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Simulating the radiofrequency dielectric response of relaxor ferroelectrics: Combination of Coarse-Grained Hamiltonians and Kinetic Monte Carlo

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The radiofrequency dielectric response of the lead-free $\text{Ba}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ relaxor ferroelectric is simulated using a coarse-grained Hamiltonian. This concept, taken from Real-Space Renormalization Group theories, allows depicting the collective behavior of correlated local modes gathered in blocks. Free-energy barriers for their thermally activated collective hopping are deduced from this *ab-initio*-based approach, and used as input data of Kinetic Monte Carlo simulations. The resulting numerical scheme allows to simulate the dielectric response for external field frequencies ranging from the kHz up to a few tens of MHz for the first time, and to, e.g., demonstrate that local (electric or elastic) random fields lead to the dielectric relaxation in the radiofrequency range that has been observed in relaxors.

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Relaxors with perovskite structure form an important family of functional materials that exhibit intriguing dielectric properties [1, 2]: the real part of the frequency-dependent dielectric permittivity has a maximum with temperature, at T_{max} , while the system remains macroscopically paraelectric down to the lowest temperature, and T_{max} depends on the frequency of the applied electric field, a phenomenon called *dielectric relaxation*. Different suggestions have been proposed to explain these macroscopic properties, such as non-local (electric or elastic) random fields (RFs) [3] (electric or elastic fields *on site i* depending on the chemical disorder *surrounding i*), and the possible existence, and interplay, of polar nanoregions (PNRs), i.e. polar instabilities that correlate the elementary dipoles on a few lattice constants. The location and properties of these PNRs would be dependent on the local chemical disorder, that relaxors can exhibit on one of their sublattices [4].

The dynamics of the electric dipoles of such structures is believed to be associated with characteristic times being much larger than typical atomic times, and being temperature-dependent (as a result of thermal activation). These large time scales are responsible for the frequency-dependence of the dielectric permittivity in the radiofrequency domain (from the kHz up to several tens of MHz). Recently, microscopic description of relaxors, based on model Hamiltonians derived from first-principles coupled to Monte Carlo (MC) or Molecular Dynamics (MD) simulations, have provided precious information about the effect of RFs on relaxor properties and the nature of these PNRs [5–12]. In heterovalent relaxors such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) [13–16], the PNRs are suggested to arise from complex phenomena including strong non-local electric RFs [17, 18]. By contrast, in homovalent relaxors such as $\text{Ba}(\text{Zr,Ti})\text{O}_3$ (BZT), Ref. [9] numerically found that PNRs appear in regions where the chemical species driving the polar instability (Ti) is more abundant, i.e., it is the *local* RFs arising from the difference in polarizability between Ti and Zr ions that induce relaxor behavior, while non-local electric and elastic RFs have a rather negligible effect. Note that local RFs can lead to very long relaxation times in disordered magnets [19], which may also be the case for relaxors [15].

In order to gain a further deeper understanding of relaxor ferroelectrics, it is highly desired to have numerical schemes able to simulate the most striking characteristics of relaxors, i.e. the radiofrequency dielectric relaxation. However, to the best of our knowledge, such schemes do not exist. One reason behind this paucity is that MD simulations are limited to a few nanoseconds, and thus cannot give access to the time scales required to mimic the radiofrequency dielectric response of relaxors. However, the Kinetic Monte Carlo (KMC) method, that we recently applied to simulate the radiofrequency dielectric response of Li-doped KTaO_3 (KLT) [20], is able to reproduce such time scales. Nevertheless, in KLT, the elementary processes driving the dielectric response involve few degrees of freedom (hoppings of individual Li impurities), with rather temperature-independent energy barriers [20], two assumptions clearly not obeyed in relaxor ferroelectrics as, e.g. evidenced by the fact that PNRs do not exist anymore above the Burns temperature, and that the processes responsible for the dielectric response involve the *collective motion* of several microscopic degrees of freedom, since a PNR should extend over several unit cells.

In this Letter, we report the development, and results, of a novel numerical approach able to simulate the radiofre-

quency dielectric response of relaxors. It is based on a Renormalization Group (RG) transformation in real space [21], combined with KMC. In particular, this new scheme allows describing radiofrequency dielectric relaxation in BZT compatible with the Vogel-Fulcher law [22, 23], therefore demonstrating the power and promise of such methodology, and that non-local electric or elastic RFs are not absolute requirements to generate relaxor behaviors. In other words, local RFs are enough to induce relaxor properties.

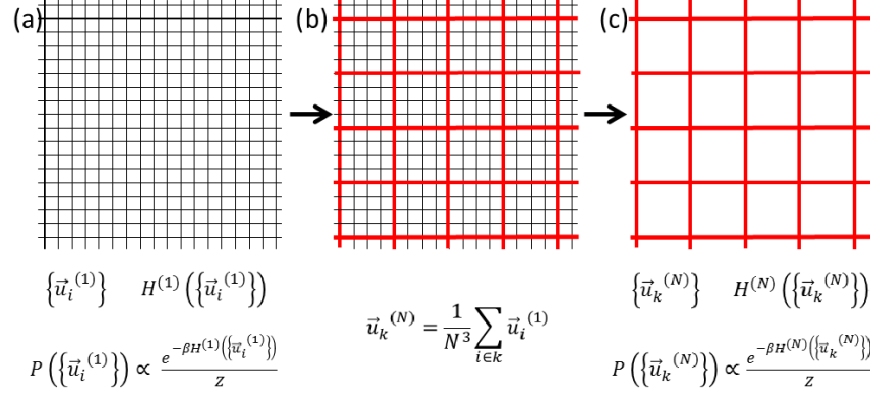


FIG. 1: Coarse-graining process. (a): real system; the microscopic local modes interact through the microscopic Hamiltonian $H^{(1)}$; (b): the unit cells are gathered by blocks, and a block variable is defined in each block, as the mean local mode; (c): the coarse-grained Hamiltonian $H^{(N)}$ is constructed, preserving the partition function and the macroscopic observables. In case a (resp. c), P denotes the density of probability of the microscopic state $\{\mathbf{u}_i^{(1)}\}$ (resp. constrained-block state $\{\mathbf{u}_k^{(N)}\}$).

We denote by $\{\mathbf{u}_i^{(1)}\}$ the set of the microscopic local modes, and associate to each elementary unit cell i a real number $x_i^{(1)}$ characterizing its composition (0 for Zr, 1 for Ti). The $\{x_i^{(1)}\}$ play the role of a set of parameters (not variables) of the microscopic Hamiltonian [24–27], for which we use the following form:

$$H^{(1)}(\{\mathbf{u}_i^{(1)}\}; \{x_i^{(1)}\}) = \underbrace{\sum_i H_{loc}^{(1)}(\mathbf{u}_i^{(1)}; x_i^{(1)})}_{\text{local random fields}} + \frac{1}{2} \sum_{\substack{i,j,\alpha,\beta \\ (i \neq j)}} \bar{C}_{SR,\alpha\beta}^{(1)}(i,j) u_{i\alpha}^{(1)} u_{j\beta}^{(1)} + \frac{1}{2} \sum_{\substack{i,j,\alpha,\beta \\ (i \neq j)}} \bar{C}_{LR,\alpha\beta}^{(1)}(i,j) u_{i\alpha}^{(1)} u_{j\beta}^{(1)}, \quad (1)$$

$\bar{C}_{SR}^{(1)}(i,j)$ and $\bar{C}_{LR}^{(1)}(i,j)$ being the matrices describing the short-range (SR) and dipole-dipole (LR) interaction between local modes in cells i and j . In such form, the chemical disorder contributes only to the *local part*, characterizing *local* RFs arising from the polarizability difference between Ti and Zr ions. Refs. [9, 28] have shown that such RFs are sufficient to reproduce several properties of BZT such as the temperature evolution of the static and hyper frequency dielectric permittivity, and the existence of small PNRs – which contrasts with heterovalent relaxors, for which *non-local* RFs (contributions of the chemical disorder from neighboring cells and related to interaction terms of $H^{(1)}$), are large and play a fundamental role in the dielectric properties [17]. We will show here, by neglecting non-local RFs, that local RFs in BZT can generate a radiofrequency dielectric relaxation by themselves.

Our approach consists in coarse-graining the system (Fig. 1), i.e. dividing it in $N \times N \times N$ cubic blocks, and defining, in each block k , a "block variable" (or local order parameter) as the mean local mode over the block: $\mathbf{u}_k^{(N)} = \frac{1}{N^3} \sum_{i \in k} \mathbf{u}_i^{(1)}$. We also define a local composition in each block, as $x_k^{(N)} = \frac{1}{N^3} \sum_{i \in k} x_i^{(1)}$, which takes fractional values $\in [0;1]$, allowing to define Ti-rich blocks ($x \rightarrow 1$) and Ti-poor ones ($x \rightarrow 0$). The set of block variables $\{\mathbf{u}_k^{(N)}\}$ is used to define an *incomplete partition function* [29, 30],

$$\tilde{Z}^{(N)}(\{\mathbf{u}_k^{(N)}\}; \{x_i^{(1)}\}) = C \int \dots \int \left\{ \prod_{\text{blocks } k} \delta(\sum_{i \in k} \mathbf{u}_i^{(1)} - N^3 \mathbf{u}_k^{(N)}) \right\} e^{-\beta H^{(1)}(\{\mathbf{u}_i^{(1)}\}; \{x_i^{(1)}\})} \left\{ \prod_i d\mathbf{u}_i^{(1)} \right\}, \quad (2)$$

by summing over all the microscopic states $\{\mathbf{u}_i^{(1)}\}$ such that $\forall k, \sum_{i \in k} \mathbf{u}_i^{(1)} = N^3 \mathbf{u}_k^{(N)}$. The $\{\mathbf{u}_k^{(N)}\}$ are thus variables of $\tilde{Z}^{(N)}$. The coarse-grained Hamiltonian [29] $H^{(N)}$ is then defined, up to an additive constant, as $H^{(N)}(\{\mathbf{u}_k^{(N)}\}; \{x_i^{(1)}\}) = -k_B T \ln \tilde{Z}^{(N)}(\{\mathbf{u}_k^{(N)}\}; \{x_i^{(1)}\})$. It has the physical meaning of an incomplete free energy, and depends on temperature (at contrast with $H^{(1)}$).

The system of the block variables interacting through $H^{(N)}$ has, by construction, the same partition function as the initial system (up to a multiplicative constant), and thus the same macroscopic observables. To calculate this coarse-grained Hamiltonian, we use the following formula [30–32]:

$$\frac{\partial H^{(N)}}{\partial \mathbf{u}_{\mathbf{n}}^{(N)}}(\{\mathbf{u}_{\mathbf{k}}^{(N)}\}; \{x_i^{(1)}\}) = - \langle \sum_{i \in n} \mathbf{f}_i \rangle (\{\mathbf{u}_{\mathbf{k}}^{(N)}\}; \{x_i^{(1)}\}), \quad (3)$$

where $\langle \dots \rangle (\{\mathbf{u}_{\mathbf{k}}^{(N)}\})$ denotes thermal conditional average [32] evaluated at fixed $\{\mathbf{u}_{\mathbf{k}}^{(N)}\}$ (see Suppl. Info). $\mathbf{f}_i = -\frac{\partial H^{(1)}}{\partial \mathbf{u}_i^{(1)}}$ is the force on local mode i . $H^{(N)}$ is a *potential of mean force*, as employed in chemical physics to study chemical reactions along a reaction coordinate [32–35]. Here, the "reaction coordinate" is multidimensional and consists in the set of all the block variables, $\{\mathbf{u}_{\mathbf{k}}^{(N)}\}$.

This coarse-grained Hamiltonian can be approximated by a form identical to that of $H^{(1)}$, i.e. $H^{(N)}(\{\mathbf{u}_{\mathbf{k}}^{(N)}\}; \{x_k^{(N)}\})$, provided some hypothesis are fulfilled. The most important is that the block size Na_0 remains lower than the correlation length $\xi(T)$, i.e. the local modes must be correlated together all over the block [36, 37]:

$$H^{(N)}(\{\mathbf{u}_{\mathbf{k}}^{(N)}\}; \{x_k^{(N)}\}) \approx \sum_n H_{loc}^{(N)}(\mathbf{u}_n^{(N)}; x_n^{(N)}) + \frac{1}{2} \sum_{\substack{n, n', \alpha, \beta \\ (n \neq n')}} \bar{C}_{SR, \alpha\beta}^{(N)}(n, n') u_{n\alpha}^{(N)} u_{n'\beta}^{(N)} + \frac{1}{2} \sum_{\substack{n, n', \alpha, \beta \\ (n \neq n')}} \bar{C}_{LR, \alpha\beta}^{(N)}(n, n') u_{n\alpha}^{(N)} u_{n'\beta}^{(N)} \quad (4)$$

The renormalized coefficients $\bar{C}_{SR}^{(N)}(n, n')$ and $\bar{C}_{LR}^{(N)}(n, n')$ describe SR and LR interactions between blocks n and n' , while the local free energy $H_{loc}^{(N)}(\mathbf{u}; x)$ describes locally the thermodynamics of a block having as local order parameter \mathbf{u} , and chemical composition x . The condition $Na_0 < \xi(T)$ ensures that the blocks contain at most one PNR. At given temperature, several values of N are thus possible, but the most convenient is $Na_0 \sim \xi(T)$. MC simulations using $H^{(1)}$ reveal that at low temperature, collective behavior of the local modes is observed within Ti-rich blocks of typical size [9] $2 \times 2 \times 2$: $N=2$ is the block size used here. This may appear as small, but within Ti-rich blocks, collective motion of 6-8 local modes is sufficient to generate a radiofrequency dielectric response, as we will see.

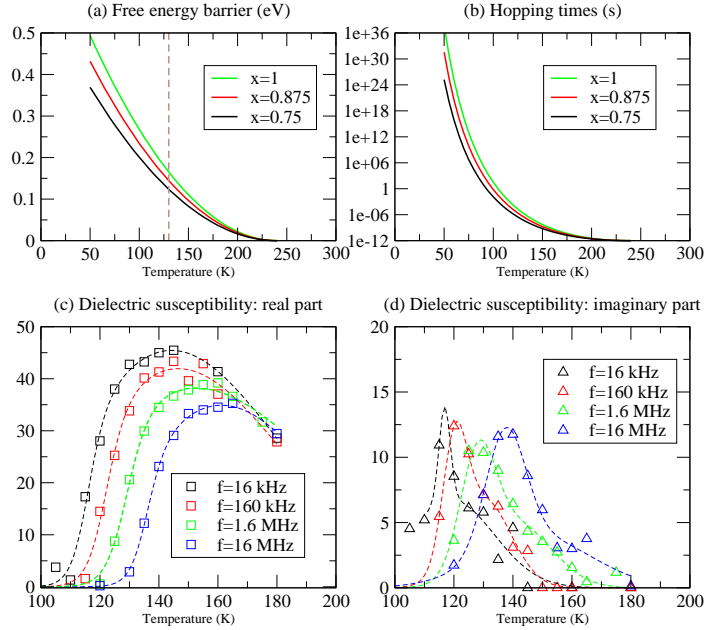


FIG. 2: Upper panel: local free energy barriers $\Delta F_{loc}(T; x)$ (eV), and hopping times, $\tau(T; x) = \tau_0 e^{+\Delta F_{loc}(T; x)/k_B T}$ (s), as a function of temperature for the three Ti-richest blocks ($x=1, 0.875$ and 0.75). Lower panel: temperature evolution of χ' and χ'' . In panel c, the lines correspond to a fit according to Ref. [38]. In panel d, the lines are guides for the eyes.

$\bar{C}_{SR}^{(N)}$ and $\bar{C}_{LR}^{(N)}$ are computed directly from the coefficients of $H^{(1)}$ (see Suppl. Info.). Ideally, the local free energy $H_{loc}^{(N)}$ could be obtained from constrained MD simulations [30, 31, 37, 39]. Here, for simplicity, we use the following

phenomenological form, expressed as an energy *per 5-atom cell*: $H_{loc}^{(N)}(\mathbf{u}; x) - H_{loc}^{(N)}(\mathbf{0}; x) = x[H_{loc,Ti}^{(N)}(\frac{\mathbf{u}}{x}) - H_{loc,Ti}^{(N)}(\mathbf{0})]$, with $H_{loc,Ti}^{(N)}(\mathbf{u}) - H_{loc,Ti}^{(N)}(\mathbf{0}) = a'_1(T - T_0)(u_X^2 + u_Y^2 + u_Z^2) + a_{11}(u_X^4 + u_Y^4 + u_Z^4)$ the local free energy for a Ti-rich block ($x=1$). Within this form, all the blocks are polar under T_0 , not above. The polar character increases with decreasing T , and with $x \rightarrow 1$. The coefficients are extracted from microscopic MD simulations: $T_0 = 240$ K (the so-called T^* of BZT, according to Ref. 9), $a'_1 = 0.053654$ eV/(Å²·K), and $a_{11} = 420.8273$ eV/Å⁴. There are 8 local minima along the $\langle 111 \rangle$ directions, and saddle points between a minimum and another are taken as the minima of $H_{loc}^{(N)}$ along $\langle 110 \rangle$. The hopping local free energy barriers $\Delta F_{loc}(T; x)$ thus depend on temperature (Fig. 2a) and on local chemical composition of the block. The associated transition rates are deduced from transition state theory [40, 41], as $r(T; x) = r_0 e^{-\Delta F_{loc}(T; x)/k_B T}$. The corresponding relaxation times $\tau(T; x) = \tau_0 e^{+\Delta F_{loc}(T; x)/k_B T}$ are plotted in Fig. 2b as a function of temperature. Above 240 K, static PNRs do not exist any more, while below ~ 130 K (freezing temperature [9]), the relaxation times increase, tending rapidly but continuously towards a freezing of the polar blocks. The phenomenon of freezing, within this phenomenological description of $H_{loc}^{(N)}$, corresponds to a sharp, but continuous increase of the relaxation times (no divergence at T_f for BZT).

Having the free energy landscape of the $\{\mathbf{u}_k^{(N)}\}$, we can perform a KMC simulation of the dielectric response. A supercell of $12 \times 12 \times 12$ blocks is constructed, starting from a $24 \times 24 \times 24$ supercell of 5-atom cells in which the Ti and Zr are randomly distributed with equal probability. Each polar block n has a local free energy surface depending on T and chemical composition x_n . However, for physical and practical reasons, we do not consider as elementary events the hoppings in *all* the blocks, because Ti-rich blocks may have large free energy barriers, and the poorest ones, very small barriers. Thus, very rare events can coexist with very frequent ones, making the KMC algorithm untractable. Moreover, our phenomenological form for $H_{loc}^{(N)}$ does not stand for Zr-rich blocks, which remain non polar down to zero K [9]. The events kept for the KMC therefore correspond to the hopping times relevant to the radiofrequency dielectric response. This is equivalent to retain only the Ti-richest blocks as polar ($x=1, 0.875$ and 0.75), the other ones being considered as a dielectric medium. The system becomes thus equivalent to a dipole glass [42] embedded in a dielectric matrix, as in KLT, at the exception that the energy barriers depend on temperature and on local chemical composition. and that each block variable has 8 possible local minima along $\langle 111 \rangle$ [9].

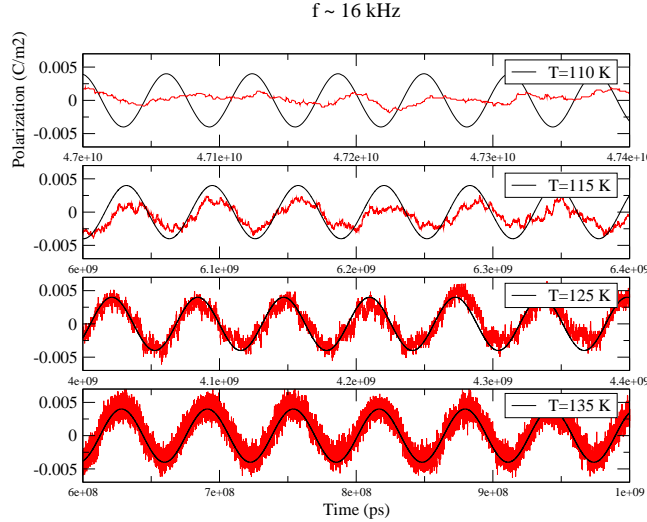


FIG. 3: Example of time evolution of the macroscopic polarization (red curve, in C/m²) under sinusoidal electric field (black curve, amplitude $1.0 \times 10^{+7}$ V/m) of frequency ≈ 16 kHz, for different temperatures.

The radiofrequency dielectric response is obtained by applying a sinusoidal external electric field along \mathbf{e}_x (unit vector along the pseudo-cubic [100] axis): $\mathbf{E}_{ext}(t) = E_0 \cos(\omega t) \mathbf{e}_x$. Each block variable n feels a local field consisting of this external field plus an internal field $\mathbf{E}_{int}(n)$ associated with the (renormalized) SR and LR interactions between blocks: $\mathbf{E}_{loc}(n) = \mathbf{E}_{ext}(t) + \mathbf{E}_{int}(n)$. We assume that $\mathbf{E}_{loc}(n)$ does not modify the position of the transition states (saddle points of $H_{loc}^{(N)}$), but changes the free energy barrier from site k to k' according to $\Delta F_{loc}(T; x) \rightarrow \Delta F_{loc}(T; x) + Z_b^*(\mathbf{u}_k - \mathbf{u}_{k,k'}) \cdot \mathbf{E}_{loc}(n)$, Z_b^* being the block effective charge, \mathbf{u}_k the position of stable site k (among the 8 possible) and $\mathbf{u}_{k,k'}$ that of the transition state from k to k' .

When \mathbf{E}_{ext} is applied, the sites \mathbf{u}_k that are in the same direction as \mathbf{E}_{ext} are stabilized, and the energy barriers towards these sites are lowered with respect to the barriers of the backwards motions. Thus the local order parameters

tend to align along the external field, producing a macroscopic polarization P_X . An example at $f \approx 16$ kHz is shown on Fig. 3. However, this alignment occurs with a delay related to the relaxation time of the block variables, compared to the external field period ($t_e = 2\pi/\omega$), so that $P_X(t) = P_0(\omega)\cos(\omega t + \phi(\omega))$ (assuming linear response). A fit is then performed, providing the amplitude $P_0(\omega)$ and the phase $\phi(\omega)$, from which the real and imaginary parts, χ' and χ'' , of the dielectric susceptibility are obtained, as $\chi' = \frac{P_0(\omega)}{\epsilon_0 E_0} \cos(\phi(\omega))$ and $\chi'' = \frac{P_0(\omega)}{\epsilon_0 E_0} |\sin(\phi(\omega))|$.

Figures 2c and d show the temperature evolution of χ' and χ'' in $\text{Ba}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$, for external field frequencies between 16 kHz and 16 MHz. As in KLT, the dielectric relaxation is well reproduced by the KMC, with a maximum of χ' , $T_{max}(\omega)$ evolving with ω , and the curves $\chi'(T)$ enveloping each other as ω decreases. The temperature T'_{max} of the maximum of χ'' are $< T_{max}$, as experimentally observed [43–45]. The peak positions are in rather good agreement with experiments [43, 45–47]. The values of χ' , however, are \sim one order of magnitude too low compared to experiments [45, 47], which we attribute, as in KLT [20], to the fact that the response of the dielectric matrix is not included, as well as its effect on the PNRs.

At low temperature, the hopping times $\tau(T; x) = \tau_0 e^{+\Delta F_{loc}(T; x)/k_B T}$ are much larger than the period t_e : the block variables have not the time to follow the external field (no dielectric response). As T increases, $\tau(T; x)$ decreases, but the emerging macroscopic polarization exhibits a delay ϕ as long as $\tau(T; x) > t_e$. When $\tau(T; x) \sim t_e$, a *resonance* between the hopping times of the PNRs and the characteristic time of external solicitation yields the maximum of the response: \mathbf{P} and the solicitation \mathbf{E}_{ext} evolve in phase (the block variables have the time to follow the external field). Above T_{max} , the hopping times are so short that the block variables instantaneously, almost adiabatically, adapt their state to the external field: the dielectric response decreases owing to the thermal agitation, that tends to equalize the probabilities of the different minima.

T_{max} therefore naturally depends on ω , and the resonance condition $\tau(T_{max}; x) \sim t_e$, i.e. $f = f_0 e^{-\Delta F_{loc}(T_{max}; x)/k_B T_{max}}$ should provide the relation between T_{max} and the external field frequency f . If there was a single relaxation time (one relaxor entity), with one single hopping barrier U not dependent on T , as in KLT, this would simply provide $f = f_0 e^{-U/k_B T_{max}}$. Here, several relaxation times $\tau(T; x)$ coexist, associated to the existence of blocks with different chemical compositions x and, moreover, interacting with each other (which changes the local barriers). The relation $f(T_{max})$ is thus complex, and mainly controlled by the form of $H_{loc}^{(N)}$. Having in mind that the phenomenological form chosen for $H_{loc}^{(N)}$ directly influences $f(T_{max})$, we can perform a fit of these data (i) on the Arrhenius law, $\ln f = \ln f_0 - \frac{U}{k_B T_{max}}$, (ii) on the Vogel-Fülcher law, $\ln f = \ln f_0 - \frac{U}{k_B (T_{max} - T_f)}$, and (iii) on a relation of the form $\ln f = \ln f_0 - \alpha \frac{(T_{max} - T_1)^2}{T_{max}}$, reflecting the temperature evolution of the free energy barriers in our phenomenological model (Fig. 2a). We find the data compatible with (ii) and (iii), with $T_f = 127.6$ K, $U = 0.019$ eV and $f_0 \sim 1.0 \times 10^{10}$ Hz in case (ii), in reasonable agreement with experiments [43], and $f_0 = 2.5 \times 10^7$ Hz, $\alpha = 1.89753$ and $T_1 = 167.3$ K in case (iii).

Finally, we add that two kinds of relaxation are observed in BZT, the first one in the hyper frequency range, the second one in the radiofrequency range [46, 48]. While the classical MD simulations of Refs. [28, 49] showed that the first relaxation is due to *single* Ti motions, our present method reveals that the second relaxation rather originates from *collective* motions of local modes inside PNRs, demonstrating the complementarity of classical MD (that can mimic the faster individual hoppings, but not the slower collective dynamics in the whole PNRs) and our developed scheme (that can model such latter dynamics, as a result of our block compartments).

In summary, we have developed a methodology to simulate the radiofrequency dielectric response of relaxor materials. It is based on a RG transformation combined with KMC. We have shown that, in BZT, it allows modeling the collective motions of correlated local modes, and reproduces the radiofrequency dielectric relaxation for the first time ever with a potentially fully atomistic-based method. In particular, the local RFs related to the difference in polarizability between Ti and Zr ions are sufficient to explain radiofrequency relaxation, an important step toward a deep understanding of relaxors (non-local electric and elastic RFs are weak in BZT [9], while they play an important role in heterovalent relaxors [17] – implying that they likely contribute to the radiofrequency response of PMN and similar systems). Our approach still needs to be tested on systems with larger correlation lengths (which will be the topic of a future study), for which theoretical difficulties have been pointed out in the past [50, 51]. As a matter of fact, in such systems, it may be more difficult to construct an approximate coarse-grained Hamiltonian as in Eq. 4. We hope that our approach will be applied and/or generalized to many complex materials and phenomena in the future.

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