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A simulation model for dielectric relaxation based on defect diffusion model and waiting time problems

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ABSTRACT

We propose a simulation model for dielectric relaxation based on defect diffusion. The defect diffusion model (DDM) has been used to interpret dielectric relaxation and other relaxation phenomena. The essential feature of the model is a cooperative interaction between the relaxing dipole and its nearest-neighbors, containing defects, and the relaxation can only occur when a defect encounters a dipole. In our model we have taken the motion of defect as a stochastic process characterized by successive waiting time problem rather than classical random walk motion. We present computer simulation result for a simple dipolar model system and the dipole correlation function obtained from this new model under various physical conditions appears to be in the form of a stretched exponential function.

1. Introduction

Defect diffusion models (DDMs) are capable of explaining many theoretical and experimental aspects of results. These theories have more physical significance than the conventional one, namely, the concept of distribution of relaxation times, and these theories also provide explanations of the microscopic origin of the non-exponential behavior in time domain and frequency domain. In the earliest theory, Glarum [1] proposed a model of molecular relaxation for condensed phases and liquids containing defects which influence the reorientation probabilities of the individual dipoles. He assumed the dipole to reorient equally likely by either rotational diffusion or instantaneous jumps due to defects. While the Debye process is normally described by a time-independent reorientation probability, the motion of defect is described by a time-dependent probability for a jump. Hence the reorientation probabilities of the individual dipoles are allowed to vary with time. In this model, defect-facilitated dipole reorientation, the turning of a dipole by a defect is a significant concept and can be interpreted in different ways. The essential feature of the model is a cooperative interaction between the relaxing dipole and its nearest-neighbors, containing defects, and relaxation can only occur when a defect diffuses to the dipole. Bordewijk [2] improved the defect diffusion calculation in 1D by considering relaxation from all defects, not just the nearest defect, and found a relaxation function of the Kohlrausch–Williams–Watts (KWW) type with $\beta = 1/2$. In this model exponential decay was obtained in 3D. The KWW type of behavior is represented by the function given by [3]:

$$\phi(t) = \exp[-(t/\tau)^{\beta}], \quad 0 < \beta \leqslant 1. \tag{1}$$

Skinner [4] developed a relaxation model for polymers based on both kinetic Ising model of Glauber [5] and Bordewijk's [2] defect diffusion model. He looked at the boundary between up and down spin domains in a kinetic Ising model and found a stretched exponential with $\beta = 1/2$ in 1D. An attempt was made by Bozdemir [6] to extend the model up to the s-th nearest-neighbor defect and the model was generalized by introducing a new one dimensional molecular chain defect diffusion model. These relaxation models were only in 1D case for normal diffusion, and not in 2D or 3D so these 1D models did not solve the stretched exponential relaxation.

The DDM has been used to explain a wide variety of experimental results included the origin of the widely observed stretched exponential, a Vogel–Fulcher–Tammann like equation, the concept that the glass transition occurs when rigidity percolates, and physical aging [7,8]. Bendler et al. [9,10] have extended the formalism to the effect of high pressure and explained the physical basis of fragility. More recently, the DDM was used to explain the widely different pre-exponentials and exponents in the Vogel-type laws that materials exhibit. In addition, a qualitative explanation was given of the liquid–liquid transition, the crystalline melting temperature, different values of the characteristic temperature, that some materials exhibit for different physical measurements, the origin of secondary relaxations such as the excess wing and the β relaxation, and the boson peak [11].

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In the present study, the relaxation behavior of a simple dipolar system is studied in the time domain using a Monte Carlo (MC) simulation. We propose an algorithm for the simulation of defect jump times and the correlation function for a single dipolar system in the time domain is obtained for the 1D case. The plan of the paper is as follows: a simulation model for dielectric relaxation based on defect diffusion process and a waiting times problem is presented in Section 2. Section 3 contains the results of MC simulation in time domain. Finally, Section 4 contains summary and conclusions.

2. Simulation model based on defect diffusion process and waiting time problems

The essential feature of the new simulation model is a cooperative interaction between the relaxing dipole and its nearest-neighbors, containing defects, and the relaxation can only occur when a defect encounters a dipole. In our model we have taken the motion of defect as a stochastic process characterized by a successive waiting times problem. The successive waiting time problem of patterns in stochastic sequences is an important topic with a wide range of applications, and it has been studied by many different methods. The first systematic treatment of the problem can be found in the book by Feller [12] who used the recurrent event theory.

Our system consists of point defect located at a distance l from a given dipole at $x = 0$ and $t = 0$. This defect arrives at the dipole as a result of successive waiting times process. We assume that the defect takes N steps to arrive at the dipole and that the defect takes each step at a discrete time interval after some trials. The trials continue up to first occurrence of a successful trial. As an example for waiting times problem we use the key problem [12] for each step: A man wants to open his door. He has n keys, of which only one fits the door. He tries the keys at random without replacement so that at each try each key has probability n^{-1} of being tried and all possible outcomes involving the same number of trials are equally likely. After any unsuccessful try, the number of keys is reduced by one. The process terminates when the man succeeds. Let us apply this process to each step from first step to last. We assume that the number of key is linearly increasing with the defect step. For the first step there is only one key so for the first trial the process terminated and the defect passes to the second step. At the second step there are two keys and after the first trial the number of keys is diminished by one so that there is one key left for the second trial. For each step the trial goes on until success is achieved and the defect passes to the next step. At the third step there are three keys and the same procedure is applied until the prescribed situation arises. There is no physics here and this is just a method for generating step times with a wide distribution. Let $i = 1, 2, 3, \ldots N$ be the step where the defect is and let $j = 1, 2, 3, \ldots i$ indicate the trial. The probability for the first step is $p_{11} = 1$. For the second step it is $p_{21} = 1/2$ for the first trial and $p_{22} = 1$ for the second trial. To pass the third step the probabilities for the each try are as follows $p_{31} = 1/3$, $p_{32} = 1/2$ and $p_{33} = 1$, respectively. The probabilities for the Nth step are become $p_{N1} = 1/N$, $p_{N2} = 1/(N-1)$, $p_{N3} = 1/(N-2), \ldots,$ $p_{NN} = 1$. The trials continue until success is achieved.

We count the trials as waiting times and they determine the time associated with a defect position. The probability that the defect arrives at the dipole is:

$$P(t) = N(t)/N, \tag{2}$$

where $N(t)$ is the number of steps made during the time interval 0 to t and N is the total number of steps. The correlation function of the dipole orientation:

$$\phi(t) = \langle m(t)m(0)\rangle / \langle m(0)m(0)\rangle, \tag{3}$$

is also the probability that the orientation at $t = 0$ persists at time t. It is related to the probability of a defect not having arrived after a time t. Consequently, we can write the decay function of the dipole as:

$$\phi(t) = 1 - P(t). \tag{4}$$

The decay function of the dipole given by Eq. (4) is obtained using a MC simulations.

3. Results and discussion

To implement this model we determine the probability of choosing the right key depending on defect position and which trial is made. As discussed, we take that to be p_{ij}. Then we generate a random number r from a uniformly distributed set of random numbers in the interval $0 \leqslant r < 1$. If $r \leqslant p_{ij}$ the defect makes a successful trial and it takes next step. Otherwise, it keeps its position and makes other trials. For each trial the waiting time is increased by one. We determine the waiting times distribution for each step and find the decay function $\phi(t) = 1 - P(t)$ due to MC time step. Here we take our time step to be $\Delta t = 1/N$. As usual, the time is measured in terms of MC steps. The values of the physical observable are recorded after each MC step and the quantity of interest here is $\phi(t) = 1 - P(t)$ where $P(t)$ is given in Eq. (2).

Let us first start with the decay function of the dipole $\phi(t)$ as a MC time step. The result of the MC simulation using algorithm given above is shown in Fig. 1 for the $N = 1000$. We have plotted $\ln[-\ln(\phi(t))]$ vs ln using the calculated values of $\phi(t)$. If the slope β of the curve is 1, then it means that $\phi(t)$ is in the form of an exponential function. If the slope is$0 < \beta < 1$, then $\phi(t)$ is in the form of a stretched exponential, which is the KWW form. The results are depicted in Fig. 2 on a logarithmic scale to test their correspondence with the KWW function. Fig. 2 is the natural logarithm and not base 10. It appears that the slope is approximately 0.5 over a wide range of times and the behavior resembles the KWW or stretched exponential function. There is a sharp upturn at long times, and this is not physical. This behavior at long times comes from the algorithm.

In our simulation model the motion of a defect is described by a time-dependent jump probability. Hence the reorientation probability of an individual dipoles varies with time according to the decay function $\phi(t)$ that is in the form of a stretched exponential. This is in agreement with the extensive observation of KWW or stretched exponential behavior such as in polymers and simple liq-

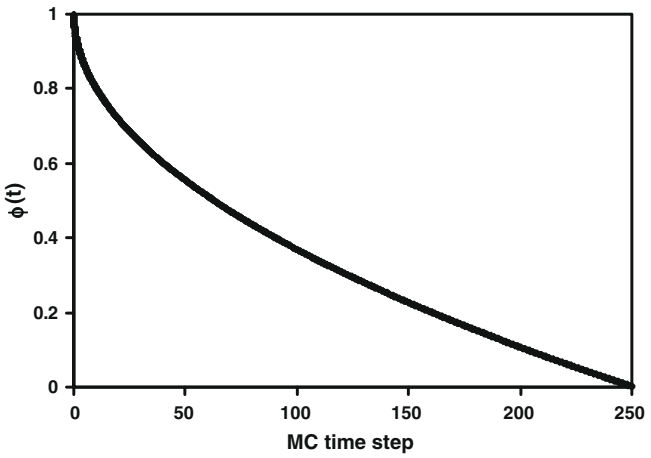

Fig. 1. The decay function of a single dipole as obtained from MC simulations.

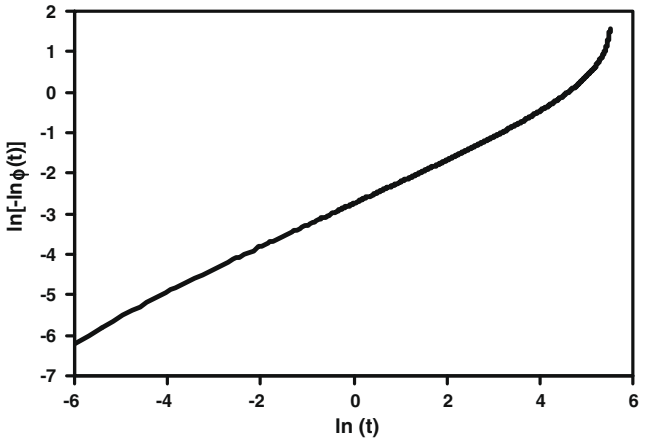

Fig. 2. The results on a natural logarithmic scale to test their correspondence with the KWW function.

uids [7,8]. It has been used to interpret dielectric relaxation, viscosity, ionic conductivity [9], the origin of fragility [10] and positron annihilation lifetime spectroscopy data [11]. These types of behavior have been represented perfectly by a KWW function which is given by Eq. (1).

4. Conclusions

We have developed a new algorithm to simulate dipole relaxation in the time domain. The essential feature of the model is a cooperative interaction between the relaxing dipole and its nearest-neighbors, containing defects, and the relaxation can only occur when a defect encounters a dipole. In our model we have taken the motion of defect as a stochastic process characterized by a successive waiting times problem rather than classical random walk motion. The motion of defect is described by a time-dependent reorientation probability. We use a method to make successive steps to have longer waiting times than previous steps. We present computer simulation results for a simple dipolar model system and a dipole correlation function obtained from this model under various physical conditions appears to be in the form of a stretched exponential function $\phi(t) = \exp[-(t/\tau)^{\beta}], \quad 0 < \beta < 1$.

Acknowledgments

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