# Evidence for a dynamics crossover and its implication on the freezing temperature determination of relaxor ferroelectrics

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**Abstract.** Relaxor ferroelectrics are characterized by a broadened and dispersive permittivity peak in their temperature-dependent dielectric spectra. Although several models have been proposed to explain the nature of these materials, understanding their relaxation dynamics still remains open and requires additional theoretical and experimental explanations. Particularly, a precise determination of the freezing temperature still remains controversial because the influence of dynamic ruptures at temperatures approaching the freezing states (dynamic crossovers) has never evaluated before. In this paper, a model-free approach for describing the super-Arrhenius behaviour in glassy systems is validated for relaxor ferroelectrics. As a result, a predicted dynamic change at a specific temperature (crossover temperature) is evidenced by a derivative-based representation of the relaxation time data. The Stickel function is suggested as a more straightforward but model-dependent method for obtaining the dynamic crossover temperature. Furthermore, the divergence (freezing) temperature is obtained on the basis of the Grüneisen-style activation energy temperature index without assuming any model equation for parameterizing the relaxation data. The influence of the dynamic change occurrences on the freezing temperature determination is also considered, showing that the dynamic crossover temperature determination is a key factor for a proper finding of the freezing temperature in relaxor ferroelectrics.

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Relaxor ferroelectrics (RFs) are functional materials believed to bear a revolutionary potential for a myriad of modern electronic applications due to their unique properties, such as an ultrahigh strain and outstanding piezoelectric behavior (hysteresis-free electromechanical response) [1, 2], and remarkable dielectric and electro-optical properties [3, 4]. However, the progress in technological implementations is notably hindered by the still unsatisfactory understanding of the physical phenomena governing their fundamental properties. RFs are compositionally disordered systems in which the arrangement of different ions on equivalent crystallographic sites is partially or fully disordered [5].

Notwithstanding the wide number of RF systems, their main feature arises from the relaxation dynamics of the nanoscale polar inhomogeneities known as polar nanoregions (PNRs) [6], which have been experimentally confirmed by practically all characterization techniques used in material science [7, 8, 9, 10, 11]. Despite the irrefutable experimental evidence of the existence of PNRs, and although it is widely accepted that the PNRs dynamic governs the functional properties of RFs, the formation mechanisms and the dynamic of these PNRs are not fully understood. The two main PNRs features are: (i) the different time-response to the applied external stimuli (usually an electric field), defined as the relaxation times, and (ii) the temperature-dependent fluctuation of the dipolar moment of the PNRs. In fact, the relaxation time differences and the temperature-dependent polarization fluctuations are the cause of the noticeable dielectric relaxation and the temperature dependence of the functional properties experimentally observed in RFs.

The different states exhibited in RFs at different temperatures may be analyzed in the context of the random field theory [12, 13, 14, 15, 16]. At high temperatures, RFs exhibit a non-polar paraelectric (PE) phase, which is similar to the PE phase of ordinary (non-relaxor) ferroelectrics. At the PE phase, RFs show a distorted local ion configuration where the ions may be dislocated. The shifts of the ions from their ideal crystallographic position, and the existence of vacancies as a consequence of the electric charge compensation of ions with different electrical charges, leads to the rise of different types of imperfections such as point charges, dilatational centers, and electric dipoles that could be considered sources of random electric fields. The quenching of the random field fluctuations with the decreasing temperature promotes the emergence of the PNRs, which is experimentally characterized by a deviation from the linear temperature dependence of the optical refractive index observed at the PE state. The temperature at which this deviation occurs is called the Burns temperature. Bellow this temperature, the small and incipient PNRs exhibit an ergodic behavior defined as the ergodic relaxor state where the PNRs may reach all the possible states in the system [5]. The slowing down of the polarization fluctuations becomes more evident with the decrease in temperature, starting to become statics at an intermediate temperature, labeled as $T^*$, at which a change in the dynamic behavior of the PNRs should become manifest [17, 18]. The temperature $T^*$ was first proposed by Viehland $et$ $al.$ [19] as a local Curie temperature. Later, other works also proposed the existence of this temperature associated with local order-disorder transitions [20, 21]. Finally, Dkhil $el$ $al.$ [22] established the intermediate temperature $T^*$ as a local order-disorder transition temperature related to the appearance of static polar nanoclusters. The polarization fluctuations continue to slow down as the temperature decreases, becoming

totally frozen below a characteristic temperature called the freezing temperature $T_f$. The kinetic behavior of the material between $T^*$ and $T_f$ becomes experimentally observable as a huge dielectric relaxation exhibiting a broadened and dispersive, frequency-dependent permittivity peak, which is usually the first experimental evidence of the relaxor behavior in ferroelectric systems [5]. Although abundant experimental investigations and numerous theoretical formulations exist, a direct determination from the dielectric relaxation data of the temperature at which a change in the dynamic behavior occurs is still lacking.

As a result of the correlation between the PNRs dynamic and the dielectric response, the study of the dielectric relaxations has always been a useful tool for gaining insights into the phenomena governing the macroscopic properties of RFs. As a matter of fact, the study of the dielectric relaxations is a fundamental tool in materials science and, in particular, one of the most helpful tools in the study of glassy systems. Several parameterizations have been used to study dielectric relaxations, among which the Arrhenius parameterization is probably the most widely used and has become a reference for relaxation behavior. The non-divergent behavior on temperature of the Arrhenius parameterization is the model's biggest handicap, precluding it for application to systems that clearly exhibit a divergent behavior at a finite temperature, such as RFs or ultraviscous glassy systems. Indeed, the deviation from the Arrhenius behavior is known as 'super-Arrhenius' (SA) behavior.

Dielectric relaxation studies are not as prolific in RFs as in glassy systems. The experimentally observable freezing temperature has discarded the non-divergent parametrizations of the dielectric relaxation in RFs [23]. Actually, the similarity to Arrhenius (i.e., the simplest parameterization) has made the divergent Vogel–Fulcher–Tammann (VFT) equation the most commonly applied parameterization in RFs. Although the VFT equation has a phenomenological origin, a broad theoretical background has subsequently emerged as a consequence of the unquestionable fitting quality of the relaxation data to this equation. In regard to RFs, percolation and thermodynamic arguments have been used to explain the dynamic relaxation in terms of the VFT equation [19, 24]. However, despite the efforts made, there is still no reliable theoretical foundation that enable this equation to be established as a trustworthy description of the relaxation dynamics of RFs. In fact, a VFT-type relationship does not necessarily imply freezing in the system [25]. Moreover, other well-known parameterizations are usually statistically indistinguishable for describing a dielectric relaxation mathematically, as shown in supplementary material.

Bearing in mind that a parameterization selection could lead to biased results in the study of the dielectric relaxations, the development of a different methodology to disentangle the dielectric relaxation in RFs seems to be mandatory. In the present work, a model-free route to study dielectric relaxations in RFs is proposed. This new approach, based on the data processing of the dielectric relaxations without an a priori parameterization selection, shows the existence of a dynamic crossover, thereby revealing a change in the dynamic behavior of RFs at a frequency-independent temperature. The implication of this finding on the determination of the freezing temperature of RFs is also analyzed herein.

Gaining insights into a system behavior without assuming any a priori theoretical or phenomenological model is one of the essential approaches in experimental physics. This
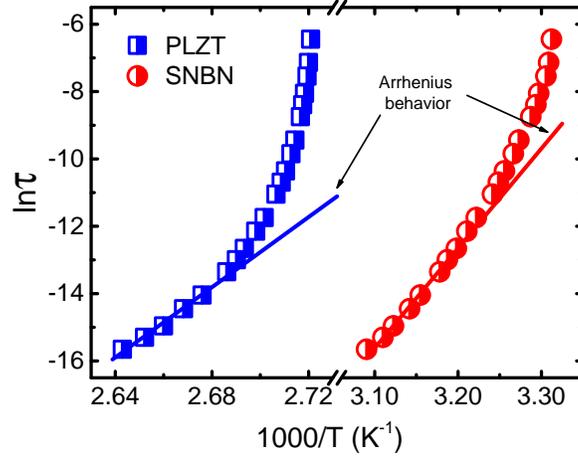
**Figure 1.** Logarithm of the relaxation time as a function of the inverse of the temperature corresponding to the maximum value of real permittivity. The linear fit corresponding to the Arrhenius model is shown as an indication of the super-Arrhenius behavior of the data.

ensure that unbiased information of the physical phenomena driving the systems behavior can be obtained. A recently introduced novel procedure for glass-forming systems takes this approach into account [26]. This procedure was first successfully applied to a wide experimental data-set, ranging from low molecular weight liquids and polymers to liquid crystals and plastic crystals [26, 27]. Furthermore, the procedure was recently applied to the study of the low-temperature dielectric relaxations of ordinary ferroelectrics, and demonstrated the effectiveness of this approach for revealing changes in the dynamic behavior of these systems [28].

Polycrystalline lead lanthanum zirconate titanate, with nominal composition $(Pb_{0.91}La_{0.09})(Zr_{0.35}Ti_{0.65})O_3$ (hereafter PLZT), and strontium sodium bismuth niobate, with nominal composition $SrNaBi_2Nb_3O_{12}$ (hereafter SNBN), are taken as models for perovskite- and bismuth-layer-structured RFs, respectively (see supplementary material for a detailed information about the samples and experimental procedure). Both PLZT and SNBN exhibit a typical dielectric relaxation where the maximum of the real permittivity shifts to higher frequencies with an increase in temperature. A typical representation of the dielectric relaxation data is shown in Fig. 1 (see the supplementary material for a detailed description about how the data shown in Fig. 1 is obtained from the permittivity versus temperature measurement). As may be observed, a clear deviation from the Arrhenius behavior (linear behavior) is verified for both PLZT and SNBN. Thus, the SA behavior may disentangle by using the proposed model-free route (MFR).

The MFR procedure is based on the assumption that the SA behavior can be described by a temperature-dependent apparent activation energy [26], such as:

$$\tau(T) = \tau_0 \exp\left[\frac{E_A(T)}{k_B T}\right], \tag{1}$$

where the function $E_A(T)$ can be obtained directly from the experimental data (see supplementary material). Taking into account that the activation energy is essential for
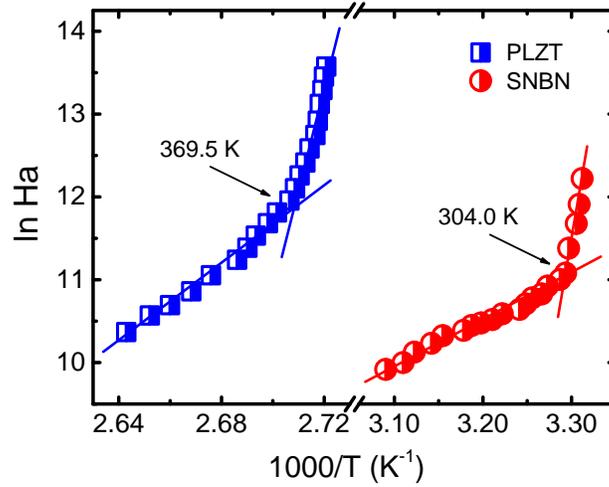
**Figure 2.** Derivative-based representation of the relaxation data. The logarithm of the apparent enthalpy function, $\ln H_a$, as a function of the inverse of the temperature displays a clear slope change, thereby evidencing two differentiated dynamical regions. A linear fit for each region is displayed for the eyes. The crossover temperature between the dynamical regions are indicated in the plot.

describing the phenomenological response of the systems, obtaining $E_A(T)$ directly from the data processing is a step forward in the unbiased study of dielectric relaxations. Note that by considering an adequate function for $E_A(T)$ it is possible to recover the most commoly used phenomenological equations. For instance,

$$E_A(T) = E_A \left(1 - \frac{T_f}{T}\right)^{-1},$$ (2)

gives rise to the well-known VFT equation:

$$\tau(T) = \tau_0 \exp\left[\frac{E_A}{k_B(T - T_f)}\right].$$ (3)

According to Drozd-Rzoska *et al.* [29], the apparent activation enthalpy can be defined as:

$$H_a(T^{-1}) = \frac{d}{dT^{-1}} \ln \tau(T^{-1}).$$ (4)

which can be easily obtained from the experimental data. Fig. 2 shows the $\ln H_a$ versus $T^{-1}$ plot, where two constant slope regions intersect at 369.5 K and 304.0 K for PLZT and SNBN, respectively. As was well-established in previous works, the slope change can be interpreted as a change in the free-volume thermal expansion coefficient of the material [30, 31], thereby evidencing the existence of two different dynamic regions. Ergo, the dynamic crossover is confirmed. An equivalent result is obtained from a model-dependent analysis proposed by Stickel *et al.* [32], as detailed in the supplementary material. The existence of a dynamic crossover in RFs is not a new concept [17, 18], but the direct determination of the crossover temperature was hitherto unexplored for RFs.

The departure from the simple Arrhenius to the SA behaviour is also characterized by the fragility coefficient introduced by Angell *et al.* [33, 34] as a measure of the dielectric relaxation metric. Although Angell's coefficient provides a metric for a wide diversity of materials, it is not the only parameter of this type [35]. Dyre [36] noted the formal importance of the Grüneisen-parameter [37] to quantify the non-linear pattern of the SA behavior in the $\log \tau$ versus $T^{-1}$ representation. This formal similarity lead to the proposal of a new equivalent steepness temperature parameter to quantify the metric of the SA behavior by the "Grüneisen-style" activation energy temperature index [36]:

$$I_N(T) = -\frac{d \ln E_A(T)}{d \ln T}.$$ (5)

This temperature index serves as an alternative metric of fragility, which can be easy correlated with Angell's parameter [36]. The $I_N(T)$ can be obtained directly from the data once $E_A(T)$ has been obtained by the MFR. This index may constitute a decisive tool for testing the validity of a given equation for fitting $\tau(T)$ experimental data [38]. Even more relevant is the linear dependence as a function of temperature that has been experimentally revealed for the inverse of the index ($I_N^{-1}$), giving rise to a universal linear dependence [26]:

$$I_N^{-1}(T) = aT + b,$$ (6)

where the values of $a$ and $b$ can be obtained by a linear fitting of the experimental data. Note that the temperature dependence of $I_N^{-1}$ for a certain phenomenological equation can be recovered by substituting the corresponding activation energy in Eq. (5). For instance, $I_N^{-1}(T) = \frac{T}{T_f} - 1$ is obtained for the VFT approach.

Considering the validity of the Adam-Gibbs model [30, 24, 39], which relates the apparent activation energy and the configurational entropy such that $E_A(T) \propto \frac{1}{S_C(T)}$, and considering the definition of the Grüneisen-index (Eq. (5)), the following relation is obtained [26, 31]:

$$\frac{I_N(T)}{T} = \frac{1}{S_C(T)} \frac{\partial S_C(T)}{\partial T}.$$ (7)

Taking into account the experimental fulfillment of Eq. (6), Eq. (7) can be transformed into a generalized power-law for the configurational entropy:

$$S_C(T) = S_0 \left(1 - \frac{T_N}{T}\right)^n,$$ (8)

where the singular temperature $T_N = -b/a$ and the exponent $n = -1/b$ are obtained from the experimental values of $a$ and $b$. It is important to point out that $T_N$ has a similar meaning of the freezing temperature $T_f$ in the VFT equation, since it is the temperature at which the entropy tends to zero; that is, $\lim_{T \to T_N} S_C(T) = 0$. Furthermore, $S_0$ represents the configurational entropy at high temperatures; that is, $\lim_{T \to \infty} S_C(T) = S_0$. Eq. (8) symbolizes a generalized new dependence for the evolution of the configurational entropy of RFs, providing a new way to obtain insight into RFs dynamics.
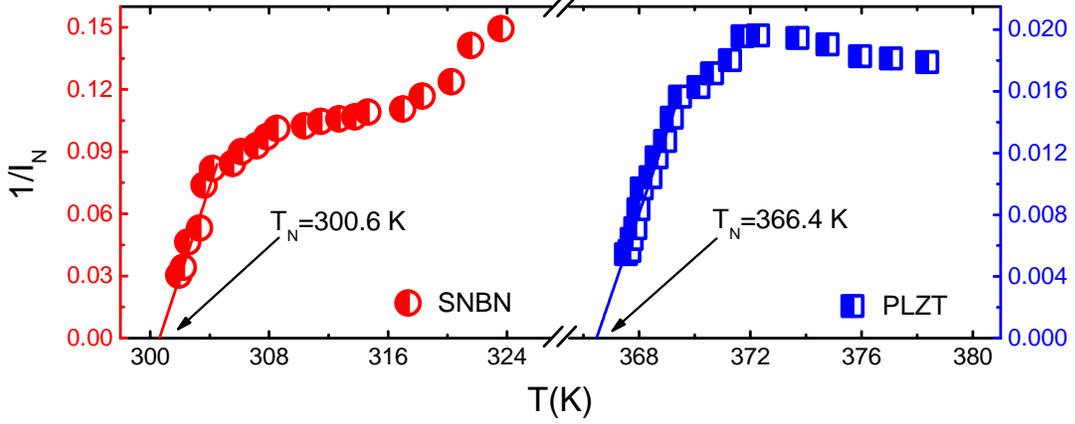
**Figure 3.** Reciprocal of the Grüneisen temperature index. Temperature evolution of the reciprocal of the index obtained directly from the experimental data for the tested materials. Only the low temperature region is considered in order to obtain the values of divergence temperatures $T_N$ for each material.

**Table 1.** Calculated divergence temperatures by using the VFT equation, $T_{VFT}$, the spin-glass model, $T_{SG}$, and the proposed model-free approach, $T_N$. The reported VFT and SG temperatures are obtained by fitting either all the relaxation data or only the data corresponding to the low temperature dynamic region.

| Materials | Dynamic region | $T_{VFT}$ (K) | $T_{SG}$ (K) | $T_N$ (K) |
|-----------|----------------|---------------|--------------|-----------|
| SNBN | All temperatures | 281.3 | 295.4 | |
| | Low temperatures | 300.4 | 300.6 | 300.6 |
| PLZT | All temperatures | 364.6 | 366.0 | |
| | Low temperatures | 366.0 | 366.0 | 366.4 |

The temperature dependence of $I_N^{-1}$ for both PLZT and SNBN is shown in Fig. 3. The linear behavior displayed in the low-temperature region of the experimental data for both samples confirms the validity of Eq. (6) for describing the low-temperature dynamic behavior of RFs (i.e., for temperatures below the dynamics crossover temperature). The values of the $T_N$ are obtained from a linear fitting of the low temperature dynamic region of the $I_N^{-1}$ versus $T$ plots, and are reported in Table 1. For comparison, the values of the freezing temperatures extracted from the VFT and the SG fittings are also reported. These freezing temperatures were extracted from the whole relaxation data and from the low-temperature region (the same region used to obtain $T_N$). Two observations should made from Table 1: The first is that the divergence temperature determination is model- and temperature region-dependent, while the second is that the values of the divergence temperature obtained by three different methods match when only the low temperature region is considered.

Summarizing, a model-free approach previously developed for glassy-systems is validated here for RFs leading to a frequency-independent characteristic temperature at which a dynamic crossover is revealed. The crossover temperature can also be determined from the

Stickel plot, which is probably a simpler approach for calculation. Based on the Grüneisen-index, the proposed methodology enables the divergence (freezing) temperature to be obtained directly from the relaxation data, without a previously defined model equation. The freezing temperature obtained by the model-free route matches the freezing temperatures obtained by the fitting of the VFT and the SG equations at the low-temperature regions, thereby proving that the existence of a dynamic crossover has a clear implication in a proper freezing temperature determination.

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