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LETTER TO THE EDITOR

Intrinsic local modes and heterogeneity in relaxor ferroelectrics

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Abstract

We suggest that ferroelectric relaxor glasses represent an important class of materials in which intrinsic spatial heterogeneity and multiscale dynamics can arise from the formation of local modes due to inherent nonlinearity in the polarizable medium. Specifically, the phenomenology of relaxor ferroelectrics in terms of the spherical random bond–random field (Binc *et al* 1999 *Phys. Rev. Lett.* **83** 424) model is explained microscopically by the formation of discrete breathers embedded in a soft but silent medium, which form in-gap local modes (IGLM) where charge and lattice are intrinsically coupled. Complete mode softening is inhibited by the IGLM and soft elasticity a prerequisite for their existence.

(Some figures in this article are in colour only in the electronic version)

Two fascinating but poorly understood current themes in condensed matter are: (i) the possibility of *intrinsic heterogeneity* in complex electronic materials [2, 3]; and (ii) the localization of energy in nonlinear systems in the form of multi-vibrational bound states (*'intrinsic local modes'* [4, 5]). We propose here that these two phenomena can come together in wide classes of *ferroelectric* materials, where the coupled electron–ion polarizability provides a self-consistent source of strong nonlinearity. Ferroelectric properties are very broadly prevalent in materials from solid state to biology and enjoy major technological applications and potentials. The technologically most important class of ferroelectrics is relaxors [6, 7]. These typically represent solid solutions of perovskites ABO_3 , i.e. $ABB'O_3$ or $AA'BO_3$ or mixtures of both, where one of the pure compounds, e.g. ABO_3 , becomes ferroelectric at a phase transition temperature T_c . The characteristics of relaxors are a strong frequency dependence of the dielectric maximum, the absence of macroscopic polarization and the occurrence of a diffuse phase transition (DFT). Since experimental evidence for

short range chemical order on a nanoscale level has been observed [2, 8], it has been proposed that the scale of inhomogeneity determines the relaxor state [2], and dynamical fluctuations of local dipole moments take place within the chemical clusters [9]. Even though it has been recognized early on that relaxors are related to dipolar glasses, the nature of the DFT has remained controversial [9–12]. A consistent phenomenological description has been given recently [1] by postulating that relaxor dynamics can be related to an Edwards–Anderson order parameter q_{EA} corresponding to a dimensionless cluster dipole moment. Due to the variations in the cluster dipole moment orientations a spherical constraint has been postulated for them with infinitely ranged, randomly frustrated interactions [13, 14]. The model corresponds then to a spherical random bond–random field (SRBRF) with distinctly different properties as compared to dipolar [13] or quadrupolar glasses [15, 16].

Here new, however related, ideas on the origin of relaxor behaviour are presented, but on a microscopic level, where the random distribution of polar ABO_3 clusters in a soft but silent $AB'O_3$ matrix is treated as *impurity* or *defect* induced heterogeneity. The inherent anharmonicity of relaxors (from the strong ion–charge coupling) then admits for the formation of intrinsic local modes (ILMs) [4] with discrete breather type character [17] whose length scale is determined by the number of *defect* ions, i.e. the chemical cluster size. The interaction between these objects is possible through phase fluctuations and is strongly dependent on their density in the soft host lattice [17]. In contrast to various previous ideas on the existence and stability regime of ILMs, we use here a much richer model, since electronic hybridization effects are explicitly incorporated. These have been shown to be of vital importance to perovskite ferroelectrics, since the transition metal d–oxygen ion p states interact through phonons, and small charge transfers between them trigger the soft mode behaviour of displacive type ferroelectric ABO_3 systems [18–21]. The p–d hybridization effects are effectively incorporated in a nonlinear shell model representation where a local anharmonic potential in the relative core shell displacement coordinate is included, which defines an integrated dipole moment [18, 19, 22]. Using a lowest two mode diatomic approximation where mass m_1 represents the polarizable cluster unit BO_3 , while m_2 is given by the rigid A ion, the Hamiltonian of our system reads [19]

$$H = \frac{1}{2} \sum_{i=1,2,n} [m_i \dot{u}_{in}^2 + m_{vi} \dot{v}_{in}^2] + \frac{1}{2} \sum_n [f'(u_{1n} - u_{1n+1})^2 + f(u_{2n} - v_{1n})^2 + f(u_{2n-1} - v_{1n})^2] + \sum_n \left[\frac{1}{2} g_2 (v_{1n} - u_{1n})^2 + \frac{1}{r} g_r (v_{1n} - u_{1n})^r \right]. \quad (1)$$

Here u_{in} are the displacements of ions $i = 1, 2$ with mass m_i , v_{1n} is the shell displacement of ion 1, f' corresponds to the next nearest neighbour core–core coupling between ions 1, f is the nearest neighbour coupling between shell 1 and ion 2, g_2 is the harmonic coupling between shell 1 and ion 1, and g_r is the anharmonic coupling between shell 1 and ion 1 with degree r of anharmonicity. It is important to note that the elastic properties of the system are explicitly included through the core–core coupling f' which defines the dispersion of the acoustic mode. Introducing the polarizability coordinate $w_{1n} = v_{1n} - u_{1n}$ and treating v_{1n} adiabatically, the following ansatz for the time periodic displacement coordinates is used [4, 5]:

$$\begin{aligned} u_{1n}(t) &= A \xi_{1n} \cos(\omega t) \\ u_{2n}(t) &= B \xi_{2n} \cos(\omega t) \\ w_{1n}(t) &= C \eta_{1n} \cos(\omega t), \end{aligned} \quad (2)$$

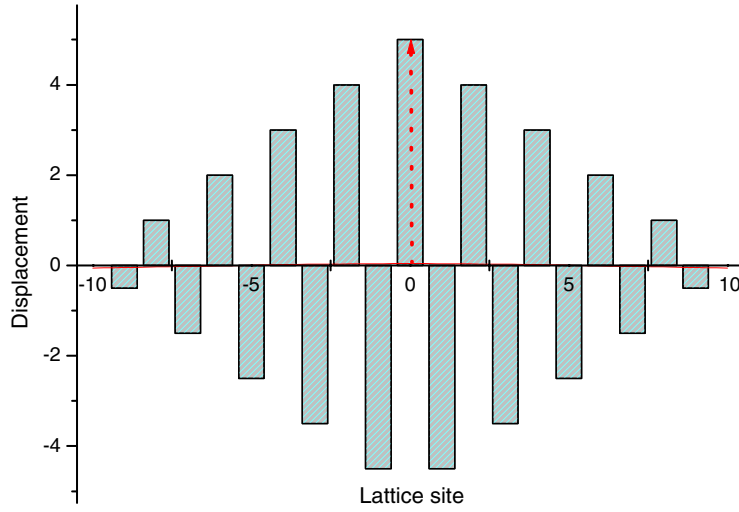


Figure 1. Displacement magnitude and pattern of the considered IGLM at lattice sites around the polar defect at site $n = 0$.

where A, B, C are amplitudes and ξ, η displacements. The equations of motion are given by

$$\begin{aligned}
 -m_1\omega^2\xi_{1n}A \cos(\omega t) &= f' A(\xi_{1n+1} + \xi_{1n-1} - 2\xi_{1n}) \cos(\omega t) + g_2 C \eta_{1n} \cos(\omega t) \\
 &\quad + g_r C^{r-1} \eta_{1n}^{r-1} [\cos(\omega t)]^{r-1} \\
 -m_2\omega^2\xi_{2n}B \cos(\omega t) &= f C(\eta_{1n+1} + \eta_{1n}) \cos(\omega t) + f A(\xi_{1n+1} + \xi_{1n}) \cos(\omega t) \\
 &\quad - 2f\xi_{2n} \cos(\omega t) \\
 0 &= -g_2 C \eta_{1n} \cos(\omega t) - g_r C^{r-1} \eta_{1n}^{r-1} [\cos(\omega t)]^{r-1} - 2f C \eta_{1n} \cos(\omega t) - 2f A \xi_{1n} \cos(\omega t) \\
 &\quad + f B(\xi_{2n-1} + \xi_{2n}) \cos(\omega t).
 \end{aligned} \tag{3}$$

In the following we consider only the so-called *worst* case $r = 4$ [5], which is relevant to ferroelectrics. By expanding the cubic term in $\cos(\omega t)$ [4, 5] and making use of the adiabatic condition, the coupled set of equations to be solved is now given by

$$\begin{aligned}
 -m_1\omega^2\xi_{1n}A &= f' A(\xi_{1n+1} + \xi_{1n-1} - 2\xi_{1n}) + g_2 C \eta_{1n} + \frac{3}{4} g_4 C^3 \eta_{1n}^3 \\
 m_2\omega^2\{ &(g_2 + \frac{3}{4} g_4 \eta_{1n}^2 C^2) \eta_{1n} C + 2f m_2 \omega^2 [C \eta_{1n} + A \xi_{1n}] \} \\
 &= -f^2 C [\eta_{1n+1} + \eta_{1n-1} - 2\eta_{1n}] - f^2 A [\xi_{1n+1} + \xi_{1n-1} - 2\xi_{1n}] \\
 &\quad + 2f (g_2 C \eta_{1n} + \frac{3}{4} g_4 \eta_{1n}^3 C^3).
 \end{aligned} \tag{4}$$

Since the *polarizability coordinate* $w = v - u$ has been introduced, solutions with $v = u$ lead to the trivial case of harmonic behaviour and are not considered. Interesting solutions which are of relevance to relaxors are obtained by the ansatz $v = -u$, by means of which $w = -2u$. Here we concentrate on odd parity solutions and consider the general displacement pattern shown in figure 1. The site labelling refers to the polarizable BO_3 units, where the vector length is a measure of the local polarization, and the rigid A ions lying in between have been omitted for simplicity. Their displacements have to be determined through the coupled equations. At sites $0, 1, 2, \dots, n_c$ the displacements are $\xi_0, \xi_1, \xi_2, \dots, \eta_0, \eta_1, \eta_2, \dots$ etc, and zero at $n = n_c$. In order to compensate for the electric field induced by the polar impurity at $n = 0$, reversed dipole moments are created at the neighbouring sites of the impurity and

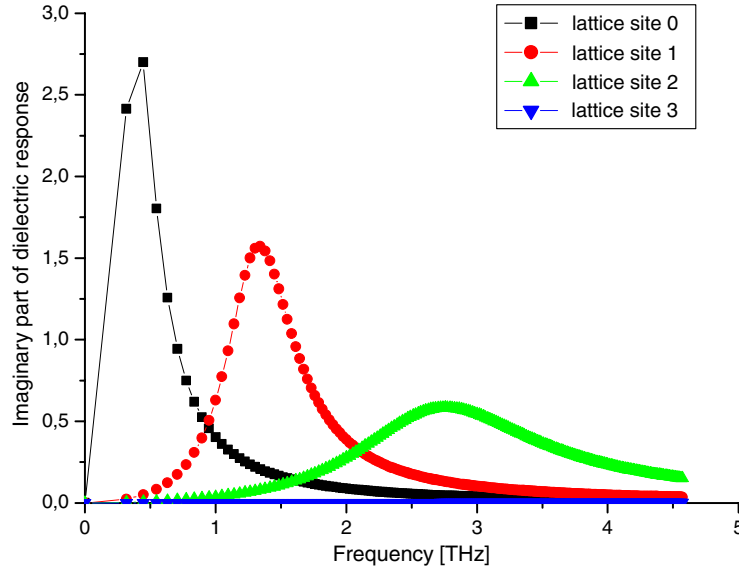


Figure 2. Frequency dependence of the dielectric response (in arbitrary units) for a cluster of size $n_c = 3$.

the corresponding lengths of the induced dipoles ξ_n, η_n are $-1/2$ of the preceding ones, i.e.

$$\xi_1 = -\left(\xi_0 - \frac{1}{2}\right), \quad \xi_2 = -\left(\xi_1 - \frac{1}{2}\right) = \xi_0 - 1, \dots, \xi_n = \xi_0 - \frac{n}{2} :$$

$$n \equiv \text{even}; \quad \xi_n = -\left(\xi_0 - \frac{n}{2}\right); \quad n \equiv \text{odd}.$$

Here it is inferred that at $n = 0$ the displacement is given in terms of a unit length scale $n_c/2$, which guarantees that at $n_c, \xi_{n_c} = 0$. In addition it follows that $\eta_n = -2\xi_n$. The two solutions for ω have to be the same over all sites until n_c is reached where both are zero. The spread of the induced polar region thus critically depends on the magnitude of the polar impurity dipole moment. A unique solution is obtained over the range n_c , with small deviations for the $n = 0$ solution, when g_4 becomes site dependent as $\tilde{g}_4^{(n)} = \frac{g_4}{2(n-n_c)^2}$. This result is entirely self-consistent since the local double-well potential is steep and broad at $n = 0$ and becomes smoother with increasing n to be pseudoharmonic for $n = n_c$ where g_4 is infinitely large.

The above scenario corresponds to an intra-cluster distribution of potential barrier heights [23] which we have used to calculate the frequency dependence of the dielectric response within the approach of [24]. The result is shown in figure 2. Since in the numerical calculation of the dielectric response the cluster size was limited to $n_c = 3$, the frequency dependence is stronger than observed experimentally but shows the characteristic behaviour observed in relaxors.

From the above it is obvious that the smaller the displacement at $n = 0$, the less the local mode is spread. The frequencies for this type of displacement patterns, using the definition $g = 2g_2 + C_r \tilde{g}_4 C^2$, are, at site $n = 0$,

$$\omega_1^2 = \frac{1}{m_1} \left[4f' + g \frac{C}{A} \right] - \frac{2f'}{n_c m_1} \quad (5)$$

$$\omega_2^2 = \frac{2f}{m_2} \left[1 - \frac{1}{n_c} \frac{1}{2 + \frac{gC}{f(2C-A)}} \right]. \quad (6)$$

At all other sites the two frequencies are

$$\omega_1^2 = \frac{1}{m_1} \left[4f' + g \frac{C}{A} \right] \quad (7)$$

$$\omega_2^2 = \frac{2f}{m_2}. \quad (8)$$

The two ILMs defined by equations (7) and (8) are different in character since mode 1 can lie below the optic mode while mode 2 is higher in energy and is typically above the optic mode spectrum. For this reason we concentrate in the following on the in-gap local mode (IGLM) equation (7), since the one defined by equation (8) always decays into the zone boundary optic mode frequency. Mode 1, however, has to be compared to the solutions obtained within the self-consistent phonon approximation (SPA) [19] where the cubic term in the polarizability coordinate is replaced like $w^3 = 3w\langle w^2 \rangle_T$ with $\langle w \rangle_T^2 = \sum_{q,j} \frac{\hbar}{m\omega_{q,j}} W^2(q, j) \coth \frac{\hbar\omega_{q,j}}{2kT}$. Here W is the displacement amplitude within the SPA and ω are the corresponding momentum q and branch j dependent frequencies. This method introduces a pseudoharmonic temperature-dependent core-shell coupling $g_T = g_2 + 3g_4\langle w \rangle_T^2$, which induces mode softening and a lattice instability towards a polar state. Such an instability clearly limits the existence regime of the IGLM, being confined to energies below the optic mode spectrum. Thus displacive type ferroelectrics are unlikely candidates to observe IGLM formation.

In order to test the interplay and competition between lattice stability and IGLM formation, we couple the displacement fields of both as $u_i = u_{i,\text{IGLM}} + u_{i,\text{lattice}}$, $w = w_{\text{IGLM}} + w_{\text{lattice}}$ [25], which introduces a renormalization of the harmonic core-shell couplings like $\tilde{g}_T = g_T + 3\tilde{g}_4 C^2$ and $g_2 = g_T$. The interesting effect arising from this coupling is that the soft lattice mode is now stabilized by the breather amplitude whereas the breather mode becomes temperature dependent. Since the existence of this mode is limited to frequencies below the zone centre optic mode energy, it appears at a certain temperature when

$$\omega_1^2 = \frac{1}{m_1} \left[4f' + g_T \frac{C}{A} \right] = \omega_{\text{TO}}^2(q=0) = \frac{1}{\mu} \frac{2f\tilde{g}_T}{2f + \tilde{g}_T}.$$

When ω_1^2 is equal to the zone boundary acoustic mode frequency, i.e.

$$\frac{1}{m_1} \left[4f' + g_T \frac{C}{A} \right] = \omega_{\text{TA}}^2 \left(q = \frac{2\pi}{a} \right) = \frac{1}{m_1} \left[4f' + \frac{2f\tilde{g}_T}{2f + \tilde{g}_T} \right],$$

strong mode-mode coupling sets in which has the crucial consequence of anomalous softening of the elastic constants. Typical temperature dependences of the three modes discussed above are shown in figure 3.

As can be seen there, the previously soft optic mode is now stabilized and only slightly temperature dependent; the same holds for the zone boundary acoustic mode, but a strong and nonlinear temperature dependence of the breather mode is observed. As soon as this mode splits off from the optic mode, an excess specific heat appears together with an entropy increase, where both increase with decreasing temperature [26]. When the energy of the breather mode reaches that of the acoustic mode, anomalies in the elastic constants appear which become more pronounced with decreasing temperature since the crossing q -value gets smaller (figure 4).

The appearance of the breather mode has the additional effect, that the optic mode related mean-square displacement deviates from linear in T behaviour at high temperatures when the breather splits from it. Also a contribution from the IGLM appears then, which has an anomalous temperature dependence since it is nearly T -independent at high temperatures, while a strong T -dependence appears as soon as its energy is comparable to the acoustic mode energy (figure 5). Correspondingly the onset of the IGLM will induce enhanced diffuse scattering, which seems to be intrinsic to relaxor systems.

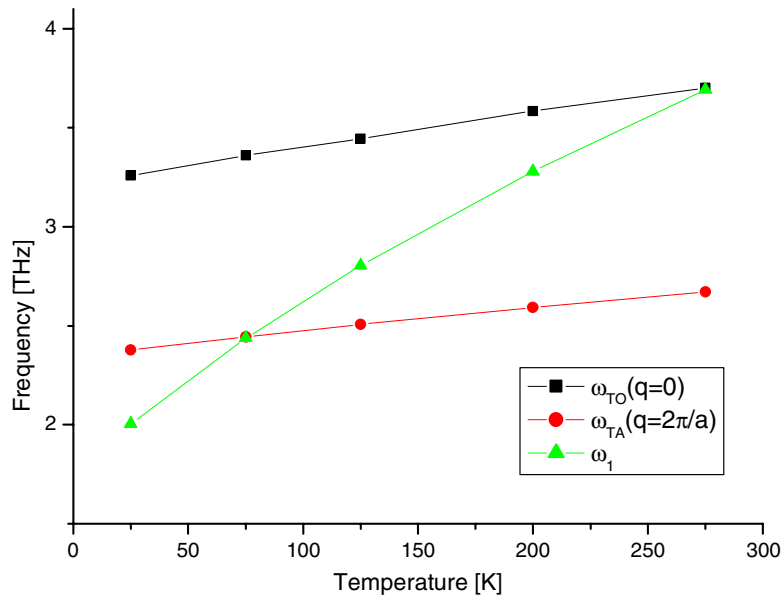


Figure 3. Temperature dependence of the transverse optic zone centre mode ω_{TO} (line with squares), the transverse acoustic zone boundary mode ω_{TA} (line with circles) and the breather mode ω_1 (equation (7)) (line with triangles). Note that ω_1 depends nonlinearly on temperature.

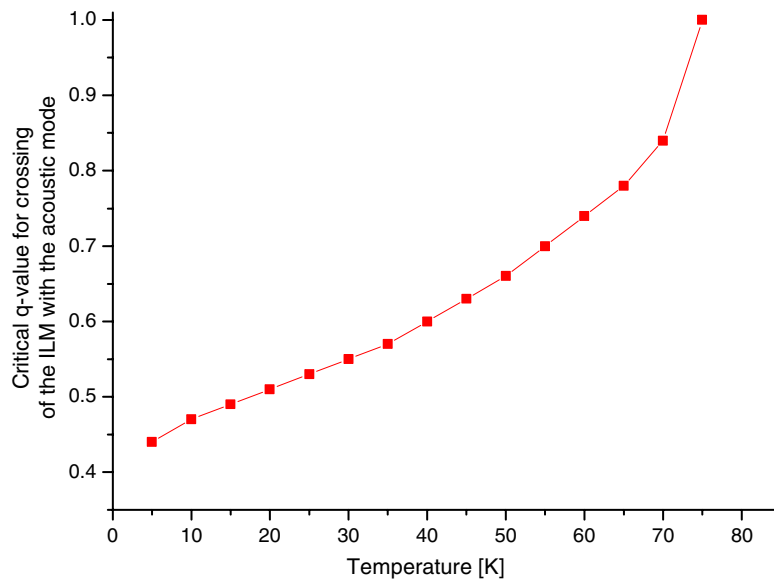


Figure 4. Variation of the q -value, where acoustic mode and IGLM cross, with temperature.

A diffuse phase transition is expected in our model system, when the IGLM freezes out. At this transition the breather patterns become static and a coexistence of locally distorted areas with the ideal host lattice structure is predicted which above the transition is dynamically present. In particular, the appearance of a macroscopic polarization is absent, since the optic

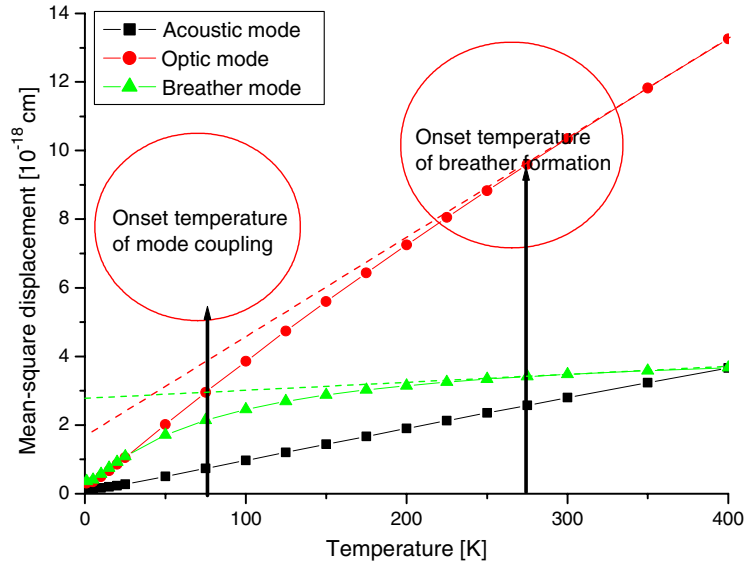


Figure 5. Temperature dependence of the mean-square displacement of the optic mode (line with circles; the dotted line is the linear in T extrapolation), the acoustic mode (line with squares) and the IGLM (line with triangles; the dashed line is the linear in T extrapolation).

mode frequency remains finite. However, $q = 0$ optic mode softening is not excluded, even though it is much less pronounced than in displacive ferroelectrics, but complete softening is prevented due to the stabilizing effect of IGLM coupling.

The relation to the SRBRF model [1] is established by introducing average dipole moments per cluster with characteristic lengths n_c like

$$\langle g_T/g_4 \rangle_{\text{average}}^{(\text{cluster})} = \frac{1}{2n_c} \sum_{n=0}^{n_c} g_T/\tilde{g}_4^{(n)} = \frac{1}{2n_c} \sum_{n=0}^{n_c} p^{(n)},$$

which are the analogue of the Edwards–Anderson order parameter when N clusters are considered. The total dipole moment per cluster i is then given by $2n_c \langle g_T/g_4 \rangle_{\text{average}}^{(\text{cluster})} = 2n_c \langle p_i \rangle_{\text{average}}$, and using the definition $S_i = 3p^{(n_i)}/n_c \sqrt{\langle p_i^2 \rangle_{\text{average}}}$ the closure relation $\sum_{i=1}^N S_i^2 = 3N$ is obtained in analogy to [1]. The reduction of temperature, which explicitly enters the average cluster dipole moments through g_T , has two effects:

- (i) it leads to smaller cluster sizes which have the advantage of becoming mobile [17] and favouring intercluster interactions;
- (ii) the breather mode softens faster than the cluster size decreases and simultaneously softens the elastic constants further because of mode–mode coupling which can lead to a ferroelastic transition prior to the glass transition [27].

The above odd IGLM is not the only solution of the model. Even symmetry solutions also exist which carry totally different character and will be discussed elsewhere. Also the chosen displacement pattern is not unique but others exist, which will be discussed in forthcoming work.

In conclusion, the IGLM discussed above is new as compared to former work on ILMs which mostly concentrate on solutions above the phonon energies and are consequently

energetically less favourable. The reported nanoscale chemical cluster formation observed in relaxors [2, 8, 23] suggests IGLM formation, and has been shown here to be due to nonlinear electron–ion (charge-transfer) interactions. The potential barrier height distribution is a self-consistent consequence of the IGLM formation and induces a frequency-dependent distribution of the dielectric constants, which simultaneously adopt an unusual temperature dependence. The model has two length scales, one related to the amplitude of the intra-cluster polarizability coordinate, and the other defined by the thermal average of the SPA displacement relevant to the long wavelength limit and following the centre of mass. The coupling to the elastic degrees of freedom arises self-consistently in our modelling, and IGLM formation is favoured in soft elastic systems. The freezing temperature is identified here as the temperature at which the IGLM freezes out without causing macroscopic polarization, but inducing a coexistence regime of locally distorted areas within the ideal lattice. The relation to the SRBRF model becomes natural through identifying the average cluster polarization with the Edwards–Anderson order parameter. Applications of the model to other than relaxor ferroelectrics are clear since heterogeneity is vital to the IGLM formation and is an intrinsic property of many complex oxides.

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