The Power of Feedback: From Dielectric to Ferroelectric Systems

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Abstract—Dielectric properties can be described using a double well potential model as introduced in dielectric theory by H. Fröhlich. Charges and/or dipoles fluctuate thermally activated between two directions. Their transition probabilities depend on the local field.

For non-interacting double well systems we find the Debye response of relaxation. With increasing dipole density and/or increasing dipole moments an interaction between the dipoles becomes significant. The mutual dipolar fields alter the local fields at the dipoles and change their transition probabilities. We focused on two approximations for this interaction.

Following the ideas of P. Weiss for a macroscopic approach, the mean local field is influenced by the polarization itself. Using this average local field within the transition probabilities of the dipoles we get a feedback loop for the polarization resulting in a second order ferroelectric phase transition. Considering also the piezoeffect we get a first order transition. Furthermore we compute: the hysteresis loops of the polarization, for the first order transition the double hysteresis loops close to the Curie temperature $T_c$, and the susceptibility for different temperatures and fields. An intrinsic asymmetry of the double well potentials can change the ferroelectric behavior to a relaxor like behavior.

In the microscopic approach we calculate numerically the local field at each dipole. In systems between parallel electrodes the local field is the superposition of the applied field and the sum over the fields of all other charges and dipoles and their images. Here the feedback enters with the sum over all dipole fields into the computation. The orientations of permanent dipoles are calculated using a dynamic Monte Carlo scheme. Simultaneously the induced dipoles in the sample are considered and computed iteratively. We compute domains and nonswitchable dead layers at electrodes and defects. The switching process is calculated to depend at low fields on the formation of a reverted stable nucleus and in high fields on the domain wall propagation speed.

Keywords—Dielectrics, ferroelectrics, relaxor materials, modeling, local electric field

I. INTRODUCTION

The properties of a dielectric depend on the behavior of the microscopic dipoles in the material. The microscopic dipoles can be modeled with charges and/or dipoles which fluctuate thermally activated between two directions in double well potentials (Fig. 1) [1], [2]. Their transition probabilities depend on the local field $E_{loc}$ ($T$ temperature, $p$ dipole moment, $W_0$ activation energy, $1/\tau_0$ phonon frequency):

$$w = \frac{1}{\tau_0} \exp \left( -\frac{W_0 + \bar{p} \cdot E_{loc}}{k_B T} \right)$$

In contrast to a dipole having a positive and a negative charge, the dipole moment of a single charge $q$ is $p = q \cdot l/2$ with $l$ as the distance between the double wells.

The local field at an atom is the superposition of all fields affecting this atom. The calculation of the local field enables the computation of the dipole orientations and in this way the simulation of the dielectric properties.

In a first approximation, the interactions between dipoles are neglected: the local field is equal to the externally applied field. After that, we present two approaches to calculate the local field for interacting dipole systems, i.e. to take a feedback into account.

1) The Weiss mean field model with an interaction contribution to the mean local field. Here this contribution is proportional to the polarization.

2) A microscopic model, where the local field at each individual dipole is computed taking into account the fields of all other dipoles.

The interaction causes an impact of the polarization on itself. This feedback can lead to ferroelectric behavior of the system, e.g. spontaneous polarization, polarization hysteresis and polarization switching.

II. FIRST APPROXIMATION: NONINTERACTING DIPOLES

Neglecting the interaction, the dipoles are influenced only by the externally applied field: $E_{loc} = E_{ext}$. In this case the polarization contribution $P(\theta)$ of the dipoles with an angle $\theta$ to the applied field follows the Debye relaxation equation [2]

$$\tau(\theta) \frac{dP(\theta)}{dt} + P(\theta) = P_{sat}(\theta) \cdot \tanh \left( \frac{E_{loc} \cdot p \cdot \cos \theta}{k_B T} \right)$$

with the saturation polarization ($n(\theta)$ dipole density)

$$P_{sat} = n(\theta) \cdot p \cdot \cos \theta$$

![Fig. 1. Single charge in a double well potential. A microscopic dipole moment is caused by the displacement of the charge from the center of the other charges.](image)

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and the relaxation time
\[ \tau = \frac{\tau_0}{2} \exp \left( \frac{W_0}{k_B T} \right) / \cosh \left( \frac{E_{loc} \cdot p \cdot \cos \theta}{k_B T} \right) \]

(4)

Beside the potential energy due to the local field, a double well potential can also have an intrinsic asymmetry \( V \) (Fig. 2), e.g. in amorphous structures. In this case the polarization contribution of all dipoles with angle \( \theta \) and intrinsic asymmetry \( V \) follows Eqs. (2)-(4), with an additional potential energy contribution \( V \):
\[ E_{loc} \cdot p \cdot \cos \theta \rightarrow E_{loc} \cdot p \cdot \cos \theta + V \]

(5)

The total polarization is the sum over all polarization contributions:
\[ P_{tot} = \int \int P(\theta, V) \, d\theta \, dV \]

(6)

Even in a bidisperse system where half of the double well potentials have an intrinsic asymmetry \( -V \), half an intrinsic asymmetry \( +V \), the asymmetry changes the graphs of the polarization \( P(E_a) \) and of the static susceptibility
\[ \chi(E_a) = \frac{1}{\varepsilon_0} \frac{dP}{dE_a} \]

(7)

Fig. 3(a) shows the polarization and Fig. 3(b) exhibits the static susceptibility in electrical fields for different values of the asymmetry \( V \).

III. MEAN FIELD APPROACH: WEISS MODEL

The Weiss model was originally developed by P. Weiss [3], [4] to describe magnetic materials. The idea of a mean local field which depends on the polarization is a simple way to consider the interactions between the dipoles. This approach of a mean local field was also introduced in the theory of ferroelectrics [2], [5]. Here the mean local field is given by the superposition of the externally applied field and an interaction field proportional to the polarization:
\[ E_{loc} = E_a + \beta P \]

(8)

The coupling parameter \( \beta \) describes the strength of the interaction. A positive coupling parameter leads to a positive feedback of the polarization on itself: the polarization increases the local field which increases vice versa the polarization. Using the Weiss field (8) instead of \( E_{loc} = E_a \), the Eqs. (2)-(4) yield:

A. Ferroelectric behavior with a second order phase transition for symmetrical double wells,

B Relaxor behavior for double wells with intrinsic asymmetry \( V \),

C Ferroelectric behavior with a first order phase transition if the piezoeffect is considered.

A. Ferroelectric with second order phase transition

We get for the polarization \( P \) with \( E_a = 0 \) and \( V = 0 \)
\[ P = \frac{1}{\beta} E_{loc} = f_1 \]

(9)

and simultaneously from (2) and (3) with \( \theta = 0 \)
\[ P = np \tanh \left( \frac{PE_{loc}}{k_B T} \right) = f_2 \]

(10)

\( f_1 \) and \( f_2 \) have stable points of intersection, \( f_1 = f_2 \), for \( T < T_C \) and thus finite values for the spontaneous polarization. With (9) and (10) we get a Curie temperature \( T_C \) proportional to the coupling parameter \( \beta \) [6]:
\[ T_C = \frac{np^2}{k_B \beta} \]

(11)

In the paraelectric phase above the Curie temperature the susceptibility follows a Curie law (Fig. 4):
\[ \chi \propto (T - T_C)^{-1} \]

(12)

For \( \beta = 0 \), the case without interaction, we find \( \chi \propto 1/T \) as can be expected. Increasing \( \beta \) leads to a pole at \( T_C \).

Below the Curie temperature \( T_C \) a spontaneous polarization and a polarization hysteresis occur (Fig. 5).
Fig. 4. Occurrence of a ferroelectric phase due to the interaction. The susceptibility has a pole at the Curie temperature which is proportional to the coupling parameter. Dipole moment \( p = 5 \times 10^{-28} \text{ C} \cdot \text{m} \), dipole density \( n = 1.85 \times 10^{22} \text{ cm}^{-3} \).

Fig. 5. Weiss model simulations: Polarization hysteresis below the Curie temperature, paraelectric behavior above the Curie temperature which depends on the strength of the coupling between the dipoles. The static susceptibility exhibits a butterfly curve for \( T < T_C \). Dipole moment \( p = 5 \times 10^{-28} \text{ C} \cdot \text{m} \), dipole density \( n = 1.85 \times 10^{22} \text{ cm}^{-3} \).

B. Relaxor behavior due to an intrinsic asymmetry

So far all calculations for the interaction of dipoles started from double wells which are symmetrical if no field is applied and the polarization is zero (Eq. (8)).

Further properties can be calculated for asymmetric double wells with an intrinsic asymmetry \( V \). In Fig. 6(a) the result of the calculation for the susceptibility vs. temperature is shown. For \( V = 0 \) we would get the curves of Fig. 4. But in asymmetric double wells the static susceptibility increases with the temperature first before it decreases finally. If the feedback mechanism Eq. (8) is employed a pronounced increase of the static susceptibility is found. The frequency dependence results from the differential equation (2). We get for example in case of an asymmetry \( V = 30 \text{ meV} \) the curves depicted in Fig. 6(b) with the frequency as parameter. Thus the typical behavior of a relaxor is found.

C. Ferroelectric with first order phase transition due to piezoeffect

So far we have neglected the influence of the piezoeffect. With the piezoeffect characteristic lengths \( R \) in the material change with the polarization:

\[
R(P) = R_0 (1 + \lambda P)
\]  \hspace{1cm} (13)

\( \lambda \) is the piezoefficient. Also the distance between the wells in the double well potentials will change thus altering the dipole moments:

\[
p(P) = p_0 (1 + \lambda P)
\]  \hspace{1cm} (14)

Using (14) and (8) with \( E_a = 0 \) for the central equation (2) yields for \( \lambda = 0 \) a transition of the second order. For \( \lambda > 0 \) a transition of the first order for the spontaneous polarization is calculated. Fig. 7 depicts the transition for \( \lambda = 0 \) and \( \lambda > 0 \).

The first order phase transition of the spontaneous polarization in external fields is directly related to the appearance of a double hysteresis loop of the polarization close to the Curie temperature (Fig. 8) \[7\], \[8\]. This double loop was observed by W. Merz in barium titanate as early as 1953 \[9\]. Far below the Curie temperature \( T_C \) the conventional \( P(E_a) \) loop is observed. Close to \( T_C \) the single loop splits into the double loop and a further temperature increase yields a single curve for \( P(E_a) \).

IV. MICROSCOPIC APPROACH: MONTE CARLO METHOD

In the framework of the microscopic model, the local field at each single dipole is computed. The local field \( E_{i\text{loc}} \) at an individual dipole \( i \) is the superposition of the applied field, the fields \( E_{ij} \) of all other dipoles and charges and of the field
Fig. 7. The spontaneous polarization without piezoeffect ($\lambda = 0$) and with piezoeffect ($0 < \lambda = 0.1/(n \cdot p)$). $\lambda = 0$ yields a second order phase transition, $\lambda > 0$ a first order phase transition. Dipole moment $p = 5 \times 10^{-28}$ C·m, dipole density $n = 1.85 \times 10^{22}$ cm$^{-3}$.

$E_{images}$ of all image charges [10]–[12] and image dipoles [13], [14] at the electrodes:

$$E_{loc}^{i} = E_a + \sum_{j \neq i} E_{ij} + E_{images}$$  \hspace{1cm} (15)

In this way, all electric fields inside the sample are considered. In particular, this microscopic method enables the simulation of heterogeneous dielectrics, because all depolarizing fields are inherently considered via the computation of the local field.

The orientations of the displaced single charges or permanent dipoles in double well potentials are simulated using a dynamic Monte Carlo method [15]–[17]: In each Monte Carlo step the local field at each permanent dipole is computed according to (15). Then Eq. (1) yields the individual switching probability of each dipole. The probabilistic flip time of a dipole depends on its deterministic switching probability $w$ and on a random factor ($\xi \in (0; 1)$ random number):

$$t_{flip} = -w^{-1} \ln \xi$$  \hspace{1cm} (16)

Only the dipole with the shortest flip time switches its orientation. The system time is increased by this shortest flip time, and the polarization is calculated from the sum over all microscopic dipole moments.

Beside displaced single charges or permanent dipoles in double well potentials, we also considered fixed ions or atoms with an induced dipole moment [18], [19]. An induced dipole moment is proportional to the local field ($\alpha$ polarizability of the atom or ion):

$$p_{ind} = \alpha E_{loc}$$  \hspace{1cm} (17)

In each Monte Carlo step, all induced dipole moments are computed iteratively [13], [14]: The initial value for the local field at each induced dipole is given by the applied field. In each iteration step, the local field is calculated using the current induced dipole moments and the permanent dipole moments. The induced dipole moments are updated according to (17).

Ferroelectric behavior like polarization hysteresis or polarization switching requires a positive feedback of the polarization on itself. That means, the permanent dipole moments shall prefer parallel orientations. Induced dipoles between the permanent dipoles can cause such a positive coupling (Fig. 9) [20].

As an example, we simulated samples with a lattice structure motivated by barium titanate. Here the titanium ions fluctuate in double well potentials whereas the oxygen and barium ions have fixed positions and an induced dipole moment [19]. The Weiss model is based on the average local field which is linear in the polarization. Indeed our microscopic simulations yield such a linear relation: the average of the local fields at all displaced titanium ions is proportional to the polarization (Fig. 10) thus confirming the Weiss equation (8).
As a further example, we simulated the polarization switching of a dipole plane motivated by the (200) - plane of barium titanate. The plane contains a defect: one missing titanium ion and two missing oxygen ions in the center.

The simulations yield intrinsic dead layers at the electrodes and around defects (Fig. 11). The intrinsic dead layers consist of dipoles which are pinned by the electrostatic interactions and which cannot be switched even in very strong applied fields.

The intrinsic dead layers are nuclei for new domains during the polarization switching after the application of an external field (Fig. 12). Dipoles at the edge of the plane and beneath the dead layer have the highest probability to switch. If by chance two or three neighbor dipoles in a row are switched, they act as nuclei for the whole switching process. Then the dipoles in the row switch one after the other in a very short time. Afterwards next neighbor rows have a high probability to switch. In this way a reverted domain grows by switching of a dipole chain next to the domain wall: the domain wall moves as observed by several authors [21].

Fig. 13 shows the polarization during the switching process.

The reversal of one chain corresponds to a step of the polarization. Between the single steps, the polarization fluctuates: single titanium ions flip forth and back for a long time, until by chance a nucleus for the next chain reversal occurs. The time to build up a stable nucleus is much longer than the reversal time of a dipole chain. Therefore, we find in Fig. 13 plateaus and jumps of the polarization curve.

The switching time of the system is defined as the time until the polarization except the nonswitchable dead layers is reverted. It strongly depends on the applied field (Fig. 14). Our simulations reproduced the empirical law found by Merz [22], [23]: In small fields, the switching time shows a decrease stronger than exponential because of the long time needed to form a stable nucleus for a new domain:

$$\tau_{\text{sys}} \propto e^{E_1/E_a}, E_1 \approx 8.6 \text{ MV/cm}$$  \hspace{1cm} (18)

At high fields the time to switch can be approximated by

$$\tau_{\text{sys}} \propto (E_a - E_0)^{-1}, E_0 \approx 7 \text{ MV/cm}$$  \hspace{1cm} (19)

Here, the nucleation time is short and the speed of the domain walls rules the process.
V. CONCLUSION

The electrostatic interaction between the dipoles inside a sample strongly influences its dielectric properties. In particular, the dipole–dipole interactions generate a feedback of the polarization on itself. Such a feedback can cause relaxor behavior and ferroelectric behavior.

The interaction is considered with the method of local fields. The local fields at each dipole consist of the applied field and the interaction fields.

REFERENCES