BZT: A Soft Pseudospin Glass

David Sherrington[*]

*Rudolf Peierls Centre for Theoretical Physics, University of Oxford, 1 Keble Road, Oxford OX1 3NP,
United Kingdom and Santa Fe Institute, 1399 Hyde Park Road, Santa Fe, New Mexico 87501, USA*
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In an attempt to understand the origin of relaxor ferroelectricity, it is shown that interesting behavior of the onset of nonergodicity and of precursor nanodomains, found in first-principles simulations of the relaxor alloy $Ba(Zr_{1-x}Ti_x)O_3$, can easily be understood within a simple mapping to a soft pseudospin glass.

For several years, there has been much interest in relaxor ferroelectric alloys based on the the generic pure ionic perovskite form ABO_3, where A, B, and O have charges $+2$, $+4$, and -2, but with the single B-type ion replaced by random mixtures of B' and B'' [1–3]. They exhibit (i) frequency-dependent peaks in their dielectric susceptibilities as a function of temperature but without any macroscopic polarization in the absence of applied fields and (ii) higher-temperature manifestations of nanoscale polar domains [4]. They have proven to be of significant application value, but there is no universally accepted understanding of the origin of their behavior. The present objective is to provide such an understanding within the context of a recently recognized system, employing only minimal modeling and simple mappings and without the need to posit *a priori* random bonds or random fields.

The originally discovered [5] and most studied relaxor is $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN). It exhibits the features mentioned above, as well as nonergodicity [6,7] beneath a temperature comparable with that of the finite-frequency susceptibility peaks. However, it is complicated by the fact that Mg and Nb are not isovalent, giving rise to perturbing extra charges and hence random fields. By contrast, in $Ba(Zr_{1-x}Ti_x)O_3$ (BZT) Zr and Ti are isovalent, of charge $+4$. Yet, it still exhibits characteristic relaxor features [8–10] for a range of relative (Zr:Ti) concentrations.

A recent first-principles and Monte Carlo computer simulation study of BZT [11] has demonstrated an ergodicity-breaking phase transition at which a separation sets in between dielectric susceptibilities measured under different protocols and has also exhibited nanodomains above this transition temperature. This communication provides a physical explanation of this transition as the onset of a soft spin-glass-like state, extends the analogy to explain the more general phase structure of BZT, and demonstrates an expected origin of the observed nanodomains.

$BaZrO_3$ and $BaTiO_3$ are ABO_3 ionic crystals with positive charges on the Ba, Zr, and Ti ions and negative charges on the O ions. Their equilibrium structures correspond to minimizing their free energies under the resultant competing (spatially frustrated) interactions. At high temperatures

both have simple perovskite structures, but at low temperature $BaTiO_3$ transforms to a ferroelectric through spontaneous coherent displacement of the Ti ions; $BaZrO_3$ remains paraelectric as the temperature is lowered. The particular current interest is in alloys in which the B sites are occupied randomly by Zr or Ti.

Akbarzadeh *et al.* [11] studied the alloy system with equal concentrations of Zr and Ti, allowing for displacements of all the ions (in a finite-size simulation) and using parameters obtained from first-principles computer modeling of small cells. They examined the susceptibilities measured (i) by directly observing the polarization when cooled in a small applied field and (ii) from the correlation function in the absence of an applied field, using the conventional equilibrium statistical physics relationship between response and correlation. These measurements increased with reducing temperature and roughly coincided above a characteristic temperature T_f but started to diverge significantly from one another at this temperature, with the directly evaluated susceptibility exhibiting a plateau beneath it while that determined from the correlations decreased, giving a cusp at T_f. This is precisely what is expected from mapping to a pseudospin glass.

As noted and utilized in Ref. [11], a crucial difference between systems with Zr or Ti at a B site lies in the strength of the effective local restoring forces associated with displacements of the ions from their positions in the pure matrix; these are weak for Ti, permitting the low-temperature ferroelectric distortion observed in $BaTiO_3$, whereas in $BaZrO_3$ the Zr restoring force is much stronger and prevents macroscopic global distortion even to zero temperature.

Akbarzadeh *et al.* [12] modeled the alloy in terms of local mode variables centered on B sites, including averaged intersite interaction terms, simple local restoring-force terms of strengths corresponding to the appropriate local B-site occupation, and associated random fields and random strains. However, they found that their results are essentially unaffected by the random-field and random-strain terms, and hence these will be ignored from the outset here. For conceptual purposes, the modeling can

be simplified further by absorbing the effects of the Ba and O ions into an effective system involving only the *B*-site ions. Ignoring any local anisotropy for illustrative simplicity, one is then left with a model characterized by an effective Hamiltonian

$$H = \sum_i \{\kappa_i |\mathbf{u_i}|^2 + \lambda_i |\mathbf{u_i}|^4\} + \sum_{ij} H_{\text{int}}^{\text{avg}}(\mathbf{u}_i, \mathbf{u}_j, \mathbf{R}_{ij}), \quad (1)$$

where the sites $\{i\}$ are occupied randomly by Ti or Zr according to the admixture concentration, with corresponding κ and λ. H_{int} represents interactions between $\{\mathbf{u}\}$ at different sites; the superscript {avg} indicates that, as in Ref. [11], the effects of the randomness are averaged and details of quenched randomness in H_{int} are ignored. The zero-temperature phase structure is given by minimizing H with respect to the $\{\mathbf{u_i}\}$.

Considering first a pure system, the sign of κ determines whether this Hamiltonian can, in principle, exhibit displacive or order-disorder transitions, with positive κ being displacive and the true order-disorder limit corresponding to strongly negative κ, in each case with λ positive. Within mean-field theory, in the order-disorder case there will always be a transition to an ordered phase as the temperature is lowered from the high-temperature paramagnetic phase, whereas in the displacive case a minimal strength of bootstrapping binding energy gain from H_{int}, through self-consistent displacements, is needed to overcome the local penalty from the κ term. For BaTiO$_3$, κ^{Ti} is small enough to permit ferroelastic, and hence ferroelectric, order being favored in this case [13]. By contrast, κ^{Zr} is too large for self-consistent displacive order and only paraelectricity $\{\mathbf{u}_i = \mathbf{0}\}$ is possible at all temperatures for BaZrO$_3$.

Turning now to the alloy and noting that the large κ^{Zr} implies that all the sites $\{i\}$ occupied by Zr atoms have $\{\mathbf{u}_i = \mathbf{0}\}$ and hence may be ignored, one is left with the effective Hamiltonian

$$H_{\text{eff}} = \sum_{i(\text{Ti})} \{\kappa^{\text{Ti}} |\mathbf{u}_i|^2 + \lambda^{\text{Ti}} |\mathbf{u}_i|^\mathbf{4}\} + \sum_{ij(\text{Ti})} H_{\text{int}}(\mathbf{u}_i, \mathbf{u}_j, \mathbf{R}_{ij}), \quad (2)$$

with sums now restricted to *B* sites occupied by Ti ions.

The fact that experimentally the low-temperature state of BaTiO$_3$ is ferroelectric shows that the dominant interaction in H_{int} is ferroelectric. However, there are both ferroelectric and antiferroelectric contributions at different separations [14,15].

This model is now recognizable as a soft pseudospin analog of canonical experimental spin-glass systems [16], such as Au$_{1-x}$Fe$_x$ or Eu$_x$Sr$_{(1-x)}$S, whose Hamiltonians may be written as

$$H = -\sum_{ij(\text{Mag})} J(\mathbf{R}_{ij}) \mathbf{S}_i \cdot \mathbf{S}_j, \quad (3)$$

where the $\mathbf{S}_i$ are hard spins [17], $J(\mathbf{R})$ is a translationally invariant but spatially frustrated exchange interaction, and the sum is restricted to sites occupied by magnetic

atoms [21]. For large x, high concentrations of magnetic atoms, these systems are periodically magnetically ordered, but for lower concentrations of magnetic atoms a nonperiodic, nonergodic, but still cooperative spin-glass phase results [22].

With this identification, it becomes clear that within some intermediate concentration range $x_c > x > x_p$ of Ti on the *B* sites in the alloy BaZr$_{(1-x)}$Ti$_x$O$_3$, there will be a pseudospin-glass transition at a critical temperature $T_g(x)$, marking the onset of nonergodicity and preparation dependence, the zero-field-cooled (ZFC) susceptibility peaking and the field-cooled (FC) susceptibility "freezing" [24]. Given that the FC susceptibility essentially measures a full Gibbs average over all pure states while the ZFC essentially measures the susceptibility restricted to a single pure macrostate [25,26], this explains the corresponding observations of Akbarzadeh *et al.* [11], with their T_f identified as T_g, their $x = 0.5$ being within this relaxor or pseudospin-glass concentration range [8], and FC and ZFC corresponding to the two different susceptibility measurements they made [27].

For $x > x_c$ the transition is to ferroelectricity at a $T_c(x)$ that increases with x, reaching the pure BaTiO$_3$ value at $x = 1$. As x is decreased below x_c, T_g is also expected to decrease with x, but initially less quickly, until a further critical concentration x_p, beyond which only paraelectricity exists as a thermodynamic phase; thus, we have the sequence with increasing Ti concentration (x) paraelectric $\rightarrow$ relaxor $\rightarrow$ ferroelectric for $0 \le x_p \le x_c \le 1$ [28], in accord with experiments [8,9].

As noted earlier, the best known signature of relaxors is the feature of frequency-dependent peaks in the susceptibility as a function of temperature, with the peak temperature increasing with increasing frequency [5,30]. It is observed experimentally for BZT [8–10]. A similar frequency-dependent peaking is also a well-known feature of spin glasses; see, e.g., Refs. [31,32]. In spin glasses, it is also well known that the peak temperature tends in the zero-frequency limit to that of the onset of nonergodicity as measured by deviation of the FC and ZFC susceptibilities. Hence, the mapping above would also lead one to expect this famous relaxor signature.

There has been much interest in the precursor observation (or interpretation) of "nanodomains" in relaxors, and these were also seen in the simulations of Akbarzadeh *et al.* [11], as well as in experiments [8]. They, too, can be understood from the above "induced-moment" soft pseudospin modeling, as corresponding to longish-lived "local moments" on statistically occurring clusters of Ti ions. To see this, H and H_{eff} may be reinterpreted as Ginzburg-Landau free energies with their parameters renormalized as a function of temperature. The effective "local nanodomains" are given by minimization with respect to the $\mathbf{u_i}$, yielding values given in simple mean-field theory by the self-consistent solution of

$$\tilde{\kappa}_i \mathbf{u_i} + 2\tilde{\lambda}_i \mathbf{u_i}|\mathbf{u_i}|^2 + \sum_j \partial\tilde{H}_{\text{int}}(\mathbf{u}_i, \mathbf{u}_j, \mathbf{R}_{ij})/\partial\mathbf{u_i} = 0, \quad (4)$$

with all the terms effectively temperature renormalized but with the most important conceptual feature that the $\{\tilde{\kappa}\}$ increase with increasing temperature relative to the interaction term. This equation is closely analogous to that for a mean-field theory of cluster-moment formation in transition metal alloys introduced in Ref. [20] and, similarly to that case, the formation of local nanodomains is relatable to an Anderson localization model [33,34].

Simplifying for illustrative purposes to a simple scalar analog of Eq. (4), we consider

$$\tilde{\kappa}_i u_i + 2\tilde{\lambda}_i u_i^3 - \sum_j \tilde{J}_{ij} u_j = 0 \quad (5)$$

and compare it with an Anderson-type eigenequation

$$\tilde{\kappa}_i \phi_i - \sum_j \tilde{J}_{ij} \phi_j = E\phi_i. \quad (6)$$

Nonzero u solutions to Eq. (5) correspond to solutions of Eq. (6) with $E < 0$. However, solutions to Eq. (6) with quenched κ disorder can be either localized or extended: localized states at the extremities of the band of eigenstates separated from a region of extended states by lower $E_{m_L}(x, T)$ and upper $E_{m_U}(x, T)$ "mobility edges." Note that the density of states and the mobility edges are temperature dependent through the renormalization of the $\tilde{\lambda}$ and $\tilde{J}$, decreasing with decreasing T. Thus, the onset of mean-field "cluster moments," observable on finite time scales as nanodomains, is given by the onset of solutions $E \leq 0$ to Eq. (6), while the true thermodynamic transition, which requires an extended state, occurs only when the mobility edge $E_{m_L}(x, T)$ becomes zero.

While in the usual electronic Anderson situation the $\{\tilde{J}_{ij}\} \geq 0$ so that extended states are ferroelectric, in the present frustrated case with $\{\tilde{J}_{ij}\}$ of both signs the extended states can also be spin-glass-like for finite x, without any periodic order or macroscopic orientation. This leads to the expectation of a true thermodynamic ferroelectric phase transition as temperature is lowered at high x, passing over to transition to a spin-glass phase as x is reduced beyond a critical x_c, and eventually, beneath x_p, exhibiting paraelectric behavior only, but also with higher-temperature nonequilibrium nanodomain precursors for all $0 < x < 1$, the size of the precursor region reducing to zero as the pure limits are approached [35].

We might also note that in the Anderson analogy above, quasifrozen nanoregions need not necessarily be internally ferroelectric and indeed deviations from collinearity were observed in the simulations of Ref. [11].

The concept of polar nanoregions (PNRs) interacting among themselves and eventually freezing cooperatively macroscopically can, in principle, be given substance by defining nanomoments in terms of negative eigenvalue eigenfunctions of Eq. (6), introducing them into an expanded partition function by adding them as variables, with delta functions ensuring their identification, and then integrating out the original variables [38].

Note that neither random fields nor random interactions were posited above [39,40]. However, H_{eff} can be mapped into a random-bond model

$$H_{\text{eff}}^{\text{EA}} = \sum_l \kappa u_i^2 + \lambda u_i^4 + \sum_{lm} J_{lm} u_l u_m, \quad (7)$$

where now the l are relabeled Ti sites, κ and λ are site independent, and all the randomness is in the $\{J_{lm}\}$. In a precise mapping, the $\{J_{lm}\}$ code the spatial distribution of Ti ions. Following the conceptualization introduced by Edwards and Anderson [41] that the important physics of spin glasses is maintained as long as one retains frustration and quenched disorder, one would expect that a further assumption of independent randomness of $\{J_{lm}\}$ would maintain the crucial physics. However, to allow for the transition between ferroelectric and relaxor phases with x, the $\{J_{lm}\}$ distribution should have a tunable (x-dependent) mean [42,43].

These analogies also suggest that, within the relevant intermediate range of x, BZT should exhibit other behaviors corresponding to those known for spin glasses, not only at the onset (where the susceptibility peaks) but also within the relaxor phase. Similar behavior and explanation might also be anticipated in other isovalent alloys of a frustrated displacive (or mixed displacive and weak order-disorder) ferroelectric (or antiferroelectric) and an appropriate paraelectric partner [44]. The corresponding analogy between hard dipolar (strong order-disorder) and other orientational glasses and hard spin glasses has long been recognized [45]; for reviews, see Refs. [46,47].

The modeling of Eq. (4) is of course only mean field and so misses both thermal fluctuation effects and dynamics. However, a similar extended simple modeling based on disorder only in local restoring terms and a spatially frustrated periodic interaction could in principle be extended to treat these.

Finally, it should be emphasized that the discussion above is minimal, a skeleton modeling to expose the physical core. More "flesh" is needed for the whole body.

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   *D.Sherrington1@physics.ox.ac.uk
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