fields. By requiring that the second moment of the distribution of dipole moments must have a fixed value, a spherical condition on the vector fields is imposed. The model has the advantage of being exactly solvable, and the general solution for an arbitrary direction of the electric field has been obtained.

The main differences between the present model and the SRBRF model of inorganic relaxors are in the physical character of polar nanoregions, the nature of the interactions between them, and the origin of the random fields. Formally, the two models are equivalent, however, the values of the physical parameters characterizing the model can vary to a significant degree. For example, relaxor polymers are usually softer than the inorganic systems and thus have a greater value of compressibility, which strongly affects the hydrostatic electrostriction constant.

The calculated temperature dependence of the static linear dielectric susceptibility agrees with the experimental values in P(VDF-TrFE) and P(VDF-TrFE-CFE) obtained previously. The parameters of the model and the corresponding Edwards-Anderson order parameter have been determined. The calculated third-order nonlinear susceptibility predicts a crossover between paraelectric behavior at high temperatures and a relaxor-like behavior near the freezing temperature, in qualitative agreement with experiments.

The model also explains the phenomenon of giant electrostriction in composites based on relaxor polymers. It can be shown that there are two competing mechanisms contributing to this effect, namely, the stress dependence of the average coupling parameter on the one hand, and the compressibility and the stress dependence of the average dipole moment on the other. The first mechanism predicts a positive value of the hydrostatic electrostrictive coefficient \( Q_h \) and is expected to be dominant in inorganic relaxors. In relaxor polymers, however, due to the large value of compressibility, the second mechanism is estimated to be mainly responsible for the giant electrostriction effect and leads to a negative value of \( Q_h \), in agreement with experiments in irradiated P(VDF-TrFE).

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