# Simulation of nonlinear dielectric properties of polyvinylidene fluoride based on the Preisach model

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The nonlinear dielectric properties of a ferroelectric material were studied based on the concepts of the Preisach model. In this work, the ferroelectric polymer polyvinylidene fluoride was chosen as an example. The electric displacement $D$ in the material when subjected to a sinusoidal electric field of a given frequency was calculated by use of the Preisach model. Both in-phase and out-of-phase components as well as higher harmonics emerged naturally from the model calculation. $D$-$E$ loops at different field amplitudes were simulated and Fourier analyzed. The Fourier coefficients obtained were compared with the experimental data [T. Furukawa, K. Nakajima, T. Koizumi, and M. Date, Jpn. J. Appl. Phys., Part 1 **26**, 1039 (1987)]. Essentially, almost all the broad experimental features were reproduced by the simulations. This model is able to account for finer features than the theoretical model used in the original paper. 
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## I. INTRODUCTION

In most virgin ferroelectric materials, the piezoelectric and pyroelectric effects are not appreciable so that they cannot be used in many applications. One common method for solving this is to polarize the materials as highly as possible to magnify the effects. Many applications, such as precision machining, also require that ferroelectrics can be operated in high stress and high electric field. However, pronounced nonlinear dielectric properties and hysteresis behavior are evident in these conditions. Moreover, domain wall contribution to dielectric properties may also be investigated by studying the nonlinearities in ferroelectric behavior. For these and other reasons, there has been much research on the nonlinear dielectricity of ferroelectric materials. One traditional approach is to write the electric displacement or polarization as a Taylor series of electric field. The disadvantage is that this approximation is only adequate in the low field range. For instance, Taylor and Damjanovic[1] reported that the amplitude and phase angle of the first and third harmonic determined from minor polarization loops could not be predicted adequately by this approach, one reason being that the maximum field amplitudes considered were quite close to the coercive field of the material.

In another approach, some investigators use the Preisach model in the study of nonlinearity and hysteresis of ferroelectrics. In Turik,[2] the Preisach model was applied to ferroelectrics under weak field. The branches of hysteresis loop and the dielectric loss of ferroelectrics were written as analytical expressions. Hughes and Wen[3] applied the Preisach model to research hysteretic behavior of piezoceramics and shape memory alloys. Hall[4] mentioned that the Preisach model has been successfully employed in piezoelectric ceramics. Huo[5] suggested that the Preisach model was combined with the Landau theory of the first-order phase transition. Stress-strain curves and strain-temperature curves were simulated, and a good agreement was obtained with experiment. In this article, we attempt to simulate $D$-$E$ loops of polyvinylidene fluoride (PVDF), measured under sinusoidal electric field excitation, by use of the Preisach model and analyze both the in-phase and out-of-phase components of $D$ by Fourier transform to obtain nonlinear dielectricity information. The resulting Fourier coefficients are compared to the experimental data given by Furukawa *et al.*[6]

## II. PREISACH MODEL

The Preisach model[7] was proposed in 1935. In the 1970s and 1980s, the mathematical properties of the Preisach model were examined and developed by Krasnoselskii.[8] The Preisach model, transcribed for use in ferroelectrics, considers a material to be a collection of square-loop hysterons having two normalized spontaneous polarization states: $\mu=-1$ and $\mu=+1$, as shown in Fig. 1(a). Each hysteron is switched up if the external field $E$ is increased to a value greater than the switch-up field $U$ of the hysteron, and is switched down if the field is decreased to less than the switch-down field $V$ of the hysteron.

For an isolated hysteron, the critical fields for switching, $E_{crit}$ and $-E_{crit}$, must be the negative of each other. However, there is an interaction among hysterons inside a material so that their individual $P$-$E$ hysteresis loops are shifted along the $E$ axis. Therefore, $U$ and $V$ of each hysteron can be expressed as the sum of the critical field $\pm E_{crit}$ and interaction field $E_{int}$, i.e.,

$$U=E_{crit}+E_{int} \quad \text{and} \quad V=-E_{crit}+E_{int}. \tag{1}$$

 

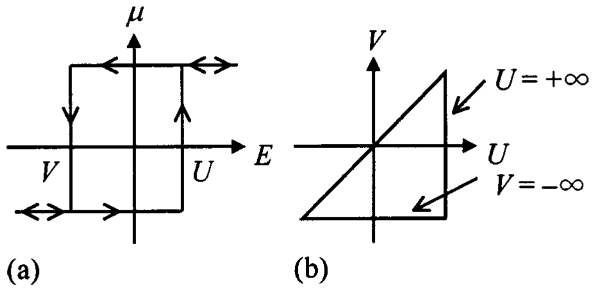


FIG. 1. (a) A single Preisach hysteron. (b) Preisach plane.

Thus $E_{\mathrm{crit}}$ and $E_{\mathrm{int}}$ are alternative coordinates for the Preisach hysterons.

For an aggregation of hysterons, both $E_{\mathrm{crit}}$ and $E_{\mathrm{int}}$ of individual hysterons may be distributed, the latter depend on their environment, leading to a distribution of $U$ and $V$. This distribution of hysterons characterizes a ferroelectric material and is described by the Preisach function $\xi(U,V)$. $\xi(U,V)dUdV$ represents the number per unit volume of hysterons with switch-up fields in the range $U$ and $U+dU$ and switch-down fields within the range $V$ and $V+dV$. $\xi(U,V)$ is defined over the Preisach plane, which is the $U$-$V$ plane with $U \geqslant V$, as shown in Fig. 1(b). With this definition, all hysterons are switched up if a sufficiently large field $E$ is applied to the material. Hence, the saturation polarization $P_s$ equals the sum of the "switch-up" state of hysterons and is given by

$$P_s=\int_{U\geqslant V}\int \xi(U,V)dUdV=\int_{-\infty}^{\infty}\int_{-\infty}^{U}\xi(U,V)dVdU. \tag{2}$$

The polarization of the material under a finite field generally is the sum of the integral of $\xi(U,V)$ weighted by $\mu=-1$ and $\mu=+1$ depending on the field history. To find the polarization change in the hysterons under an arbitrary field history, it is convenient to consider its trace on the Preisach plane. An example of such a construction is shown in Figs. 2 and 3. Let the field history be given in Fig. 2(a), where $\beta_1$ is a large negative field. The material is therefore first polarized by $\beta_1$ to negative saturation $-P_s$. When $E$ increases to $\alpha_1$ and is then decreased to $\beta_2$, the polarization $P$ of the material increases along the rising branch of the major hysteresis loop and then heads off to the inside of the loop. The corresponding $P$-$E$ curve is shown in Fig. 2(b). Figure 3 shows the construction on the Preisach plane in each step of the process. The field $E$ is initially decreased to $\beta_1$ (assumed to be a large negative number, say $-\infty$), thus switching all hysterons down. As $E$ increases progressively to $\alpha_1$, it switches hysterons having $U$ smaller than the instantaneous $E$ value to the up state; this action is representable by a vertical line sweeping along the $U$-axis changing hysteron states to $\mu=+1$ along its way. $E$ is then decreased to $\beta_2$; its action is representable by a horizontal line sweeping down the $V$-axis changing hysteron states to $\mu=-1$. It follows that the Preisach plane is divided into two parts $S^+$ where each hysteron has $\mu=+1$, and $S^-$ where each hysteron has $\mu=-1$. Mathematically, the overall polarization is given by

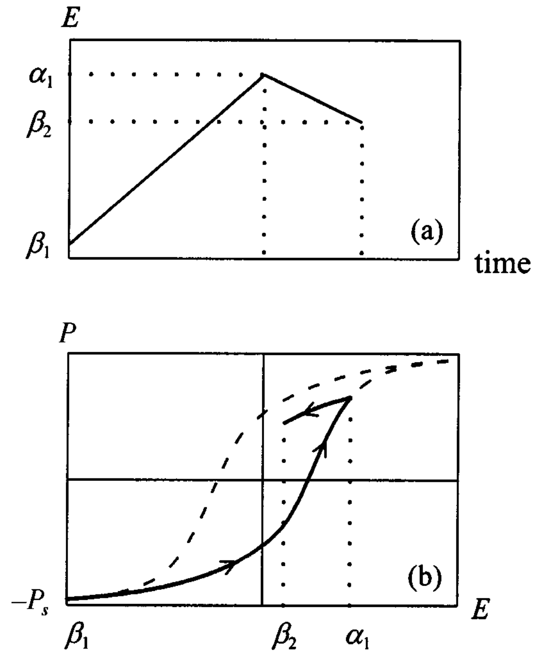


FIG. 2. (a) A field history is applied to a material in a poling process. (b) The solid and dashed line denotes the *P-E* history during the poling process and the major loop of the material, respectively.

$$\begin{aligned}P(E)&=\int\int_{S^+}\mu(U,V)\xi(U,V)dUdV\\&\quad+\int\int_{S^-}\mu(U,V)\xi(U,V)dUdV\\&=\int\int_{S^+}\xi(U,V)dUdV\\&\quad-\int\int_{S^-}\xi(U,V)dUdV.\end{aligned} \tag{3}$$

In this work, the Preisach function is divided into two components: irreversible and reversible components, i.e.,

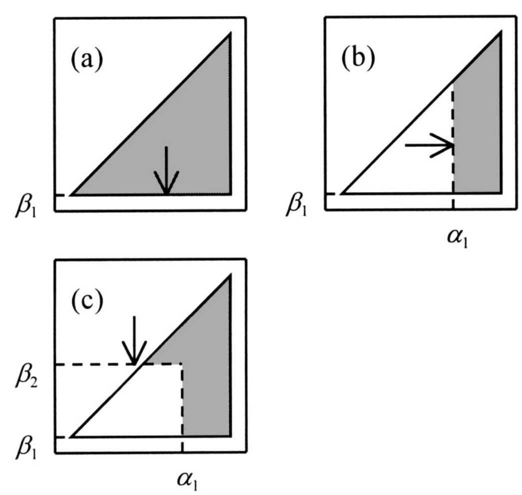


FIG. 3. The corresponding status represented on the Preisach plane after applying (a) $\beta_1$, (b) $\alpha_1$, and (c) $\beta_2$. The gray and white regions in the Preisach plane ($U \geqslant V$) denote the region in which $\mu=-1$ and $\mu=+1$, respectively.

$$\xi(E_{\mathrm{crit}},E_{\mathrm{int}})=\xi_{\mathrm{irr}}(E_{\mathrm{crit}},E_{\mathrm{int}})+\xi_{\mathrm{rev}}(E_{\mathrm{crit}},E_{\mathrm{int}}). \tag{4}$$

The irreversible Preisach function $\xi_{\mathrm{irr}}(E_{\mathrm{crit}},E_{\mathrm{int}})$ is assumed to be the product of a distribution of $E_{\mathrm{crit}}$ and a distribution of $E_{\mathrm{int}}$ and is given by[9]

$$\xi_{\mathrm{irr}}(E_{\mathrm{crit}},E_{\mathrm{int}})=SP_s\frac{E_{c0}}{\sqrt{2\pi}\sigma_c E_{\mathrm{crit}}}\exp\left[-\frac{\ln^2(E_{\mathrm{crit}}/E_{c0})}{2(\sigma_c/E_{c0})^2}\right]\times\frac{1}{\sqrt{2\pi}\sigma_i}\exp\left[-\frac{E_{\mathrm{int}}^2}{2\sigma_i^2}\right], \tag{5}$$

where $S$ is the weight of the irreversible component in the total polarization of the material, $\sigma_c$ describes the dispersion of the critical field, $\sigma_i$ is the standard deviation of the interaction field, and $E_{c0}$ is related to the maximum position of the distribution of $E_{\mathrm{crit}}$. The reversible Preisach function $\xi_{\mathrm{rev}}(E)$, which is only defined on the $E_{\mathrm{int}}$ axis, is given by[9]

$$\xi_{\mathrm{rev}}(E)=\frac{(1-S)P_s}{2\sigma_r}\times\exp\left[-\frac{|E|}{\sigma_r}\right], \tag{6}$$

where $E$ is the applied field, and $\sigma_r$ is the standard deviation of the exponential function.

This model is limited by its deletion property and congruency property.[10] The deletion property is that the output of a model is only affected by the alternating series of dominant input extrema. The effect of all other inputs is wiped out. The congruency property is that all minor loops between the same pair of external fields are congruent.

However, many materials generally do not observe the congruency property. For this reason, many modifications have been suggested. One of the modifications is the moving Preisach mode,[10] which can remove the congruency property. Mathematically, the polarization is expressed as

$$P(E)=\int\int_{S^+}\xi(E_{\mathrm{crit}}+\alpha P(E),E_{\mathrm{int}})dE_{\mathrm{crit}}dE_{\mathrm{int}}-\int\int_{S^-}\xi(E_{\mathrm{crit}}+\alpha P(E),E_{\mathrm{int}})dE_{\mathrm{crit}}dE_{\mathrm{int}}, \tag{7}$$

where $\alpha$ is the moving parameter.

## III. METHODOLOGY

In this work, the electric displacement $D(E)$ of a ferroelectric is written as $P+\varepsilon E$, where $P$, $\varepsilon$, $E$ are switchable polarization, permittivity, and field, respectively. Clearly, $\varepsilon$ may be determined from the slope of the $D$-$E$ relation in the "saturation" region where $P=P_s$. Suppose a sinusoidal field $E(t)=E_0\cos(\omega t)$ is applied on this nonlinear material. Using the Fourier transform techniques, the polarization $P$ and the electric displacement $D$ of a nonlinear dielectric can be expressed as

$$P(t)=P_0+\sum_{n=1}^{\infty}[P_n'\cos(n\omega t)+P_n''\sin(n\omega t)], \tag{8}$$

$$D(t)=D_0+\sum_{n=1}^{\infty}[D_n'\cos(n\omega t)+D_n''\sin(n\omega t)], \tag{9}$$

where $P_0$ and $D_0$ are constants, and $P_n'$ and $P_n''$ are the $n$th order Fourier coefficients of $P(t)$, and $D_n'$ and $D_n''$ are the $n$th order Fourier coefficients of $D(t)$. Since $D(t)=P(t)+\varepsilon E(t)$, the electric displacement is

$$D(t)=P_0+(\varepsilon E_0+P_1')\cos(\omega t)+P_1''\sin(\omega t)+\sum_{n=2}^{\infty}[P_n'\cos(n\omega t)+P_n''\sin(n\omega t)]. \tag{10}$$

Comparing Eq. (10) with Eq. (9), we have

$$\begin{cases} D_0=P_0 \\ D_1'=\varepsilon E_0+P_1' \quad \text{and} \quad D_i'=P_i' \\ D_j''=P_j'', \end{cases} \tag{11}$$

where $i\geqslant 2$ and $j\geqslant 1$. Note that the Presiach model can describe major as well as minor loops.[10] So, the $P$-$E$ loops of the material corresponding to sinusoidal excitations of different amplitudes can be calculated by using the Preisach model, and the Fourier coefficients of $D(t)$ can be analyzed by using Eq. (11). The $D_n'(E_0)$ and $D_n''(E_0)$ curves therefore can be simulated.

In the calculation of the polarization $P$, we use the Everett integral[8] defined as

$$\Psi(x,y)=\int_0^{(x-y)/2}\int_{y+E_{\mathrm{crit}}}^{x-E_{\mathrm{crit}}}\xi_{\mathrm{irr}}(E_{\mathrm{crit}},E_{\mathrm{int}})dE_{\mathrm{int}}dE_{\mathrm{crit}}+\int_y^x\xi_{\mathrm{rev}}(E)dE. \tag{12}$$

Consider a minor loop between the same pair of fields $E_0$ $-E_0$. The polarization of the loop at $E_0$ is

$$P(E_0)=\Psi[E_0+\alpha P(E_0),-E_0-\alpha P(E_0)]. \tag{13}$$

The descending ($P_{\mathrm{down}}$) and the ascending ($P_{\mathrm{up}}$) branches of the minor loop are given by

$$P_{\mathrm{down}}(E)=P(E_0)-2\Psi[E_0+\alpha P(E_0),E+\alpha P_{\mathrm{down}}(E)] \tag{14}$$

and

$$P_{\mathrm{up}}(E)=-P(E_0)+2\Psi[E+\alpha P_{\mathrm{up}}(E),-E_0-\alpha P(E_0)]. \tag{15}$$

## IV. EXPERIMENTAL NONLINEAR DIELECTRIC PROPERTIES OF PVDF

In Ref. 6, Furukawa *et al.* investigated the nonlinear dielectric properties of PVDF at 20 °C. Minor loops were traced using an electric field with frequency 0.8 Hz. When the field amplitude $E_0$ was less than 20 MV/m, the $D$-$E$ relation tended to be linear. As the amplitude was increased to values greater than 40 MV/m, the nonlinearity of the $D$-$E$ relation grew, as shown in Fig. 4 (solid lines). The coercive field $E_c$ of the PVDF was 75 MV/m and its remanent polarization $P_r$ was 60 mC/m$^2$. Then, these experimental $D(t)$ curves corresponding to different field amplitudes were analyzed by using digital Fourier transforms. The results are shown in Fig. 5 (open and closed circles).

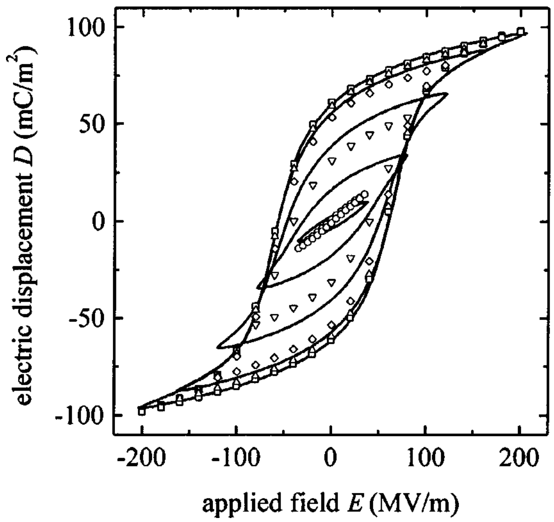


FIG. 4. *D-E* loops of PVDF at 20 °C. The simulation results (open symbols) are compared with experimental results in Ref. 6 (solid line).

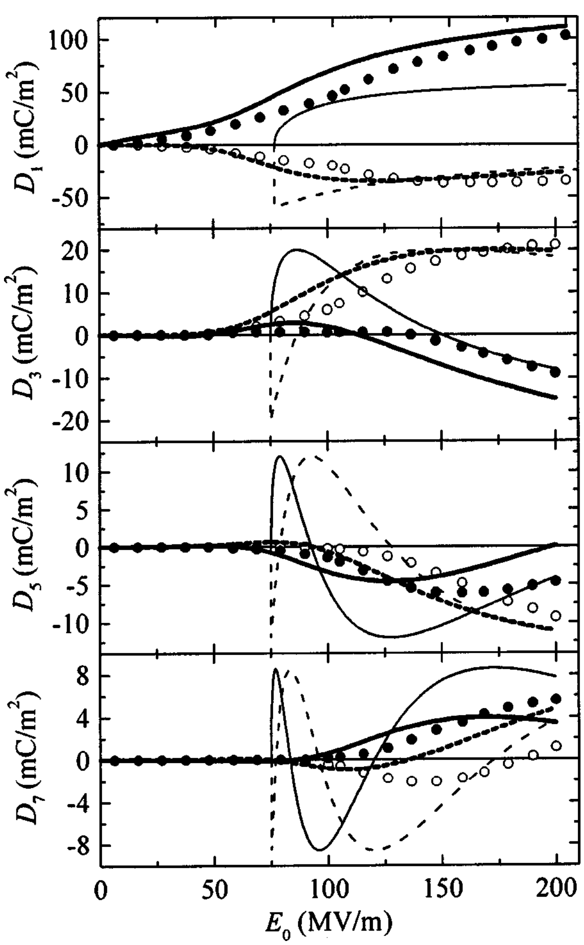


FIG. 5. Plot of in-phase, $D_n'$, and out-of-phase, $D_n''$, components of the first-, third-, fifth-, and seventh-order of $D$ against $E_0$ for PVDF. (●) and (○) denote the experimental $D_n'(E_0)$ and $D_n''(E_0)$, respectively. The thick solid (—) and dashed lines (- - -) and denote $D_n'(E_0)$ and $D_n''(E_0)$ simulated by using the Preisach model. The thin solid (—) and dashed lines (- - -) denote $D_n'(E_0)$ and $D_n''(E_0)$ calculated from Eqs. (16) and (17).

Furukawa *et al.* proposed a model to explain this behavior. They considered an ideal square *D-E* relation for the material. The displacement $D$ was switched up if the field $E$ was increased to a value greater than the coercive field $E_c$, and was switched down if the field was decreased to lesser than $-E_c$. Their method is as follows. The phase angle of the electric displacement $\delta_D$ is defined as

$$E_0 \sin \delta_D = -E_c, \tag{16}$$

where $E_0$ is the amplitude of $E$. Using the Fourier transforms, the Fourier coefficients are given by

$$\begin{cases} D_0 = 0; \\ D_n' = (P_r/n)\cos(n\delta_D), \quad n \geq 1; \\ D_n'' = (P_r/n)\sin(n\delta_D), \quad n \geq 1. \end{cases} \tag{17}$$

The $D_n'(E_0)$ and $D_n''(E_0)$ curves are calculated by using Eqs. (16) and (17) with $E_c = 75$ MV/m and $P_r = 60$ mC/m$^2$, as shown in Fig. 5 (solid and dashed lines).

## V. SIMULATION OF NONLINEAR DIELECTRIC PROPERTIES BASED ON PREISACH MODEL

Table I shows the Preisach parameters for PVDF fitted from the steady-state major hysteresis loop.[6] Using these parameters, the simulated *D-E* curves for the PVDF are compared with the experimental results,[6] as shown in Fig. 4. From Fig. 4, we see that for large $E_0$ the simulated $D(E_0)$ minor loop is larger than the experimental $D(E_0)$ loop. It is because, in the Preisach model, every minor loop must lie inside the major loop, but this is not strictly so with the experimental data here.

$D_n'(E_0)$ and $D_n''(E_0)$ may then be calculated from the simulated loops, as explained earlier. The $D_n'(E_0)$ and $D_n''(E_0)$ curves are shown in Fig. 5. For the first-order, third-order and fifth-order components, the broad experimental features are essentially reproduced by the simulations. However, this is not the case with the seventh-order curves. This is because it is quite impossible to find an accurate Preisach function which can reproduce all the fine structures of the experimental curves. From Fig. 5, it is seen that the experimental curve for the first-order in-phase component is lower than the simulated curve. This discrepancy is related to the limitation that the simulated $P(E_0)$ minor loops must be inside the simulated major loop.

In Fig. 5, by comparing our simulation results with results calculated from the original model used in Ref. 6, it is seen that the Preisach model gives reasonable $D_n'(E_0)$ and $D_n''(E_0)$ curves with $E_0 < E_c$ (75 MV/m), but the original model cannot. The sharp changes in the original model are missing in the Preisach model. Also, the curves based on the Preisach model are able to account for finer features than the original model.

## VI. CONCLUSIONS AND DISCUSSION

The nonlinear dielectric properties of PVDF is analyzed by the concepts of the Preisach model. *D-E* loops of different field amplitudes are simulated and Fourier analyzed. Both in-phase and out-of-phase components of the Fourier coeffi-

TABLE I. The Preisach parameters and permittivity of PVDF used in the simulation.

| $E_{c0}$ (MV/m) | $\sigma_c$ (MV/m) | $\sigma_i$ (MV/m) | $\sigma_r$ (MV/m) | $\alpha$ | $S$ | $P_s$ (mC/m$^2$) | $\varepsilon$ ($10^{-9}$ F/m) |
|---|---|---|---|---|---|---|---|
| 69.8 | 29.9 | 32.2 | 67 | 0.38 | 0.73 | 77 | 0.11[a] |

[a]Reference 6.

cients obtained are compared with the experimental data reported in Ref. 6. Essentially, almost all the broad experimental features are reproduced by the simulations. This model is able to account for finer features than the theoretical model used in the original paper.[6]

The model considered in the article by Furukawa *et al.* is a square *D*-*E* hysteresis loop with coercive fields $\pm E_c$ and remanent polarization $P_r$, where $E_c$ and $P_r$ are obtained from the experimental major loop of the PVDF material. When the amplitude of the applied field, $E_0$, is varied, the phase angle of $D$, $\delta_D$, changes. Using the technique of the Fourier analysis, both in-phase and out-of-phase components of the Fourier coefficients of $D$ are obtained and depend on $E_0$. Although the predictions of this model are more or less consistent with experiment in the high field range, it cannot describe the nonlinearity behavior at low field, especially $E_0 < E_c$. It is because the coercive field of the square *D*-*E* hysteresis loop in the model is a constant. If $E_0 < E_c$, then the applied field $E$ is impossible to switch the material and thus $\delta_D$ is not well defined. In the region near $E_c$, a sharp change of the Fourier coefficients of $D$ occurs due to the sudden dipolar switch in the model, however this is not the case in the experiment. Experimentally, a different *D*-*E* hysteresis loop is formed for any given amplitude of the applied field, leading to field-dependent $P_r$ and $E_c$. As a finer point, a fixed $P_r$ value limits $D_1'(E_0)$ to values smaller than $P_r$, so that in high field range the predicted $D_1'(E_0)$ comes out to be much smaller than the experimental value.

To understand the behavior of a ferroelectric material under arbitrary field magnitudes, it is important to have a model which can describe its major loop as well as *D*-*E* histories within. In our simulations, we use the moving Preisach model to simulate *D*-*E* loops with different field amplitudes. The model produces a sequence of *D*-*E* loops with increasing remanent polarization as the field amplitude increases from 0 to $E_c$ ($E_c$ is the coercive field of the experimental major loop). Sudden changes in the calculated $D_n'(E_0)$ and $D_n''(E_0)$ are avoided because of the gradual growth of hysteresis loops. Essentially, our simulations not only reproduce the broad experimental features of nonlinear dielectric behavior in ferroelectric PVDF, but also are indicative of the usefulness of the Preisach model in studying other ferroelectric responses.

## ACKNOWLEDGMENTS

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