Crossover in a non-analytical behaviour of dielectric non-linearity in $PbMg_{1/3}Nb_{2/3}O_3$ relaxor ferroelectric

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Abstract. The dielectric response of the relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) is found to be a non-analytical function of the ac field, with the absolute value of the non-linear component of the polarization given by $|P_{nl}| \propto E_m^{\gamma(\omega, T)}$. The dependence on the temperature, T, and frequency, ω, of the exponent γ manifests itself in the form of a crossover in $\gamma(T)$ from approximately 2 to 3 upon cooling, whose position depends upon the frequency of the applied ac field. From the comparison of $\gamma(\omega, T)$ with the linear complex dielectric permittivity, $\varepsilon_l^*(\omega, T)$, of PMN, the following can be correlated: (i) $\gamma \approx 2$ in the regime of the quasi-static response, and γ starts deviating from 2 simultaneously with the onset of the frequency dispersion; and (ii) $\gamma \approx 3$ when the spectrum of relaxation times in PMN becomes flat. These findings can be understood in terms of the change in the type of the motion of the interphase boundaries of the microscopic polar regions existing in PMN, namely in the change of the scale on which the interphase boundaries can move.

1. Introduction

In the contemporary physics of relaxor ferroelectrics (relaxors), there are several key problems which still remain open and challenge both experimentalists and theoreticians. One of these problems is that of the nature of the dielectric response of relaxors, and, primarily, that of their 'classical' representative—$PbMg_{1/3}Nb_{2/3}O_3$ (PMN).

In fact, the name 'relaxor' identifies the most characteristic feature of these materials: a relaxation dispersion of the linear dielectric permittivity. The dispersion is observed over a wide frequency interval, from millihertz to gigahertz [1]. This is distinct from the simple Debye relaxation which is present only over 2.3 decades in frequency. Owing to detailed experimental studies of the linear dielectric response of PMN, its relaxation dispersion has recently received a clear interpretation on the phenomenological level [2–4]. It was shown that there exists an exponentially broad and smooth spectrum of relaxation times, τ, which changes with temperature and controls the frequency dependence of the real, ε_l', and imaginary, ε_l'', parts of the linear dielectric permittivity.

At the same time, on the microscopic level, the understanding of the relaxation dispersion in PMN is yet to be developed. Although it is commonly believed that the dielectric response of PMN is related to small—about 10 nm in size—polar regions which are randomly distributed in a non-polar matrix [5], it is still not clear how the polar regions respond to applied electric fields. Several possible models have been proposed, which with certain

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assumptions could equally well describe the frequency dispersion of the linear permittivity. They are:

(a) a superparaelectric [6, 7];
(b) a dipolar glass [2, 8, 9];
(c) a dipolar dielectric with random fields [10–12];
(d) a domain wall or interphase boundary motion [13–15]; and
(e) the model which comprises the approaches (c) and (d) invoked according to the temperature interval discussed [16].

In this situation, additional experimental evidence is required in order to distinguish among models (a)–(e).

In previous work, we showed that such evidence could be obtained from the systematic study of non-linear dielectric properties of PMN [14, 17–20]. It was shown that a set of experimental data, which included an increase in the real part of the dielectric permittivity with increasing ac-field amplitude [14], and a large qualitative difference between the effects of the dc bias and ac driving fields on the dielectric permittivity of PMN single crystals [17–19], provide several arguments against models (a)–(c) and (e), and, at the same time, in favour of model (d). Thus, at present, the scenario in which the ac-field-induced displacements of the boundaries of the polar regions (rather than a reorientation of the regions) controls the dielectric response looks rather convincing for PMN. Following Cross [21], we will call this mechanism of the dielectric response a 'breathing' mechanism, because the motion of the interphase boundary between the polar regions and the non-polar matrix looks like breathing of the polar regions under the applied ac field.

It is the purpose of this paper to continue our study of the non-linear dielectric response of PMN and to report the experimental data which, on one hand, look rather surprising and, on the other hand, lend additional support to the 'breathing' model. We investigate the non-linear response to the ac field by measuring the dielectric permittivity and the third-harmonic component of the induced polarization of PMN. The analysis of the field dependence of both quantities leads to the conclusion that at small ac-field amplitudes, down to 0.04 kV cm^{-1}, the non-linear polarization, P_{nl} (defined as the difference between the total induced polarization, P, and its linear component: $P_{nl} = P - \varepsilon_0 \varepsilon_l' E_m$, where $\varepsilon_0 = 8.854 \times 10^{-12}$ F m^{-1}), is a non-analytical function of the field. We find that its absolute value is given by the following relationship:

$$|P_{nl}| \propto E_m^{\gamma(\omega,T)} \tag{1}$$

where the exponent γ is temperature and frequency dependent. As a function of temperature γ exhibits a *crossover*, changing from $\gamma \approx 2$ at high temperatures to $\gamma \approx 3$ at low temperatures. The position of the crossover depends upon the frequency, ω, of the applied ac field, and can be correlated with the frequency dispersion of the linear dielectric response:

(i) $\gamma \approx 2$ in the regime of the quasi-static response, and, upon cooling, γ starts deviating from 2 simultaneously with the onset of the frequency dispersion of ε_l';

(ii) with increasing temperature, the deviation of γ from its low-temperature limit occurs simultaneously with the appearance of the frequency dispersion of the imaginary part of the permittivity, ε_l''.

The theoretical part of the discussion of the experimental results has two sections. First, we will compare the data for PMN with the known examples of non-analytical behaviour of the non-linear response in disordered systems [22, 23], which have already received a solid theoretical interpretation. From this comparison, it will become clear that PMN is a unique

example, which does not fit the existing models of non-analytical behaviour [22, 23], and thus requires a new approach for describing the field dependence of its non-linear response. Therefore, in the second section we will discuss the data reported in this paper within the 'breathing' model. Even though this model is comparatively new, recently it has already been successful in explaining some other features of the non-linear dielectric response of PMN [14, 17–20]. It will be shown that, within this model, the observed crossover in the field exponent $\gamma(\omega, T)$ may imply a change in the type of the interphase boundary motion.
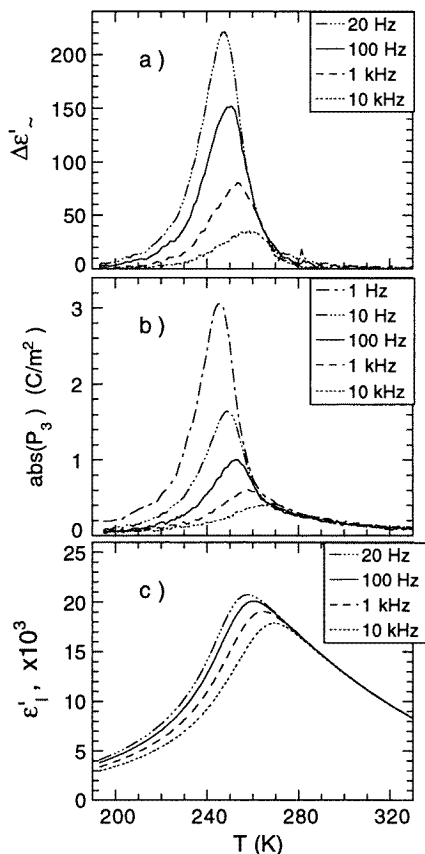

Figure 1. The temperature and frequency dependence of: (a) the non-linear part of the dielectric permittivity, $\Delta\varepsilon'_\sim = \varepsilon'(E_m) - \varepsilon'_l$, measured at $E_m = 0.1$ kV cm^{-1}; (b) the absolute value of the third-harmonic component of the polarization, P_3, measured at $E_m = 0.04$ kV cm^{-1}; and (c) the linear dielectric permittivity, ε'_l, of PMN single crystal.

2. Experimental procedure

The experiments were performed on PMN single crystal, in which case the electric field was applied along a $\langle 111 \rangle$ direction, and ceramic samples. The typical sample dimensions were about $3 \times 3 \times 0.1$ mm^3. The third harmonic of the polarization, P_3, was measured using a SR 830 digital lock-in amplifier. The frequency range was from 1 Hz to 10 kHz, and the ac-field amplitude, E_m, varied from 0.04 kV cm^{-1} to 0.20 kV cm^{-1}. The dielectric

permittivity, ε', was measured using an HP 4284A LCR meter. The amplitude of the ac field changed from 0.02 kV cm^{-1} to 2.0 kV cm^{-1}, and the frequency interval investigated was from 20 Hz to 10 kHz. The non-linear effect was characterized by the non-linear component of the dielectric permittivity, $\Delta\varepsilon'_\sim$, which was calculated as the difference between the permittivity measured at a given amplitude, E_m, and the linear permittivity, ε'_l, corresponding to $E_m = 0.02$ kV cm^{-1}:

$$\Delta\varepsilon'_\sim = \varepsilon'(E_m) - \varepsilon'_l.$$

Both experiments were performed as functions of temperature, always upon cooling from 380 K to 180 K. This special study showed that there were no effects of the cooling rate on non-linear dielectric data for the rates within 0.4 to 2 K min^{-1}. In this paper, we report the data which were obtained using the cooling rates of 1 K min^{-1} for ε' and of 0.5 K min^{-1} for P_3. For all of the samples, we used Cr/Au electrodes deposited by evaporation.

3. Results

In figures 1(a) and 1(b), we plot typical data for $\Delta\varepsilon'_\sim$ and the absolute value of P_3, respectively, measured at a fixed ac-field amplitude. These plots clearly demonstrate that, like the linear dielectric permittivity (figure 1(c)), the non-linear components of the response have two regimes: quasi-static (at high temperatures) and frequency dispersive (at low temperatures), and that for a given frequency of the applied field, the transition from the non-dispersive to the dispersive regime occurs simultaneously in the linear, ε'_l, and non-linear, $\Delta\varepsilon'_\sim$ and P_3, dielectric responses.
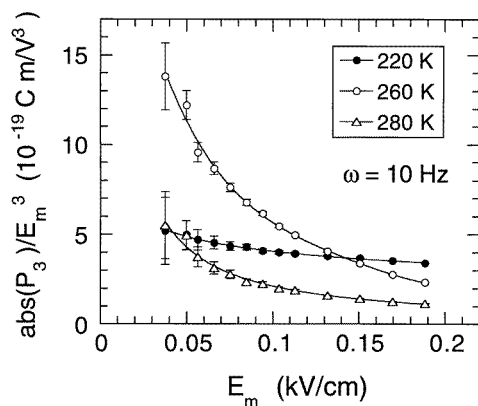

Figure 2. The plot shows that the ratio between the amplitude of the third harmonic of the polarization and the cube of the ac-field amplitude, P_3/E_m^3, strongly depends upon the applied electric field even at field levels as small as 0.04 kV cm^{-1}. The symbols show the experimental data for a single crystal of $\langle 111 \rangle$ orientation measured at 10 Hz at three temperatures, and the solid lines are drawn to guide the eye.

In this work, we focused on the analysis of the field dependences of $\Delta\varepsilon'_\sim$ and P_3. The analysis showed that, at temperatures above approximately 240 K, the non-linear components of the dielectric response strongly deviate from the $\Delta\varepsilon'_\sim \propto E_m^2$ and $P_3 \propto E_m^3$ functions which are predicted by the simple phenomenological scheme based on the symmetry considerations (see the more detailed discussion in the next section). This is evident, for example, from figure 2, where one can see that the ratio P_3/E_m^3 exhibits substantial field dependence,

even at a field as small as 0.04 kV cm^{-1}. Moreover, we could not fit the measured dependence $P_3(E_m)$ to a polynomial function containing only odd powers of the field (which is consistent with the macroscopic symmetry of PMN—cubic, with the $m\bar{3}m$ point group [5, 24, 25] unless an unreasonably large number, from 5 to 8, of terms were taken into account. A similar problem was encountered when we tried to fit $\Delta\varepsilon'_\sim$ to a polynomial function containing only even powers of the field.
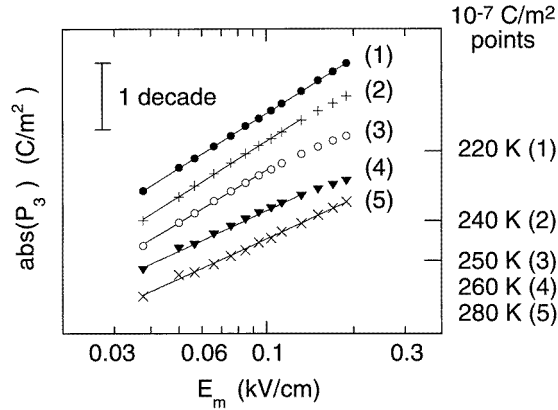

Figure 3. The data for the electric field dependence of the absolute value of the third harmonic, P_3, of PMN (symbols) and their fits to the power function $|P_3| \propto E_m^\gamma$, shown with the solid lines. The sample is a single crystal of $\langle 111 \rangle$ orientation, and the frequency of the ac field is 10 Hz. The markers on the right indicate the positions of the point $P_3 = 10^{-7}$ C m^{-2} for each temperature.

Trying to choose an appropriate function for describing the field dependence of $\Delta\varepsilon'_\sim$ and P_3, we found that the data can be nicely fitted to a power law. For example, figure 3 shows a plot of the absolute value of P_3 as a function of the ac-field amplitude for PMN single crystal. First, one can see here that, plotted on a log–log scale, the data lie well on the straight line, implying a power-type dependence. In the plot, the solid lines correspond to a fit to the power function $|P_3| \propto E_m^\gamma$, using γ as an adjustable parameter. Second, one can clearly see the difference between the exponents γ at the lowest and highest temperatures, as represented by the slopes of the straight lines. For the whole temperature interval investigated, the temperature dependence of the exponent γ is plotted in figure 4(a) for two frequencies of the applied ac field, 10 Hz and 1 kHz. The plot demonstrates that, as a function of temperature, γ undergoes a step-like change: at high temperatures, $\gamma = 2.00 \pm 0.05$ with a good accuracy, while at low temperatures, it is close to 3 ($\gamma = 2.75 \pm 0.05$). Also, the position of the 'step' depends upon the frequency, ω, of the ac field, shifting toward higher temperatures with increasing ω.

Similar analysis using the power function can be performed for the amplitude dependence of the non-linear component of the dielectric permittivity. Figure 5(a) shows $\Delta\varepsilon'_\sim$ for a PMN single crystal as a function of E_m plotted on a log–log scale, where the symbols correspond to the experimental data obtained at 1 kHz at two temperatures, and the solid lines show their fits to the power function $\Delta\varepsilon'_\sim \propto E_m^\xi$. The exponent ξ obtained from the fit is plotted in figure 5(b) as a function of temperature, and, like $\gamma(T)$, it exhibits a step-like change. For the same frequency, 1 kHz, the position of the 'step' in $\xi(T)$ almost coincides with that in $\gamma(T)$ obtained from the third harmonic. Also, the comparison of the plots in figures 4(a) and 5(b) shows that, for the same frequency, these exponents are
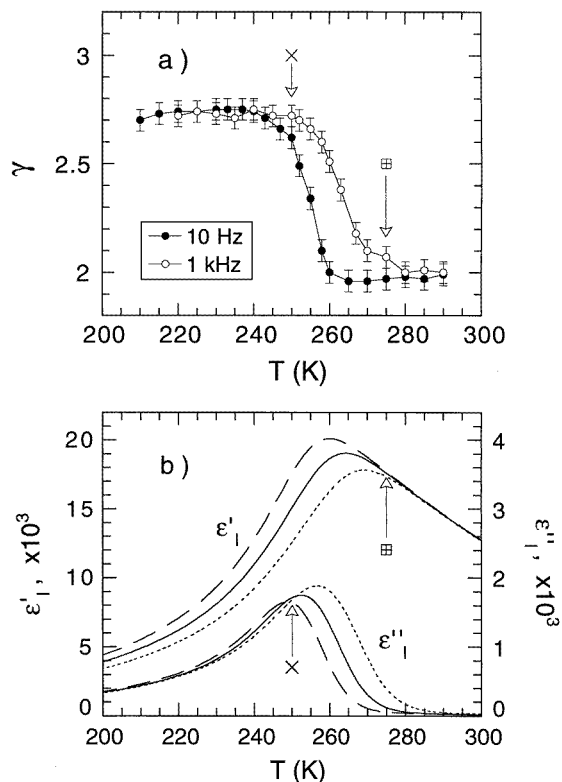
Figure 4. (a) The temperature dependence of the exponent γ corresponding to the fit of the data for $P_3(E_m)$ for a PMN single crystal to a power function, for two frequencies of the ac field: 10 Hz and 1 kHz (in the plot, the lines are drawn to guide the eye). (b) The temperature and frequency dependence of the real, ε_l', and imaginary, ε_l'', parts of the linear dielectric permittivity of the same PMN single crystal (dashed line: 100 Hz; solid line: 1 kHz; dotted line: 10 kHz). One can see that for the same frequency of the ac field, 1 kHz, the following are correlated: (i) $\gamma = 2$ in the regime of the quasi-static response, where $\varepsilon_l' = \varepsilon_s$ and $\varepsilon_l'' \approx 0$, and γ starts to deviate from 2 simultaneously with the onset of the frequency dispersion (shown by the box); (ii) $\gamma \approx 3$ when ε_l'' becomes nearly frequency independent at $\omega > 1$ kHz (shown by the cross).

related by $\gamma - \xi = 0.85$; their difference is in reasonable agreement with the expected value of 1 [26].

For the power-type dependence, a comparative analysis of the data for the field exponents, $\gamma(\omega, T)$ and $\xi(T)$, with those for the linear dielectric permittivity, ε_l' and ε_l'', for the same PMN single crystal enables us to correlate several events. We demonstrate them by plotting in figure 4(b) the data for ε_l' and ε_l''. For a given frequency of the applied ac field, the quadratic field dependence of the third harmonic, $\gamma = 2$, is observed in the regime of the quasi-static response, and, upon cooling, the temperature at which $\gamma(\omega, T)$ starts to grow from 2 coincides with the onset of the frequency dispersion of ε_l' (the box in figure 4(b) for 1 kHz). At the same time, for a given ω, the transition to the nearly cubic field dependence of P_3 occurs simultaneously with the event of ε_l'' becoming nearly independent of the frequency at frequencies higher than ω (the temperature corresponding to this event is marked with the cross in figure 4(b) for 1 kHz).

Thus, there are two ways to describe the non-linear dielectric data for PMN: using either
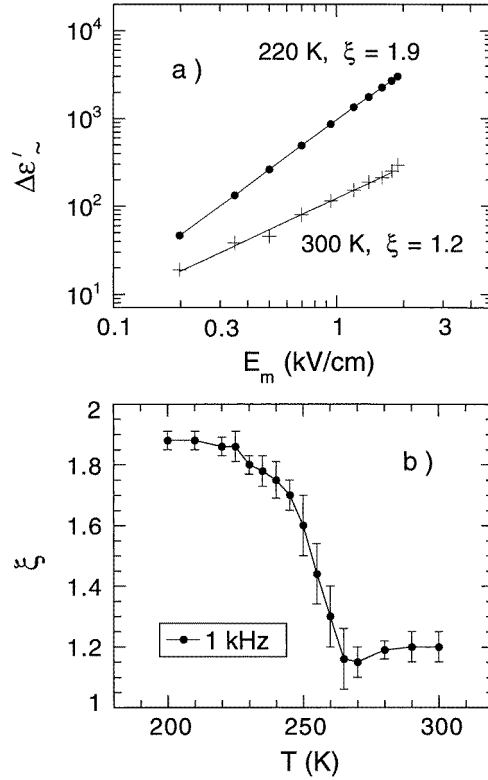
Figure 5. (a) The electric field dependence of the non-linear component, $\Delta\varepsilon'_{\sim} = \varepsilon'(E_m) - \varepsilon'_l$, of the dielectric permittivity of a PMN single crystal measured at 1 kHz, and its fit to the power function, $\Delta\varepsilon'_{\sim} \propto E_m^{\xi}$, which is shown by the solid lines. (b) The temperature dependence of the exponent ξ corresponding to the frequency of the ac field of 1 kHz.

the polynomial expansion or the power function with the field exponents γ and ξ different from the values predicted by the symmetry of the crystal (as has already been mentioned, for the macroscopically centrosymmetrical crystal of PMN, the expected values are equal to $\gamma = 3$ and $\xi = 2$). For the power function, the similarity of the behaviours of the exponents γ and ξ which correspond to two different characteristics, P_3 and $\Delta\varepsilon'_{\sim}$, of the non-linear dielectric response leads us to suggest that the absolute value of the non-linear component of the polarization of the sample, P_{nl}, should change according to equation (1): $|P_{nl}| \propto E_m^{\gamma}$, where the exponent γ is temperature and frequency dependent. Equation (1) is a non-analytical function at the point $E = 0$, which actually implies non-analytical behaviour of the induced polarization, $P(E)$, in PMN in the limit of very small fields, $E \to 0$. In the following part of this paper, we are going to work only with this function. The reason for this is that a similar type of non-analytical field dependence, with the field exponents different from the values corresponding to the symmetry of the material, has been observed previously for some disordered systems; see, e.g., references [22, 23]. Therefore, since PMN is also a disordered material [1, 2, 6, 13], it seems both interesting and physically reasonable to investigate the possibility of it having a non-analytical dielectric response.

Before concluding this section, we will pay special attention to the behaviour of the dielectric non-linearity of PMN in the quasi-static regime. Here, the third harmonic,
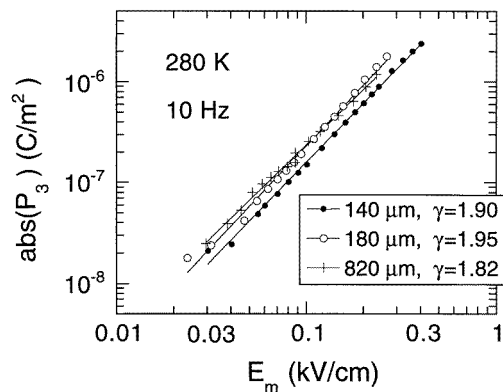
Figure 6. The absolute value of the third harmonic of the polarization of PMN ceramics is plotted as a function of the ac-field amplitude on a log–log scale. The symbols correspond to the experimental data for different sample thicknesses, and the solid lines show a fit to the power function $|P_3| \propto E_m^\gamma$. The temperature is 280 K and the frequency of the ac field is 10 Hz.

P_3, changed quadratically, and $\Delta\varepsilon'_\sim$ changed almost linearly with the field. Taking into account the fact that the magnitude of the non-linear effect is fairly small—for example $\Delta\varepsilon'_\sim/\varepsilon'_l \leqslant 10^{-2}$ at 300 K for $E_m \leqslant 1$ kV cm^{-1} (cf. figures 5(a) and 1(c))—such behaviour is very unusual for a macroscopically centrosymmetrical crystal of PMN, for which it is expected that the induced polarization should contain only odd powers of the electric field. It looks suspiciously close to the non-linear response of a 'non-centrosymmetrical' object, like an electrically asymmetric surface layer of the sample. Thus, in order to eliminate this possibility, and to be sure that we are dealing with 'true' bulk properties of PMN and not with surface-related effects, we performed an additional experiment and carried out device modelling. The sample was considered as consisting of two dielectric layers: one layer represents the bulk properties of the material, and the second layer, whose non-linear response behaves as E_m^2, represents the near-surface part of the sample. A detailed analysis of this problem is presented in the appendix. It shows that if the non-linear response of the sample is controlled by a surface layer, the third harmonic of the polarization should be inversely proportional to the thickness of the sample, h_s, and change as follows: $P_3 \propto E_m^2/h_s$. In order to investigate $P_3(E_m)$ as a function of the sample thickness, PMN ceramic samples were used. The result of this study is demonstrated in figure 6, where one can see that even though h_s varies by a factor of 4, the measured values of the third harmonic almost coincide for all of the samples, and that they all show a nearly quadratic field dependence (the value of γ corresponding to each sample thickness is given in the caption to the plot). This gives us enough confidence that the measured components, P_3 and $\Delta\varepsilon'_\sim$ (and therefore P_{nl}), represent true material properties of PMN.

4. Discussion

4.1. Crossover in the field exponent versus evolution of the relaxation time spectrum

The correlation indicated between the beginning and the end of the temperature crossover of the field exponent γ (equation (1)), and the onset of the frequency dispersion of the real and imaginary parts of the linear dielectric permittivity, ε'_l and ε''_l (figure 4), lets us relate this crossover to the evolution of the relaxation time spectrum. We take advantage of the

fact that in relaxors the spectrum $G(\ln \tau, T)$ of relaxation times τ is broad and smooth [4], which allows us to write down the following expressions for ε'_l and ε''_l for a relaxor [27]:

$$\varepsilon'_l(\omega, T) = \varepsilon_s(T) \int_{\tau=0}^{\tau=1/\omega} G(\ln \tau, T) \, \mathrm{d}(\ln \tau) \tag{2}$$

$$\varepsilon''_l(\omega, T) = \frac{\pi}{2} \varepsilon_s(T) G(\ln \omega^{-1}, T) \tag{3}$$

where the spectrum has a normalizing condition:

$$\int_{\tau=0}^{\tau=\infty} G(\ln \tau, T) \, \mathrm{d}(\ln \tau) = 1$$

and ε_s is the linear static permittivity. We note that these expressions are for the contribution of the 'relaxor' degrees of freedom to the dielectric response. They give a low-frequency relaxation dispersion of ε'_l and ε''_l typical of relaxors, at frequencies below the gigahertz range. The lattice contribution is neglected in the discussion throughout the paper.
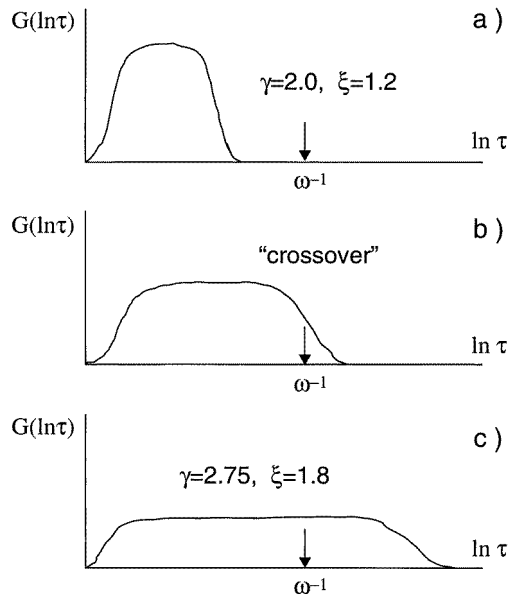

Figure 7. The correlation between the crossover in the field exponents γ and ξ of the non-linear dielectric response of a relaxor and the temperature evolution of the relaxation time spectrum $G(\ln \tau, T)$ which controls its linear dielectric response. A schematically shown relative position of the spectrum and the reciprocal frequency, $1/\omega$, of the ac driving field: (a) for the quasi-static regime; (c) for the regime in which the spectrum is perfectly flat; and (b) for an intermediate regime in which (a) changes to (c) upon cooling. The values of the field exponents γ and ξ are indicated in the figures. These exponents control the field dependence of the third harmonic of the polarization, $|P_3| \propto E_m^\gamma$, and the non-linear component of the dielectric permittivity, $\Delta\varepsilon'_\sim \propto E_m^\xi$.

Using equations (2) and (3), one can distinguish three separate regimes of the dielectric response, which are shown schematically in figure 7. If the spectrum is relatively narrow, with the result that its maximum relaxation time, τ_{max}, is smaller than ω^{-1}, the quasi-static regime is realized (figure 7(a)): from equations (2) and (3), one has $\varepsilon'_l = \varepsilon_s$ and $\varepsilon''_l = 0$, respectively. This corresponds to the behaviour of PMN at high temperatures.

With decreasing T, the spectrum $G(\ln \tau, T)$ broadens—that is, τ_{max} increases. When τ_{max} becomes larger than ω^{-1}, the frequency dispersion of both ε'_l and ε''_l appears (figure 7(b)). Finally, at low temperatures, the spectrum becomes almost flat (figure 7(c)). According to equations (2) and (3), this manifests itself in a logarithmic dependence [28] of the real part, ε'_l, and in a virtually frequency-independent [3, 29] imaginary part, ε''_l, of the permittivity. From the data presented above, one can conclude that these three regimes correspond exactly to the three regimes of the non-linear dielectric behaviour of PMN, which are also indicated in figure 7. Thus we see that the crossover in the field exponents γ and ξ is related to the temperature evolution of the relaxation time spectrum $G(\ln \tau, T)$ when the edge of the spectrum τ_{max} passes by the period $1/\omega$ of the ac driving field, the width of the crossover being controlled by the smearing of this edge.

4.2. Non-analytical dielectric non-linearity in the quasi-static regime

As is seen from figures 4(a) and 5(b), at high temperatures in the quasi-static regime, the non-linear component of the polarization is close to a quadratic function of the amplitude of the ac field:

$$|P_{nl}| \propto E_m^2. \tag{4}$$

However, for a macroscopically centrosymmetrical crystal such as PMN [5, 24], the symmetry arguments require that the polarization P should be a function of just the odd powers of the field E. This means that in the quasi-static regime, a weak non-linear dielectric effect can be described by the expansion

$$P = AE + BE^3 + \cdots \tag{5}$$

in which the coefficients A and B are independent of E. Therefore, the difference between the experimental fact, given by equation (4), and the phenomenological expansion, equation (5), implies that at high temperature we are dealing with a non-analytical non-linear dielectric behaviour of PMN. This behaviour persists down to the amplitudes of the field $E_m = 0.04$ kV cm^{-1} which is close to that used in standard small-signal dielectric measurements.

Let us discuss a possible origin of this phenomenon. Recently, a similar dielectric behaviour was reported by Lyons *et al* [22]. They observed that in disordered ferroelectric $KTa_{0.991}Nb_{0.009}O_3$ (KTN), the non-linear component of the polarization changed quadratically with the field, i.e., $\gamma = 2$, and they attributed this behaviour to a manifestation of the Rayleigh-type dynamics of two-level systems. Later, the Rayleigh law was observed for another ferroelectric material, lead zirconate titanate (PZT) [30, 31], for which it was related to the domain wall motion in the media with randomly distributed pinning centres. However, we argue that the interpretation in terms of the Rayleigh law cannot be applied to the case of PMN, even though in the quasi-static regime we have $\gamma = 2$ (figure 4(a)). The main argument is that the Rayleigh law, given by [22]

$$P(E) = (\varepsilon_0 \varepsilon'_l + \nu_R E_m)E \pm (\nu_R/2)(E_m^2 - E^2) \tag{6}$$

(ν_R is a Rayleigh coefficient, and '+' corresponds to increasing field and '−' to decreasing field), predicts that, for $E(t) = E_m \sin \omega t$, the higher harmonics $P_k(t)$ of the polarization should be in quadrature with the field, i.e., $P_k(t) \propto \sin(k\omega t + 90°)$, as was observed for KTN [22]. At the same time, in our experiments we observed $P_3(t) \propto \sin(3\omega t + 180°)$ when we had the exponent $\gamma = 2$ in the quasi-static regime; cf. figure 8 and figure 4(a).
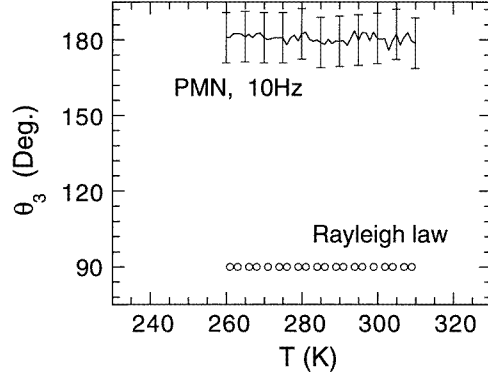
Figure 8. The phase angle θ_3 of the third harmonic of the polarization is defined from $P_3(t) \propto \sin(3\omega t + \theta_3)$ when the applied field is $E \propto \sin \omega t$. In the plot, the line shows the data for θ_3 for PMN at 10 Hz, at temperatures corresponding to the regime of the quasi-static dielectric response. The open circles show the value of $\theta_3 = 90°$ corresponding to the classical Rayleigh law, equation (6).

Table 1. Values calculated in terms of two models (represented by equations (6) and (7)) and measured experimentally for the following parameters: the exponents γ and ξ which control the field dependence of the absolute value of the third harmonic of the polarization, $|P_3| \propto E_m^\gamma$, and the non-linear component of the dielectric permittivity, $\Delta\varepsilon'_\sim \propto E_m^\xi$; the phase angle θ_3 of the third harmonic defined from $P_3(t) \propto \sin(3\omega t + \theta_3)$ when the applied field is $E \propto \sin \omega t$; and the ratio $\Delta\varepsilon'_\sim \varepsilon_0 E_m/|P_3|$.

	Rayleigh law	$P_{nl} \propto \pm E_m^2$	Experiment ($T = 280$ K)
γ	2	2	2
ξ	1	1	1.2
θ_3	90°	180°	180°
$\Delta\varepsilon'_\sim \varepsilon_0 E_m/|P_3|$	$15\pi/4 \approx 12$	5	18

The phase shift of 180° between the field and the third harmonic of the polarization observed in our experiments suggested to us considering another non-analytical expression for the polarization, namely

$$P = AE \pm BE_m^2 \tag{7}$$

where '+' corresponds to increasing field and '−' to decreasing field. One can easily check that the dielectric response controlled by this expression possesses a field exponent and a phase shift of the third harmonic which are both consistent with our observations (table 1). However, we found that equation (7) most probably does not describe our data. This conclusion was suggested by the comparison of the ratio $\Delta\varepsilon'_\sim \varepsilon_0 E_m/|P_3|$ calculated using equation (7) with that measured experimentally. According to equation (7), one has $\Delta\varepsilon'_\sim \varepsilon_0 E_m/|P_3| = 5$, whereas the experiment gives $\Delta\varepsilon'_\sim \varepsilon_0 E_m/|P_3| = 18 \pm 0.5$ (the data at $T = 280$ K and $\omega = 1$ kHz). A more detailed comparison of the two models discussed above, i.e. given by equations (6) and (7), and the experimental data is summarized in table 1. One can see that even on the phenomenological level these models cannot describe the non-analytical non-linearity of PMN.

Very recently, another type of non-analytical non-linear dielectric response has been

reported for PZT by Mueller and Zhang [32]. It was observed that P_{nl} scaled as follows:

$$P_{nl} \propto \left[(E - E_c)/E_c \right]^{\varphi}$$

where $\varphi \approx 2.2$ and E_c has the meaning of a threshold field. The authors interpreted these results in terms of the motion of randomly pinned domain walls. In their interpretation, they used the results of a theoretical analysis of the problem of the charge-density-wave (CDW) motion [33]. Concerning possible extension of this approach to a description of our results, several remarks should be made. First, in the framework of the 'breathing' model, in which the ac dielectric response is attributed to the field-induced vibrations of the polar region boundaries, there could be a relationship between our results and those reported in reference [32]. Second, being applied to the case of a quasi-static dielectric response in PMN, this approach would imply that the threshold field E_c should tend to zero when one reaches the quasi-static regime upon heating. This is consistent with the disappearance of the experimentally observed hysteresis loops in $P(E)$ in this regime [1, 6]. Third, even though the system of the charge-density wave, the results on which were employed in the discussion in reference [32], has some common features with the problem of interface pinning, it is very different from the latter. For example, the Hamiltonian studied in reference [33] cannot be used directly for the problem of the dielectric response of a randomly pinned interface. All in all, the origin of the non-analytical dielectric non-linearity in PMN might be related to the origin of the non-linear current response in a CDW system. However, at present, the theoretical results derived for the CDW can hardly be used for the interpretation of the data obtained for PMN until an adequate theory for relaxors is developed.

4.3. 'The breathing' model and the crossover in the field exponent

It has already been indicated in the introduction that many features of the dielectric response of PMN can be interpreted in the framework of the so-called 'breathing' model (d), and that this model looks the most realistic among the various options. However, at present, we are not aware of any exact theoretical result which could explain the crossover in the field exponents γ and ξ in this framework. Also, currently we are not able to develop an adequate theory of the non-linear phenomena discussed. But we can show that in the framework of the 'breathing' model a crossover of the dynamics of polar region boundaries is expected, and that it can be responsible for the experimentally observed crossover in field exponents of the non-linear dielectric response. Our arguments are given below.

The approach is based on the interface-roughening theory of randomly pinned interfaces [34]. In the previous work [18], we developed this approach for PMN and showed that it could successfully explain the large difference between the ac and dc non-linear effects. The idea of this approach is as follows.

According to the 'breathing' model [18, 20], the ergodic phase of PMN [35] is treated as a system of polar regions embedded in a non-polar matrix. They are elongated along the direction of the local spontaneous polarization, $\boldsymbol{P}_s$, the shape of which minimizes the effect of the depolarizing field. Polar regions have a fixed orientation in the crystal, along one of eight $\langle 111 \rangle$ pseudocubic directions allowed by the rhombohedral symmetry of the polar phase [5]. The orientation does not change under the thermal agitation. The polar region pattern is determined by the spatial distribution of the pinning centres (as has been pointed out in reference [13], the internal random fields induced by the charge disorder can act as a source of pinning centres in PMN). Following the interface-roughening arguments [34], due to the random distribution of the pinning centres, the interphase boundary between a polar region and the non-polar matrix will not stay flat. Instead, it will become 'rough' with a
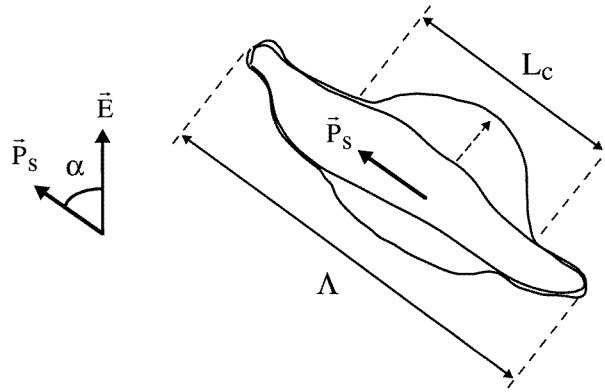
Figure 9. A schematic drawing of a polar region elongated along the direction of the local spontaneous polarization, P_s. Λ is the length of the polar region, and L_c is the scale on which the boundary of the polar region is effectively free. Application of an external electric field, E, produces a bending of the boundary on the scale L_c, and that gives the major contribution Δp_E (equation (8)) to the dielectric response of the material. For the single polar region, Δp_E depends also upon the angle α between the directions of P_s and E.

characteristic length scale L_c, which is determined by the spatial distribution of the pinning centres and elastic properties of the interphase boundary. In other words, if L_c is smaller than the length Λ of the polar region (figure 9), the boundary will not be able to move as a whole. The motion of the boundary will be determined by the motion of the 'free' pieces, of length L_c, each of them behaving as an elastic 'drum head'.

Now, the application of an external field E will exert pressure $(E \cdot P_s)$ on the interphase boundary. The bending of the 'free' piece, of length L_c, under the pressure will change the volume of the polar region (figure 9), and, therefore, also its dipole moment. Along the lines of reference [34], one can easily show [18, 20] that, for a small electric field, the dipole moment Δp_E induced in the direction of the field due to the bending of the interphase boundary of a single polar region can be written as [36]

$$\Delta p_E \propto E \frac{S P_s^2}{\Gamma} (\cos^2 \alpha) L_c^2 \tag{8}$$

where Γ is the surface tension of the interphase boundary, S is the area of the boundary, and α is the angle between the direction of P_s and E (figure 9). The total polarization, P, induced in the crystal will be equal to the average of the values of Δp_E for the individual polar regions:

$$P = V_{cr}^{-1} \sum_i \Delta p_{E,i}$$

where V_{cr} is the volume of the crystal.

Let us show now that in this model there is room for a temperature crossover in the dynamics of the interphase boundary motion which is accompanied by the disappearance of the frequency dispersion of the small-signal dielectric permittivity.

First, consider the origin of the frequency dispersion of the dielectric response within this model. According to reference [34], the bending of the interphase boundary is characterized by the relaxation time τ, which has the meaning of the time required to bend the piece of the boundary on the scale L_c. The longer the piece, the longer the relaxation time. Also, it

is assumed that, due to the randomness, both L_c and τ are characterized by the distribution functions. This will lead to the frequency dispersion of the induced polarization, P. The frequency ω of the applied ac field sets a characteristic time for measuring P equal to ω^{-1}. If one waits a longer time, the larger pieces, of length L_c, of the interphase boundaries can bend. Therefore, both Δp_E and P will increase with decreasing frequency of the ac field. The quasi-static limit is realized if the measurement time, ω^{-1}, becomes so long that for all of the polar regions $L_c \to \Lambda$ (where Λ is the size of the region itself; see figure 9). In this case, the polarization will not change if ω is reduced again, since Λ stops L_c from growing further. To calculate the dielectric response of the interphase boundary of a polar region in the quasi-static regime, in equation (8) one should, thus, substitute Λ for L_c (but noting the reservation of reference [36]).

Likewise, if one fixes the measurement frequency and reduces the temperature starting from the quasi-static regime, the length scale L_c will change because it is temperature dependent (according to reference [34], L_c decreases with decreasing temperature). At a certain temperature, one will have a drop in Δp_E and P (and in ε'_l too), because, for some polar regions, L_c will become smaller than Λ at a given ω, leading to a decrease in their contribution to the dielectric response. Note that the temperature dependence of Λ may also contribute to this phenomenon. Thus, there will be a frequency-dependent drop in $\varepsilon'_l(T)$, which is typically observed in relaxors; see, e.g., figure 1(c).

Let us consider now the response of the interphase boundaries to the ac field in the non-linear regime. Here one should note that the exact theoretical predictions (like those in reference [34] for the linear response) are still lacking. Nevertheless, in the regime of small non-linearity we still can try to use equation (8) in order to evaluate the trend. This can be done if we consider the length L_c of 'free' pieces to be dependent not only on ω and T, but also the ac-field amplitude, E_m. On the basis of the above picture for the linear response, one can expect the non-linear response to be qualitatively different in the quasi-static and frequency-dispersive cases.

In the regime with the frequency dispersion, the increase in the length L_c can be achieved either by decreasing ω or by increasing E_m. The reason for this is essentially the same: a depinning of the interphase boundaries by the applied field [14]. However, the situation is different in the absence of frequency dispersion. Here there is no possibility for a 'further' depinning of the interphase boundary, because on the scale Λ the boundary is assumed to be already 'free'. The non-linear effect will now be related to a growth of Λ itself. Even though the growth of the polar regions is also related to the motion of their interphase boundaries, the dynamics of the boundaries is quite different from that in the frequency-dispersive case. When $L_c < \Lambda$, the motion of the interphase boundary on scale L_c is essentially a motion at the bottom of a single potential well of the random pinning potential [34], whereas for $L_c > \Lambda$, it is an over-barrier motion. This is because now the size Λ of the moving interface becomes smaller than the scale on which the interface would be free if it were not restricted by the size of the polar region. We believe that these two cases can correspond to different types of field dependence of the non-linear response of PMN, $P_{nl}(E)$.

To summarize, within this picture, the observed crossover in the field dependence of P_{nl} can be related to the following regimes of the dynamics of the interphase boundary motion.

(i) At low temperatures, for which the field exponent γ is close to its classical value of 3, the dielectric response is controlled by the field-induced vibration of the polar region boundaries on a scale smaller than the size of the regions.

(ii) At high temperatures, in the quasi-static regime, for which the field exponent γ is

close to 2, the dielectric response is controlled by the field-induced breathing of the polar region as a whole.

(iii) A temperature crossover between the cases (i) and (ii) takes place when the maximal size of the polar regions becomes comparable with the scale on which the interface of the polar region can be considered as 'free'.

5. Conclusions

We have shown experimentally that the non-linear dielectric response of PMN relaxor ferroelectric has the following features:

(1) it is a non-analytical function of the field, with the absolute value of the non-linear component of the polarization given by $|P_{nl}| \propto E_m^{\gamma(\omega,T)}$;

(2) the dependence on the temperature, T, and frequency, ω, of the exponent γ manifests itself in the form of a crossover in $\gamma(T)$ from 2 to 3 upon cooling, whose position depends upon the frequency of the applied ac field;

(3) the crossover begins (i.e. γ starts growing from the value 2) simultaneously with the onset of the frequency dispersion of the dielectric response, and ends (i.e., γ becomes approximately equal to the value 3) when the spectrum of relaxation times in PMN becomes flat.

We indicated that the non-analytical behaviour of PMN is different from that of the Rayleigh dynamics [22, 30, 31], and thus requires another approach. We showed that this approach could be developed within the framework of the interface-roughening theory of randomly pinned interfaces [34], and demonstrated that it could explain the origin of the crossover in $\gamma(\omega, T)$ and its relationship to the frequency dispersion in PMN. Certain—important—details of the observed behaviour remain unexplained—namely, the exact forms of the field dependence of P_{nl} in the quasi-static ($\gamma = 2$) and frequency-dispersive ($\gamma \approx 3$) regimes. These details require a thorough theoretical investigation.

Acknowledgments

Appendix. The non-linear response due to the surface layer

As was indicated in section 3, a possible origin of the quadratic field dependence of the non-linear component of the polarization of PMN, which was observed at high temperatures, could be the surface of the sample. That is, there exists a near-surface layer in the sample, which contributes a component to the total induced polarization, which changes quadratically with the applied field, whereas the properties of the bulk of the sample are described by the 'normal' cubic field dependence, which is determined by the macroscopic cubic symmetry of PMN. Thus, the fact that at high temperatures the experimentally measured polarization changed as $|P_{nl}| \propto E_m^2$ could be explained by the fact that, at such temperatures, the properties of the surface determined the total non-linear dielectric response of the sample.
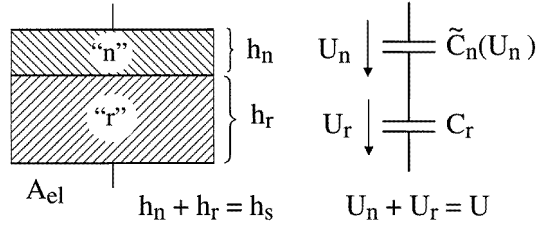
Figure A1. On the left: the double-layer structure, with one layer ('*r*') which represents the properties of the bulk material, and the other ('*n*') which represents the properties of the surface of the sample. On the right: an equivalent circuit consisting of two capacitors connected in series, which corresponds to the double-layer structure.

In order to investigate the effect of the surface, let us replace the sample with a double-layer structure (see figure A1) in which one layer, '*r*', represents the bulk properties of the material, and the second layer, '*n*', represents the surface of the sample. The behaviour of the double-layer structure can be described using an equivalent circuit consisting of two capacitors connected in series (figure A1), C_r and $\tilde{C}_n$, which correspond to the layers '*r*' and '*n*', respectively. The non-linear properties of the surface are taken into account by the fact that the capacitance of $\tilde{C}_n$ depends upon the applied voltage U_n (figure A1), whereas the bulk of the material gives only a linear contribution to the dielectric response; thus C_r is a linear capacitor. The behaviour of the equivalent circuit is described by the following equations:

$$Q_r = C_r U_r \tag{A1}$$

$$Q_n = \tilde{C}_n(U_n)U_n = C_n U_n \pm \psi U_n^2 \tag{A2}$$

$$Q_r = Q_n \tag{A3}$$

$$U = U_r + U_n \tag{A4}$$

where U_r and U are the voltages applied to the layer '*r*' and to the entire sample, respectively, and Q_n and Q_r are the charges of the two capacitors. In equation (A2), '+' corresponds to $U_n > 0$ and '−' corresponds to $U_n < 0$, and ψ is a constant. Thus, the response of the surface is modelled using $Q_n(U_n)$, which is a quadratic function of the applied voltage, centrosymmetrical with respect to the point $U_n = 0$; $Q_n = 0$, in order to maintain the symmetry of the total dielectric response of the sample. The linear capacitors in equation (A1) and equation (A2) have capacitances equal to $C_r = \varepsilon_r \varepsilon_0 A_{el}/h_r$ and $C_n = \varepsilon_n \varepsilon_0 A_{el}/h_n$, where the thicknesses of the bulk and surface layers are related by $h_r \gg h_n$. From equations (A1)–(A4), one can obtain the following equation for the equivalent circuit:

$$C_r(U - U_n) = C_n U_n + \psi U_n^2 \tag{A5}$$

where we limited ourselves to the case in which $U_n > 0$.

The response of the sample to the applied voltage U can be found by solving equation (A5) to find $U_n(U)$, and by substituting this solution into equation (A2) for Q_n. The solution of the quadratic equation, equation (A5), corresponding to the positive values of U_n, is equal to

$$U_n = \frac{\sqrt{b^2 + 4\psi U C_r} - b}{2\psi} \approx \frac{U C_r}{C_r + C_n}\left[1 - \frac{\psi U C_r}{(C_r + C_n)^2}\right] \tag{A6}$$

where $b = C_r + C_n$, and in the last step we performed a series expansion of U_n with respect to small U leaving only the first non-linear term in the brackets. After the substitution of U_n into equation (A2) and rearrangement of the coefficients, one can obtain (again, for the positive branch of $Q_n(U)$)

$$Q_n = U \frac{C_r C_n}{C_r + C_n} + \psi U^2 \frac{C_r^3}{(C_r + C_n)^3}. \tag{A7}$$

The first term on the right-hand side is the linear component of the charge induced on the electrodes of the sample. Since $C_r \ll C_n$, due to the difference in the thicknesses h_r and h_n, this term is equal to $C_r U$, which means that the linear dielectric response of the sample is totally determined by the properties of the bulk material. For the non-linear term, $Q_n^{nl} \propto U^2$, from equation (A7) we can obtain

$$Q_n^{nl} \approx \psi U^2 \left(\frac{C_r}{C_n} \right)^3 = \psi E^2 h_s^2 \left(\frac{\varepsilon_r}{h_r} \frac{h_n}{\varepsilon_n} \right)^3 \tag{A8}$$

where in the first step we neglected C_r compared to C_n in the denominator, and in the last step we substituted in C_r, C_n, and $U = E h_s$ (where E is the field applied to the sample, and h_s is the sample thickness, equal to $h_s = h_r + h_n$). Taking into account the fact that due to the small thickness of the near-electrode layer, $h_s \approx h_r$, and that the induced polarization is related to the charge as $P = Q_n / A_{el}$, we can obtain the final expression

$$P_{nl} = \frac{\psi}{A_{el}} \left[\frac{\varepsilon_r}{\varepsilon_n} h_n \right]^3 \frac{E^2}{h_s} \tag{A9}$$

which describes the dependence of the non-linear component of the polarization on the sample thickness, h_s.

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