

Modeling relaxor characteristics in systems of interacting dipoles



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ABSTRACT

We present a model which derives typical relaxor characteristics from simple and plausible microscopic assumptions. The model is based on charges which fluctuate thermally activated in double well potentials. The double well potentials are asymmetric due to disorder in the system. The electrostatic interaction between the charges is considered via a mean field approach. This model yields the typical relaxor features: we find high susceptibilities in a broad temperature range with dynamics following the Vogel–Fulcher law. In the framework of the model no spontaneous polarization arises at cooling without strong external field in accordance to experimental findings for relaxors. Furthermore the model yields hysteresis loops which depend on the amplitude of the external field and which become more and more thin and deformed above the maximum temperature of the susceptibility.

1. Introduction

Relaxors, due to their exceptional dielectric properties, are interesting candidates for many applications, e.g., in energy storage [1–4].

Typical relaxors have high susceptibilities, comparable to the susceptibilities in ferroelectrics. In contrast to ferroelectrics, where the susceptibility has a pole at the Curie temperature, relaxors have high susceptibilities in a broad temperature range [5–8]. The maximum of the susceptibility does not clearly mark a phase transition. The temperature dependence of the dynamics of the susceptibility in relaxors can be described by the empirical Vogel–Fulcher law [8–11].

In alternating fields with sufficient high amplitudes relaxors have polarization hysteresis loops like ferroelectrics [5,7]. This ferroelectric-like response slowly degenerates to the paraelectric response above the temperature of the maximum of the susceptibility [5,7]. Furthermore no spontaneous polarization occurs in relaxors without external field [5,7].

Relaxor characteristics have been observed e.g. in disordered perovskites [5,8] but also in polymers (e.g. defect-modified poly(vinylidene fluoride)) [1,12–14]. A common characteristic of all relaxor materials is disorder [6–8,11,15–17].

Dielectric properties can be simulated by a model based on charges fluctuating thermally activated in double well potentials [18]. In this work we extend this model by considering intrinsic asymmetries of the double wells caused by disorder in the system. In that way we derive a model which enables simulating the typical features of relaxors [19,20].

2. Model

The macroscopic dielectric properties depend on the behavior of the microscopic dipole moments in the material. In this work microscopic dipole moments are modeled with charges which fluctuate thermally activated in double well potentials (Fig. 1) [18]. The local electric field E_{loc} also deforms the double well potentials: each double well gets an extrinsic asymmetry $q \cdot R \cdot E_{loc}$ (q charge, R distance between the wells). In a first step to consider the effect of disorder in the material, we extend the model with intrinsic asymmetries of the double well potentials [19]. In contrast to the extrinsic asymmetry, an intrinsic asymmetry V is caused by heterogeneous surroundings and can exist even without external field or interactions. In Appendix B it is illustrated how this asymmetry can be deduced from electrostatic calculations.

The local electric field E_{loc} at a double well potential is the superposition of the externally applied field E_a and the fields of the other charges. For non-interacting systems E_{loc} is equal to E_a . To consider the electrostatic interactions inside the system we employ a mean field approach which was originally developed by Weiss [21,22] to describe magnetic materials and which was later successfully applied to ferroelectrics [18,23–26]. Here all double wells are influenced by the same mean local field E_{loc} which includes the applied field E_a and a mean interaction field proportional to the polarization P :

$$E_{loc} = E_a + \beta P. \quad (1)$$

The coupling parameter β describes the strength of the interactions inside the system. The linear relation between local field and polariza-

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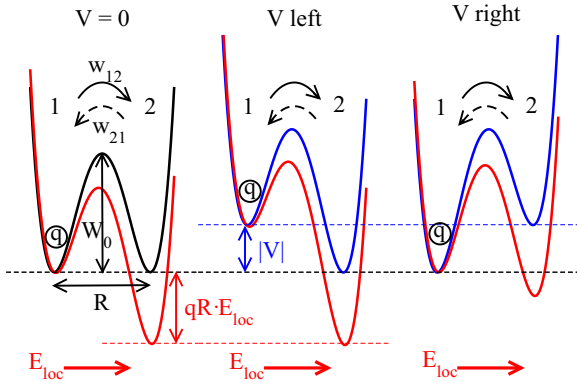


Fig. 1. Basic model element: A charge q fluctuates thermally activated in a double well potential (activation energy=barrier height W_0 , distance R of the wells). The potential can be symmetrical (black curve), $V=0$, or it has an intrinsic asymmetry V due to disorder in the sample (blue). The local electric field E_{loc} evokes an additional extrinsic asymmetry (red). The transition rates w_{12} and w_{21} depend on W_0 , on the intrinsic and extrinsic asymmetry and on the temperature T . (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

tion has been confirmed by microscopic Monte–Carlo simulations considering all electrostatic interactions (see Appendix A).

The macroscopic polarization P is given by the microscopic dipole moment $p = q \cdot R/2$ of the displaced charges and by the densities n_1 and n_2 of charges in well 1 or in well 2 respectively (Fig. 1): $P = p \cdot (n_2 - n_1)$. The densities follow the rate equations:

$$\frac{d}{dt}n_1 = -w_{12}n_1 + w_{21}n_2 = -\frac{d}{dt}n_2 \quad (2)$$

and the condition $n_1 + n_2 = n = const$ (n total density of the double wells). The transition rates w_{12} and w_{21} of the charges at the temperature T depend on the average barrier height W_0 and on the intrinsic and extrinsic asymmetries of the double well potentials ($1/\tau_0$ phonon frequency):

$$w_{12} = \frac{1}{\tau_0} \cdot \exp\left[-\frac{W_0 - (q \cdot R \cdot E_{loc} \pm V)/2}{k_B T}\right] \quad (3a)$$

$$w_{21} = \frac{1}{\tau_0} \cdot \exp\left[-\frac{W_0 + (q \cdot R \cdot E_{loc} \pm V)/2}{k_B T}\right]. \quad (3b)$$

Here V has a positive sign for an intrinsic asymmetry on the left side, a negative sign for an intrinsic asymmetry on the right side (Fig. 1).

The rate equation (2) yields for the polarization the relaxation equation [18,24]

$$\frac{d}{dt}P = \frac{1}{\tau}(P_\infty - P). \quad (4)$$

That means the polarization P depends on the equilibrium polarization

$$P_\infty(V, E_{loc}) = n \cdot p \cdot \tanh\left(\frac{q \cdot R \cdot E_{loc} \pm V}{2k_B T}\right) \quad (5)$$

and on the relaxation time

$$\tau(V, E_{loc}) = \frac{\tau_0}{2} \cdot \exp\left(\frac{W_0}{k_B T}\right) \Big/ \cosh\left(\frac{q \cdot R \cdot E_{loc} \pm V}{2k_B T}\right). \quad (6)$$

Without interaction and intrinsic asymmetry, (4) reduces to the classic Debye relaxation. With interaction between the charges P_∞ and τ in (4) are functions of the polarization itself via local field E_{loc} according to (1). In that way we have a feedback loop for P .

Generally one expects in disordered materials a distribution of barrier heights W_0 , of intrinsic asymmetries V , of distances R between the double wells and of angles θ between the field and the axis of the double wells. With a distribution of R and θ one has also a distribution of the effective microscopic dipole moments p . Because of the

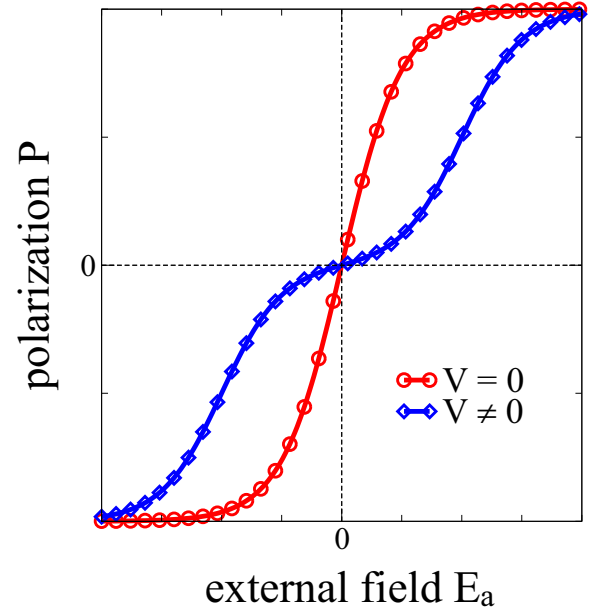


Fig. 2. Static polarization $P_\infty(V=0)$ of a system consisting of charges in symmetrical double wells and static polarization $P_\infty(+V) + P_\infty(-V)$ with $V \neq 0$ of a system with half left asymmetric double wells and half right asymmetric double wells. $P_\infty(V=0)$ according to (5).

distributions one has to solve a system of relaxation equations of the form (4) which differ in P_∞ and in τ according to Eqs. (5) and (6). The total polarization is the sum of all polarization contributions given by the different relaxation equations. All the relaxation equations are coupled via the local field which depends on the total polarization according to (1).

Here we consider a first simple approach for disordered systems where all charges in double wells have the same barrier height and cause the same effective dipole moment. The double wells differ only in the intrinsic asymmetry: 50% have an intrinsic asymmetry on the left side, 50% on the right side. With total dipole density n , a density $n/2$ belongs to left asymmetric double wells and the other half belongs to right asymmetric double wells. In this case the polarization is the sum of the contributions P_{left} and P_{right} of the charges in double wells with V on the left side and on the right side respectively: $P = P_{left} + P_{right}$. Each polarization contribution follows a relaxation equation of the form (4). The two relaxation equations differ in the sign of V in P_∞ and in τ according to Eqs. (5) and (6). Fig. 2 depicts qualitatively the static polarization for a system with symmetrical double wells and for a system with half left asymmetric double wells and half right asymmetric double wells. The electrostatic interaction between the charges couples the relaxation equations for P_{left} and P_{right} via the local field according to (1).

3. Computation method

In the static case, the time derivative of the polarization is zero and the differential Eq. (4) reduces to the algebraic equation

$$P_\infty(P) - P = 0. \quad (7)$$

The static susceptibility is computed from the static polarizations, i.e. the solutions of (7), via (here: $\Delta E_a = 10^{-12}$ MV/cm)

$$\chi_{stat} = [P(\Delta E_a) - P(-\Delta E_a)]/(2\Delta E_a). \quad (8)$$

The integration of the relaxation equations (4) for all polarization contributions yields the dynamic polarization $P(t)$ in the time domain.

In this work we also present computation results for the ac – small signal response. To that we apply an oscillating external field with a frequency f and with a small amplitude \hat{E}_a :

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