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Simulation of thermally stimulated polarization current (TSPC) based on the Frohlich two-state model and the complexity of the amorphous phase

George Collins

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Abstract Numerical simulations of thermally stimulated polarization current profiles have been performed using rate expressions based on the Frohlich two-state model. The qualitative behavior of simulations previously published by other researchers can be reproduced. The important feature examined is a peak in the evolution of polarization with temperature, which results in a change in sign for the polarization current profile. The previous researchers have assigned this to a crossover of the kinetic transient polarization with the equilibrium polarization described by the Langevin approximation. The origin of the peak in the evolution of polarization has been reexamined and found to be the kinetic consequence of the structure of the Frohlich model. When the field is applied, the two-state model requires that half the available dipoles are initially polarized. This high level of polarized dipoles contributes to an increased rate of the reverse process, depolarization, at high temperatures and results in the calculated decrease in polarization. The constraints of the Frohlich two-state model are too severe to represent the kinetics of a physically plausible polar solid. Further the multiple modes of aggregation in the amorphous state impose complications on the computation of polarization current.

Keywords Thermally stimulated polarization current · Thermally stimulated current · Frohlich model · Polarization simulation

Introduction

Thermally stimulated current, TSC, is the general term applied to a category of thermal analysis techniques that involve the measurement of current generated by the temperature activated relaxation of charged structures in response to the application of a static electric field. For organic materials, the basic unit of material structure is the molecule, and in the idealized description of the behavior of molecular materials, the charged structure of interest is the structural dipole. The application of a static electric field to a molecular material results in a torque stress on the structural dipoles that tends to displace them in a manner that brings them in alignment with the electric field. That alignment reduces the stress on the dipole and thus is referred to as a dipole relaxation. The physical motion involved in the reorganization of the molecular dipoles that occurs as a result of this stress can be experimentally detected a dipole displacement current.

Thermally stimulated polarization current, TSPC, is the term most often given to experiments that involve the observation of current generated as the dipolar structures orient in response to the application of the field [1]. Thermally stimulated depolarization current, TSDC, is the term given to experiments that involve the observation of the current generated when the static field is removed and the dipolar structures fall away from the orientation imposed by the previous application of the field [2]. Both these techniques are non-isothermal in that the displacement current is observed as a function of temperature. It must be pointed out that in response to the applied electric field, only the mobile dipoles can respond. The mobile dipoles will be those dipoles in the amorphous phase of a material.

G. Collins (✉)
Department of Biomedical Engineering, Medical Device Concept Laboratory, New Jersey Institute of Technology, 111 Lock St, Newark, NJ 07103, USA
e-mail: collins@adm.njit.edu

Based on what is available in the technical literature, TSDC has been much more widely applied to research in solid materials than TSPC [3, 4]. Irrespective of this difference in the number of articles available, both techniques involve polarization. In TSDC, the dipoles must first be polarized in order to observe a depolarization, and in TSPC, it is the polarization that is observed directly. Because the initial state of the dipoles is well defined in TSDC experiments, quantitative descriptions of depolarization have been developed. In TSPC experiments, however, there is an ambiguity on the initial state of the dipoles which imposes a difficulty on the development of computational models for polarization. A detailed understanding of the factors controlling polarization of structural dipoles in the molecular framework of solid organic materials would be fundamentally useful for interpreting results from TSPC experiments.

Theory

Frohlich [5] has summarized the simplified, basic theory of the behavior of dipoles in the solid state in the presence of an electric field in his classic monograph. In the Frohlich treatment, the dipoles are considered to have two equilibrium positions with opposite directions separated by a potential barrier. An electric field is applied in the direction on one of the dipoles, which means that the other dipole is 180° opposed to the direction of the field. His analysis proceeds to articulate the factors that control the transition of the dipole from one direction to the other with respect to the field.

The essential features of the analysis are represented in Fig. 1. Before the field is applied, the bistable Frohlich model is depicted in terms of two configurations, State 1 and State 2, with the same potential energy. The transition from State 1 to State 2 or from State 2 to State 1 requires the input of sufficient energy to surmount the potential energy barrier indicated by the solid curve with height E_0. The rate of transition from one state to the other can be expressed in terms of the statistical formalisms from transition state theory [6]. Using this structure, rate of change of the number of dipoles from State 1 to State 2 and from State 2 to State 1 can be expressed as

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -N_1\upsilon_0\mathrm{Exp}\left(-\frac{E_0}{kT}\right) + N_2\upsilon_0\mathrm{Exp}\left(-\frac{E_0}{kT}\right) \tag{1}$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = N_1\upsilon_0\mathrm{Exp}\left(-\frac{E_0}{kT}\right) - N_2\upsilon_0\mathrm{Exp}\left(-\frac{E_0}{kT}\right) \tag{2}$$

where N_1 and N_2 are the number densities of idealized dipoles in configuration 1 and configuration 2, respectively. Since these two dipoles differ only in their relative directions, the pre-exponential factor, v_0, is taken to be the same for transitions in both directions.

Frohlich simplifies these relationships and maintains uniform charge distribution for the physical system before the field is applied by assuming the following relationships.

$$N_0 = N_1 + N_2 \tag{3}$$

$$N_1(t=0) = N_2(t=0) = \frac{N_0}{2} \tag{4}$$

Before the field is applied, the rate of transmission from State 1 to State 2 is the same as the rate of transmission from State 2 to State 1. As a consequence, there is a kinetic steady state with no net accumulation of one state or the other. There is no preferred state, and in the absence of a field, polarization cannot be defined. It is only when the field is applied that this situation is altered.

The electric field and the dipole have a directional nature to them, and thus are described as vectors. These directional aspects are manifested in the physical interaction of the dipole with the field. A stress is imposed that tends to orient the dipole in the direction of the field. In the Frohlich analysis, the field is taken to be in the direction of the dipole in State 2. In Fig. 1, the dotted lines for States 1 and 2 represent the impact of the field on the potential energy each of the configurations. Because the field is directional, it affects dipoles in State 1 and State 2 differently. In the direction opposite to the field, State 1, the initial potential is destabilized by the μf, where μ in the dipole moment and f is the electric field. In the direction of the field, State 2, the potential energy is lowered by the amount μf. State 1 and State 2 no longer differ only by direction, they also differ by potential energy. In the presence of the field, State 2 is more stable and can be defined as the polarized state. The activation energy for the transition of State 1 to State 2 is now $(E_0 - \mu f)$, and the

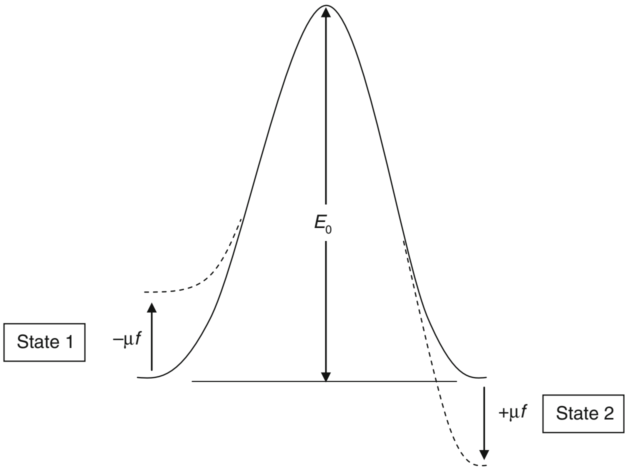

Fig. 1 Potential energy diagram for the Frohlich two-state model of dipoles in the solid state

activation energy for the transition of State 2 to State 1 is now ($E_0 + \mu f$). Polarization will be retained because, in the presence of the field, the height of the barrier for loss of polarization is higher.

Using these new values for activation energy and the conditions represented in Eqs. 3 and 4, Eqs. 1 and 2 can be rewritten as

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -N_1\upsilon_0\mathrm{Exp}\left(-\frac{(E_0-\mu f)}{kT}\right) + (N_0-N_1)\upsilon_0\mathrm{Exp}\left(-\frac{(E_0+\mu f)}{kT}\right) \tag{5}$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = (N_0-N_2)\upsilon_0\mathrm{Exp}\left(-\frac{(E_0-\mu f)}{kT}\right) - N_2\upsilon_0\mathrm{Exp}\left(-\frac{(E_0+\mu f)}{kT}\right) \tag{6}$$

In the Frohlich model, polarization is given as proportional to ($N_2 - N_1$); more specifically, the time dependence of polarization in the presence of a field will be given by

$$P(t) = \mu(N_2(t) - N_1(t)) = \mu(N_0 - 2N_1(t)) = \mu\left(N_0 - 2\int_0^t \frac{\mathrm{d}N_1}{\mathrm{d}t}\right) \tag{7}$$

Using the assumptions of this model, Eq. 7 provides a means to calculate polarization. Expressed in this manner, the evolution of polarization with increasing temperature is defined in terms of the loss of unpolarized dipoles.

Simulation of thermally stimulated polarization current

Equation 5 can be rearranged to a more convenient form,

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = \left[-N_1\mathrm{Exp}(\frac{\mu f}{kT}) + (N_0-N_1)\mathrm{Exp}\left(-\frac{\mu f}{kT}\right)\right] \times \upsilon_0\mathrm{Exp}\left(-\frac{E_0}{kT}\right) \tag{8}$$

Vanderschueren et al. [7, 8] have used an expression similar to Eq. 8 to implement a numerical simulation of polarization. The expression they used has the form (see Eq. 3, reference [8]),

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = \left[-N_1 + (N_0-N_1)\mathrm{Exp}\left(-\frac{\mu f_\mathrm{v}}{kT}\right)\right]\upsilon_0\mathrm{Exp}\left(-\frac{E_{\mathrm{v}0}}{kT}\right) \tag{9}$$

where $E_{\mathrm{v}0}$ and f_v, respectively, are the activation energy and electric field as formulated in the Vanderschueren treatment. Equations 8 and 9 will yield identical results as long as the barrier height and field are chosen in a manner such that

$$\frac{E_0-\mu f}{E_0+\mu f} = \frac{E_{\mathrm{v}0}}{E_{\mathrm{v}0}+\mu f_\mathrm{v}} \tag{10}$$

Recognizing this similarity, the analysis can proceed using the Vanderscheuren expressions.

Thermally stimulated polarization current is a thermal analysis method that profiles the evolution of polarization as the temperature of the test specimen is uniformly increased using a linear heating program. The heating rate can be specified as

$$T = T_0 + \beta t \tag{11}$$

where T_0 is the initial temperature and β is the linear heating rate. By employing the differential relationship known as the chain rule, Eq. 9 can be expressed in terms of the change in temperature,

$$\frac{\mathrm{d}N_1}{\mathrm{d}T} = \frac{\mathrm{d}t}{\mathrm{d}T}\frac{\mathrm{d}N_1}{\mathrm{d}t} \tag{12}$$

$$\frac{\mathrm{d}N_1}{\mathrm{d}T} = \frac{1}{\beta}\left[-N_1(T) + (N_0 - N_1(T))\mathrm{Exp}\left(-\frac{\mu f_\mathrm{v}}{kT}\right)\right] \times \upsilon_0\mathrm{Exp}\left(-\frac{E_{\mathrm{v}0}}{kT}\right) \tag{13}$$

Equation 13 has been written to explicitly indicate that N_1 is a function of temperature. The polarization as a function of temperature can be expressed using Eq. 7,

$$P(T) = \mu(N_0 - 2N_1(T)) = \mu\left(N_0 - 2\int_0^t \frac{\mathrm{d}N_1}{\mathrm{d}T}\right) \tag{14}$$

In TSPC experiments, it is the polarization current that is detected and not the polarization. As stated in the "Introduction" section, the incremental polarization current originates from the motion of the dipole as it changes its configuration from its initial direction to the direction in alignment with the field. This allows the polarization current to be expressed in terms of the rate of change in polarization,

$$j(T) = \frac{\mathrm{d}P(T)}{\mathrm{d}t} = \frac{\mathrm{d}T}{\mathrm{d}t}\frac{\mathrm{d}P(T)}{\mathrm{d}T} = -2\beta\mu\frac{\mathrm{d}N_1}{\mathrm{d}T} \tag{15}$$

Using appropriate values for N_0, v_0, $E_{\mathrm{v}0}$, μ, f_v, and β, the behavior of a TSPC experiment can be simulated.

Analysis of theory and simulation

The numerical solution of Eq. 13 has been implemented using the NDSolve object in Mathematica 3.0 [9]. This utility allows $N_1(T)$ to be determined at specified values of T. Using this method and the values for the parameters listed in the Vanderschueren publications, the qualitative features of the simulated TSPC reported previously could be reproduced.

Figure 2a shows the calculated evolution of polarization with increasing temperature. Figure 2b shows the simulated TSPC that results from that evolution according to Eq. 15. The calculated behavior reported here is qualitatively similar to Fig. 1 in reference [8]. The important feature of the Vanderschueren simulation and the simulation given in Fig. 2 is the calculated increase in polarization followed by a decrease, resulting in a peak in the polarization profile. The impact of this on the TSPC is to produce a negative current at high temperature, because the $dP(T)/dT$ changes sign.

It is of primary interest to understand the origin of the TSPC current reversals embodied in the kinetic equations. The Vanderschueren researchers have asserted that the peak in polarization that produces the current reversal occurs at the temperature where the numerically calculated buildup in polarization is the same as the polarization calculated from the approximation of the Langevin formulation of the equilibrium polarization. In their view, there is a crossover from behavior controlled by discrete kinetics to behavior controlled by a temperature-dependent equilibrium in a continuum. Implicit in this assertion is that there is a change in the behavior of the system of such magnitude that it imposes a change in the model required to describe it.

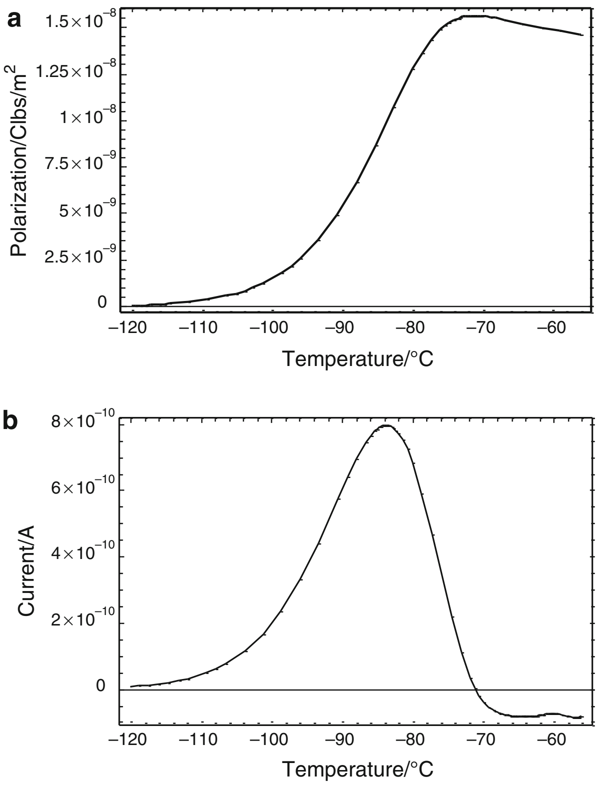

Fig. 2 **a** Polarization calculated using Eq. 14 with parameters from Vanderschueren et al.: $N_0 = 2.0 \times 10^{25}/\text{m}^3$, $N_1(0) = 0.50N_0$, $v_0 = 2.5 \times 10^9$ Hz, $E_{v0} = 0.4$ eV, $\mu = 6.60 \times 10^{-30}$ Clbs m, $f_v = 10^5$ V/m and $\beta = 1$°K/min, $k = 1.38 \times 10^{-23}$ J/°K. **b** Current calculated using Eq. 15

That there is a peak in the polarization calculated in this manner cannot be questioned, but the reason for it must be examined more closely because of its fundamental importance in understanding how this model describes orientational polarization. The Frohlich two-state model is an extreme idealization of a dipolar solid. It requires that the dipoles exist only in one of two discrete states. The numerical simulation of polarization using the conditions of this model is discrete in the sense that polarization is calculated by counting the number of dipoles that change their state to the polarized direction. The Langevin formulation of equilibrium polarization starts with randomly oriented dipoles that are free to continuously rotate into the direction of the field when it is applied opposed only by thermal agitation. The Langevin polarization expression applies to gases and low viscosity liquids in thermal equilibrium [10]. It would seem that a transition of the system of dipoles from the discrete behavior of an assumed solid state configuration to the free rotation of gases or low viscosity liquids would imply the occurrence of a phase transition. The computation of polarization current in this treatment and the Vanderschueren treatment is performed under non-isothermal conditions over a temperature range within which the only changes allowed are those determined by the initial conditions and the given kinetic equations. On this basis, the Vanderschueren assertion must be questioned.

The polarization defined by Eq. 14 depends on $N_1(T)$. Figure 3 shows the calculated values of $N_1(T)$ and $N_2(T)$ as functions of temperature. In Fig. 3a, the numerical simulation clearly indicates that the density of N_1 dipoles decreases and then increases within the constraints to the Frohlich model. Figure 3b shows that the N_2 dipoles increase and then decrease. In terms of the kinetics, this can occur because the rate of the reverse process, State 2 to State 1 in Fig. 1, becomes larger than the forward process at higher temperature. The number of dipoles in each state and the transmission rate over the barrier in each direction controls the rate in either direction. Examining the initial conditions for the number of dipoles in each state, a severe constraint of the Frohlich bistable model is revealed. The Vanderschueren simulation and the simulation reported here in Fig. 2 started with the initial dipole densities as represented in Eq. 4, which means that half of the initial density was in one configuration and half was in the opposite configuration. With this constraint, it is unavoidable that half the available dipoles are in the polarized state when the field is applied. The stress of the field initially causes a further accumulation of dipoles in the polarized state, but at higher temperatures, the kinetic condition of a high number of dipoles in the polarized state and a high reverse transmission rate results in polarized dipoles being converted to the unpolarized state.

This kinetic situation can be explicitly examined by evaluating the rate of each component. The rate of conversion of unpolarized dipoles to polarized dipoles as a function of temperature is given by Eq. 13. Since this is a two-state model, the rate of conversion of polarized dipoles to unpolarized dipoles is simply the negative of Eq. 13,

$$\frac{\mathrm{d}N_1}{\mathrm{d}T} = -\frac{\mathrm{d}N_2}{\mathrm{d}T} \tag{16}$$

In Fig. 4, the calculated rates of formation for polarized and unpolarized dipoles are plotted together. The derivative of Eq. 14 with respect to temperature will give Eq. 15 with the heating rate factor, β, removed. It is clear from this derivative that polarization will increase as long as $\mathrm{d}N_1/\mathrm{d}T$ is negative. If $\mathrm{d}N_1/\mathrm{d}T$ becomes positive, polarization will decrease. In Fig. 4 at about −71 °C, the sign of $\mathrm{d}N_1/\mathrm{d}T$ changes from negative to positive. It is clear from the crossover of the rates at this temperature that the rate of generation of unpolarized dipoles becomes greater than the rate of generation of polarized dipoles. The consequence of this is a peak in the evolution of polarization with temperature as observed in Fig. 2a.

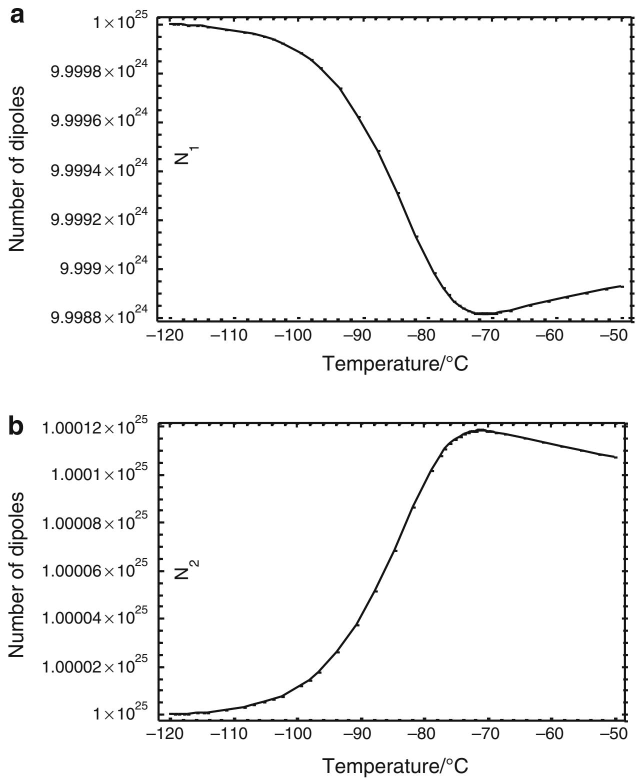

Fig. 3 **a** Number density of unpolarized dipoles, N_1, as a function of temperature. **b** Number density of polarized dipoles, N_2, as a function of temperature

The overall process changes from increasing polarization to decreasing polarization. The peak in the temperature evolution of the polarization is kinetic in origin. It represents the temperature-induced shift in the kinetic ratio of the forward and reverse processes. Polarization is lost to maintain the kinetic conditions as defined by the model equations at the higher temperatures. No changes in the model are required to account for this behavior. This situation is encountered because in the Frohlich model, when the field is applied, half the dipoles are already polarized.

The constraint represented by Eq. 4 is too severe for a semi-quantitative description of physically plausible solids. In no typical real solids are half the dipoles already polarized when the field is applied. The difficulty can easily be shown by varying the initial number density of the unpolarized dipole, $N_1(0)$. If $N_1(0)$ is increased, it means that in the initial state, there are a higher number of dipoles that are opposed to the field than are aligned with the field. Figure 5a shows the behavior of the calculated polarization with $N_1(0) = 0.51N_0$. It is immediately obvious that this small increase in $N_1(0)$ eliminates the previously observed peak in the evolution of polarization. The absence of that peak is reflected in the TSPC shown in Fig. 5b that does not change sign over the calculated temperature range. It should be noted that, however, the polarization in Fig. 5a is negative over the entire calculated temperature range. This is a direct consequence of polarization defined by Eq. 14, which reflects the Frohlich constraints. If $N_1(0) > 0.50N_0$, then the initial charge is not uniformly distributed. There exists a net initial polarization in the direction opposite to the applied field.

A more dramatic consequence of the Frohlich constraints can be observed if $N_1(0) < 0.50N_0$. Figure 6a shows the calculated polarization with $N_1(0) = 0.49N_0$. Under these conditions, once again, the initial charge is not uniformly distributed. There is an excess of dipoles initially in the direction of the field. The calculated kinetic adjustment of this system is to reduce the number of dipoles in the field direction. The result shown in Fig. 6a is that polarization does not occur. Only loss of polarization is the calculated result. The current observed in Fig. 6b is not a polarization current. It is a depolarization current and, by the Vanderschueren convention, is negative.

Considerations in summary

While the Frohlich two-state model is very useful in articulating the conceptual structures that are necessary to describe dipole polarization in the solid state, care must be exercised when the attempt is made to employ it to

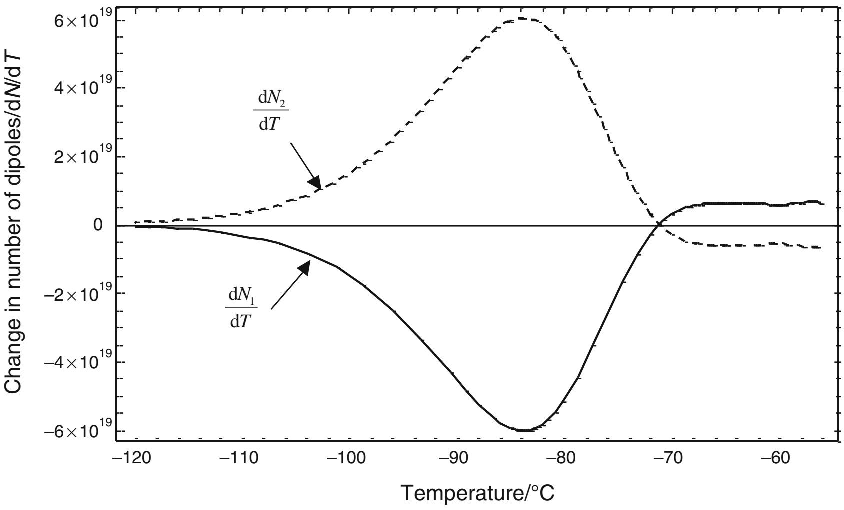

Fig. 4 *Solid line* Temperature dependence of rate of generation of unpolarized dipoles, dN_1/dT, using Eq. 13. *Dotted line* Temperature dependence of rate of generation of polarized dipole, dN_2/dT, using Eq. 16

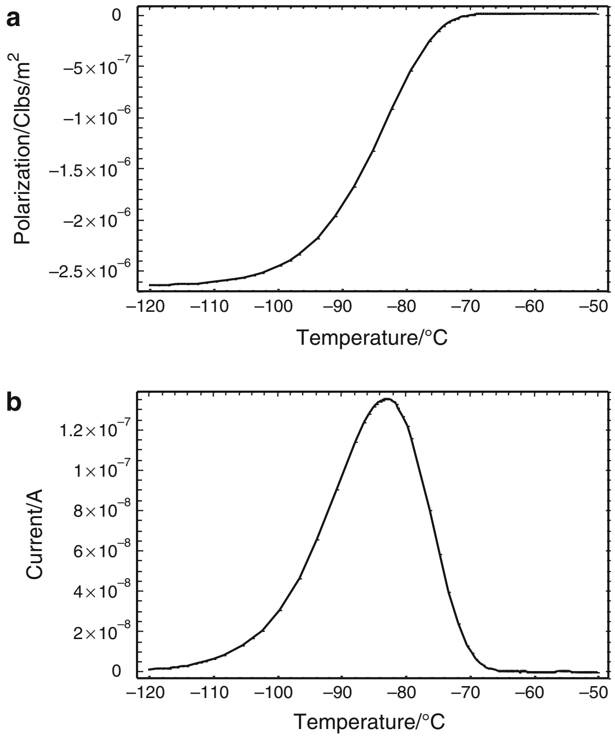

Fig. 5 **a** Polarization calculated using Eq. 14 with $N_1(0) = 0.51N_0$. **b** Current calculated using Eq. 15 with $N_1(0) = 0.51N_0$

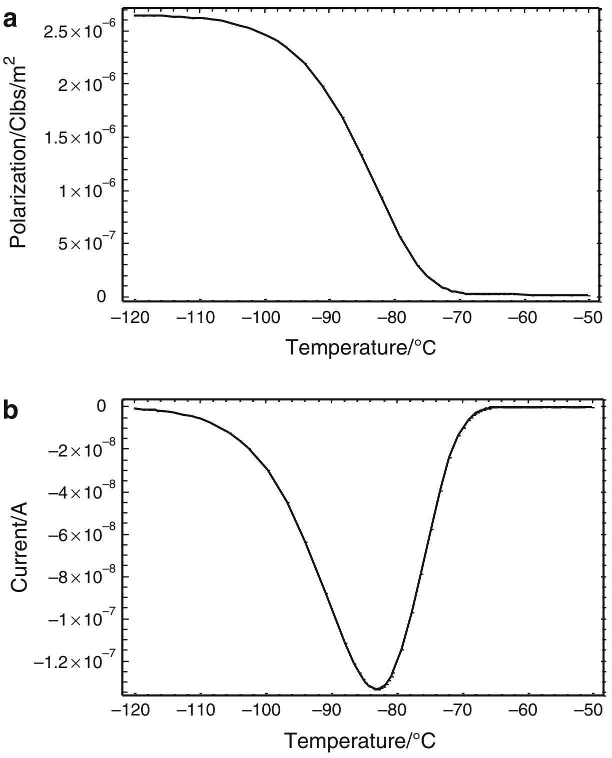

Fig. 6 **a** Polarization calculated using Eq. 14 with $N_1(0) = 0.49\ N_0$. **b** Current calculated using Eq. 15 with $N_1(0) = 0.49N_0$

describe physically plausible systems. The conceptually simplifying assumption that dipoles exist in only two states with opposite directions requires that before the field is applied, the number of dipoles in one direction equals the number of dipoles in the other direction. This condition is necessary in order to preserve the initial uniform charge distribution.

The basic conceptual structure involved in the kinetic treatment of polarization is that the rate of orientation will depend on the number of unoriented dipoles and the factors that influence the height of the potential barrier for that change. Similarly, the rate at which an oriented dipole will become unoriented will depend on the number of oriented dipoles and the factors that influence the height of the potential barrier for that change. The Frohlich assumptions require that initially, the number of oriented and unoriented dipoles be equal. With these conditions, the kinetics of polarization is determined only by the difference in the potential barriers of the polarized and unpolarized states. If that difference is relatively small, the rate of the reverse process, loss of polarization, becomes large at high temperature. From the numerical simulations presented here, it appears that this kinetic feature calculated directly from the constraints of the Frohlich model is what accounts for what has been observed as a reversal in the polarization current versus temperature curves. The Frohlich assumptions impose the constraint that half the available dipoles are already polarized when the field is applied. To depart from this assumption means a departure from the conceptual simplicity of the Frohlich model.

In solids that do not exhibit piezoelectric behavior, it less restrictive to assume that dipoles are initially randomly oriented. By adopting an initial state with randomly oriented dipoles, Fig. 1 is no longer adequate to describe the impact of the application of the field on the potential barriers. The situation, however, is even more complex because of the nature of the amorphous phase where the mobile dipoles will reside. Debenedetti and Stillinger [11] have described the formation of amorphous materials in terms of the distribution of minima on the potential energy hypersurface. The consequence of this description is that the amorphous state is more accurately described as multiple states of aggregation characteristic of this distribution of minima on the hypersurface. This means that the dipole response to the external electric field cannot be described in terms of single activation energy. There must be a distribution of activation energies. To account for this Eq. 15 would have to be revised to reflect this distribution,

$$j(T_\mathrm{k}) = -2\beta\mu \sum_{i=1}^{n} \frac{\mathrm{d}N_i}{\mathrm{d}T} = -2\beta\mu\upsilon_0 \sum_{i=1}^{n} N(E_i)\exp\left(\frac{E_i}{RT_\mathrm{k}}\right) \tag{17}$$

where E_i represents the activation energy of the individual dipoles in a particular state of aggregation.

Using single molecule microspectroscopy, Deschenes and Vanden Bout [12] have provided experimental evidence that indeed there are multiple states of aggregation in the amorphous state.

Conclusions

The evolution of polarization with temperature and TSPC profiles from Vanderschueren et al. has been examined. Numerical simulations have been performed using the same parameters used in the Vanderschueren calculations producing qualitatively similar results. The important feature pointed out is a peak in the evolution of polarization, which results in a change in sign for the TSPC profile. The Vanderschueren researchers have assigned this behavior to a crossover from polarization behavior controlled by the discrete kinetics to behavior controlled by the Langevin approximation.

Based on the analysis of the kinetic behavior, the peak in polarization and the resulting change in sign of the TSPC originate in the kinetic behavior of the system as defined by the Frohlich assumptions. The constraint of the basic model that in the initial number of polarized and unpolarized dipoles is equal has consequences in the kinetic computation. The impact of the initial high number density of polarized dipoles is that the reverse process of depolarization becomes important at high temperatures resulting in the observed loss in polarization. The observed peak in the calculated evolution of polarization with temperature is a kinetic consequence of the Frohlich model itself. Considering the complex nature of the amorphous phase with multiple states of aggregation, any computational description of TSPC experiments would have to account for both a random distribution of dipole orientations as well as multiple activation energies characteristic of each mode of aggregation.

The computations performed here and by Vanderschueren represent idealizations. The behavior of this idealized system is completely determined by the equations that are formulated to describe it. It has been shown here that the kinetic equations can describe what was previously thought to be a fundamental change in polarization behavior. It should be pointed out that while the behavior of this model system is deterministic, in the performance of TSPC experiments on real materials, the situation can be quite different. Over the temperature range of a TSPC experiment, it is possible that a real material can undergo structural relaxations, mechanical relaxations or phase changes that can, indeed, alter the fundamental polarization behavior. Under those circumstances, at the temperatures where those processes take place, the equations that describe polarization would have to be altered to account for those changes in polarization behavior.

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