International Conference on
Dielectric and Related Phenomena'98

Characterization and
Applications of
Dielectric Materials

Andrzej Wlochowicz
Chair/Editor

Elżbieta Targosz-Wrona
Coeditor

24-27 September 1998
Szczyrk, Poland

Organized by
Textile Institute, Technical University of Łódź,
Branch in Bielsko-Biała, Poland,
in co-operation with
Institute of Polymers, and Institute of Physics,
Technical University of Łódź

Sponsored by
United States Air Force European Office
of Aerospace Research and Development,
United States Army Research Development
and Standardization Group (UK),
Committee for Scientific Research, Poland
Rector of the Technical University of Łódź
Stefan Batory Foundation, Warsaw, Poland
SPIE-The International Society for
Optical Engineering in association with
the SPIE Poland Chapter

Vol. 37DP
NUMERICAL INVESTIGATIONS OF RELAXING SYSTEMS

Krzysztof Kosmulski

Institute of Physics
Wroclaw University of Technology
Wyspiańskiego 27, 50-370 Wroclaw, Poland
e-mail: kosma@im.pwr.wroc.pl

Agnieszka Jurlewicz

Institute of Mathematics
Wroclaw University of Technology
Wyb. Wyspiańskiego 27
50-370 Wroclaw, Poland
e-mail: agniesz@im.pwr.wroc.pl

ABSTRACT

In this paper we perform numerical investigations of a fractal model of relaxation phenomena in which the effective relaxation rate is obtained as a sum of relaxation rates over all clusters in the system. We show that in order to describe relaxation process expressed by the Cole-Cole and Cole-Davidson susceptibility functions a long-tailed distribution of cluster size must be assumed which is in accordance with the fractal structure of clusters. Having chosen the cumulated Pareto distribution for the cluster size, we calculate the empirical distributions of number of clusters in the system and approximate the distribution of the effective relaxation rate. We compare the obtained results with the theoretically derived distributions of the effective relaxation rates of the Cole-Cole and Cole-Davidson functions. We show that it is enough to take system consisting of $10^7$ particles to make the difference between the approximated and theoretically derived distributions negligible.

Key words: relaxation phenomenon, fractal clusters, effective relaxation rate, Lévy-stable distribution, Pareto distribution, random summation.

1. INTRODUCTION

It is widely known (see e.g. [1–3] and refs. therein) that most materials exhibit nonexponential relaxation. One of the first attempts [1, 3] to describe this phenomenon was to present relaxation function as a weighted average of relaxation rates with respect to some probabilistic density function $p(b)$

$$\phi(t) = \int_0^\infty e^{-bt}p(b)db.$$  

The above formula can be rewritten in the following form

$$\phi(t) = \left\langle \exp(-\tilde{\beta}t) \right\rangle,$$  

(1)

where $\tilde{\beta}$ is the random variable distributed according to the density function $p(b)$ and considered to be the effective relaxation rate representing the entire system. (Here $\langle \cdot \rangle$ denotes the mean value.) In a natural way there arises a question of the form and origins of the effective relaxation rate $\tilde{\beta}$.

Following the probabilistic models of relaxation phenomena based on the notion of the first passage relaxation function [4–6] we postulate that the effective relaxation rate $\tilde{\beta}$ can take the form of an averaged sum of relaxation rates over all $K_N$ clusters in the system of $N$ particles:

$$\tilde{\beta} = \lim_{N \to \infty} \frac{1}{A_N} \sum_{i=1}^{K_N} \beta_i,$$  

(2)
where $A_N$ is a sequence of positive scale constants and the random variable $\beta_i$ expresses the relaxation rate of $i$-th cluster.

The number $K_N$ is equal to the number of clusters in the system. In the case corresponding to the first passage relaxation function, $K_N$ is simply the function of the number $N$ of all particles in the system (e.g. $K_N = N$). In general, this quantity remains unknown to us and therefore it should be considered as a random variable. As it has been postulated [7–9] both the whole cluster and its surface form fractals with fractal dimensions $D$ and $D_S$, respectively. Moreover, the fractal property of cluster is reflected in the following surface - volume relation:

for any $k > 0$ if $S_i \rightarrow k S_i$ then $N_i \rightarrow k^{1/a} N_i$,

where $S_i$ is the number of surface particles, $N_i$ is the total number of particles of $i$-th cluster, and $a = D_S/D_1$ (so that $0 < a < 1$). It is worth noting that both $S_i$ and $N_i$ are integer–valued random variables and that the probability distribution of cluster size $N_i$ belongs to the domain of attraction of the one–sided Lévy–stable law [10]. The number $K_N$ of clusters is directly obtained by the sequence of the cluster sizes $N_1, N_2, \ldots$, namely,

$$K_N = \max \left\{ k : \sum_{i=1}^{k} N_i \leq N \right\}.$$  \hspace{1cm} (3)

The random variable $K_N$ takes, hence, the value $k$ if the sum $N_1 + \ldots + N_k$ of particles in $k$ clusters reaches the total number $N$ of particles in the system, so that it is not possible to create another cluster.

The formulas (2) and (3) provide an easy way to simulate the properties of a relaxing system, and therefore it can be useful for numerical investigations of the relaxation phenomena. In the next section we analyze the two special cases that yield the effective relaxation rate $\beta$ corresponding to the Cole–Cole and Cole–Davidson relaxations [11, 12].

2. EFFECTIVE RELAXATION RATE FOR EMPIRICAL RELAXATION FUNCTIONS

In order to describe the relaxation phenomenon in the frequency domain one uses the normalized susceptibility function $\phi^*(\omega)$ which is the Fourier transform of the response function $f(t) = \frac{-d\phi(t)}{dt}$ [1]

$$\phi^*(\omega) = \int_0^\infty e^{-i\omega t} \frac{-d\phi(t)}{dt} dt.$$

The Cole–Cole and Cole–Davidson functions are the special cases of the Havriliak–Negami form [13, 14] of susceptibility function

$$\phi^*(\omega) = \frac{1}{1 + (i\omega \beta)^a}, \quad A > 0, \quad 0 < a, b < 1,$$

which is commonly used to fit the relaxation data. The relaxation function $\phi(t)$, and hence the susceptibility function $\phi^*(\omega)$, correspond to the effective relaxation rate $\beta$ via formula (1). In this section we study the effective relaxation rates $\beta_{CC}$ and $\beta_{CD}$ corresponding to the Cole–Cole and Cole–Davidson functions, respectively. We present the theoretically derived forms of random variables $\beta_{CC}$ and $\beta_{CD}$. Then we show what should be assumed about the cluster size distribution and the law of relaxation rate of single cluster in formula (2) to obtain as a limit the Cole–Cole and Cole–Davidson effective relaxation rates.

2.1 Cole–Cole relaxation rate

For the empirical Cole–Cole susceptibility function, namely,

$$\phi^*(\omega) = \frac{1}{1 + (i\omega \beta)^a}, \quad A > 0, \quad 0 < a < 1,$$

we can get the following form of the effective relaxation rate $\beta_{CC}$

$$\beta_{CC} = \frac{\beta_a}{AT_a}. \hspace{1cm} (4)$$
The random variable $T_a$ in (4) is distributed according to one-sided Lévy-stable law [10] defined by the Laplace transform

$$L(T_a, t) = e^{-at}, \quad 0 < a < 1.$$  

The random variable $\tilde{\beta}_a$ is independent and identically distributed as $T_a$.

On the other hand it is possible to obtain the effective relaxation rate $\tilde{\beta}_{CC}$ by means of formula (2) if one assumes that the cluster size $N_i$ and the cluster relaxation rate $\beta_i$ are independent random variables having the same distribution that belongs to the domain of attraction of Lévy-stable law. Under these conditions we get that

$$\tilde{\beta}_{CC} = \lim_{N \to \infty} \frac{1}{AN} \sum_{i=1}^{KN} \tilde{\beta}_i,$$

where $K_N$ is given by formula (3).

2.2 Cole–Davidson relaxation rate

In case of the empirical Cole–Davidson function

$$\phi^*(\omega) = \frac{1}{1 + iA\omega^b}, \quad A > 0, \quad 0 < b < 1,$$

we obtain that the effective relaxation rate $\tilde{\beta}_{CD}$ has the following form

$$\tilde{\beta}_{CD} = \frac{1}{A\tilde{\tau}_b},$$  

(5)

where the random variable $\tilde{\tau}_b$ in (5) is distributed according to the law defined by the probability density function

$$g_b(z) = \frac{\sin(\pi b)}{\pi} z^b - 1 (1 - z)^{-b}, \quad 0 < z < 1,$$

with the parameter $0 < b < 1$.

In order to obtain the effective relaxation rate $\tilde{\beta}_{CD}$ by means of formula (2) one has to assume that (as in the Cole–Cole case) both the cluster size $N_i$ and the cluster relaxation rate $\beta_i$ have the same distribution belonging to the domain of attraction of Lévy-stable law. However, in contrary to the previous case, the two random variables are linearly dependent, i.e., $\beta_i = \rho N_i$ for some positive constant $\rho$. Under these conditions we get that

$$\tilde{\beta}_{CD} = \lim_{N \to \infty} \frac{1}{AN} \sum_{i=1}^{K_N+1} \beta_i,$$

where $K_N$ is given by formula (3).

3. NUMERICAL INVESTIGATIONS

In this section we present numerical results illustrating the presented attempt to relaxation. For the size $N$ of the system we approximate the distributions of the effective relaxation rates for the Cole-Cole and Cole-Davidson functions by means of respective cases of formula (2). Then we compare the distribution obtained for different sizes $N$ with the law of $\tilde{\beta}$ derived theoretically. We show that it is enough to take system consisting of $N = 10^7$ particles to make the difference between the approximated and theoretically derived distributions of the effective relaxation rate negligible.

In order to obtain numerically the distribution of the effective relaxation rate $\tilde{\beta}$ we use the following algorithm.

1. Choose the cluster size distribution. (e.g. cumulated Pareto($\lambda, a$) [15])
2. Choose the magnitude $N$ of the system. (e.g. $N = 10^7$ particles)
3. Generate cluster size \( N_i \) according to the distribution chosen in step 1 in order to obtain by formula (3) the number \( K_N \) of clusters in the system.

4. Generate the cluster relaxation rates \( \beta_i, \ i = 1, 2, \ldots, K_N \). (For the Cole-Davidson system \( \beta_i = N_i \)).

5. Using the random summation formula (2), calculate the value of the effective relaxation rate \( \bar{\beta} \).
   Repeat the steps 3-5 \( P \) times, where \( P \) is the statistical sample size.

6. Using statistical methods obtain the probability distribution of \( N_i, K_N \) and \( \bar{\beta} \).

7. Return to step 2 and change \( N \).

(Ad. 1) As it has been stated in the previous section, in order to obtain the Cole–Cole or Cole–Davidson relaxation functions, a long-tailed, i.e. belonging to the domain of attraction of a Lévy–stable law, distribution of cluster size \( N_i \) must be chosen. One of the most popular examples of such distributions is the Pareto\((\lambda, \alpha)\) law [15] defined by its distribution function

\[
F(x) = 1 - \left( \frac{x}{\lambda + x} \right)^\alpha, \quad x > 0,
\]

for the shape parameter \( \alpha \) restricted to the range \((0, 1)\) and any scale parameter \( \lambda > 0 \). Since the cluster size \( N_i \) is an integer-valued random variable, so we have to use the cumulated rather than the ordinary Pareto law as a cluster size distribution. The parameter \( \lambda \) should be chosen to reflect the size of the smallest cluster in the system. Below in Fig. 1 we present a typical cluster size distribution.

![Figure 1: Empirical distribution of cluster size (number of dipoles in a cluster) for \( \alpha = 0.8 \) (solid line stands for Pareto(1,0.8)).](image)

(Ad. 2) The magnitude of the system, i.e. the number of particles \( N \) in the system can be chosen arbitrarily. It appears that the quantity \( N = 10^7 \) is large enough to obtain good approximation of theoretical densities of \( \bar{\beta} \). It is worth noting that this quantity is relatively small when compared to the real physical systems.

(Ad. 3) In this step we generate the cluster sizes \( N_i \) according to the cumulated Pareto distribution until the sum \( N_1 + N_2 + \ldots + N_k \) reaches the number of particles in the system \( N \). As a result we obtain the number \( K_N \) of clusters in the system. We repeat this operation \( P \) times to get the statistical sample. In the presented calculation we have chosen \( P = 30000 \). Using standard statistical methods, we obtain empirical distribution of \( K_N \) (see Fig. 2 and Fig. 3).

(Ad. 4 and 5) For the Cole–Davidson case, having the number of clusters in the system we can calculate the approximate value of the effective relaxation rate \( \bar{\beta} \) by means of formula (2) using \( \beta_i = N_i \). In the Cole–Cole case,
Figure 2: Histogram of a number of clusters in a system of $N = 10^7$ dipoles for $a = 0.2$.

Figure 3: Histogram of a number of clusters in a system of $N = 10^7$ dipoles for $a = 0.8$. 
first we have to generate $k$ random numbers according to the same cumulated Pareto distribution as we have used for generating $N_i$. We repeat this step $P$ times and by applying statistical methods we obtain the empirical distribution of the approximated effective relaxation rate $\tilde{\beta}$, which now can be compared to the distribution derived theoretically (see Fig. 4).

![Figure 4: Effective relaxation rate $\tilde{\beta}$ for Cole-Davidson function. The dotted line stands for empirical density obtained through simulations. $N = 10^7$, $a = 0.4$.]

4. CONCLUSIONS

In the presented paper we have discussed the fractal model of relaxation phenomena in which the effective relaxation rate, representing the system as a whole, takes the form of a random sum (2) of relaxation rates over all clusters in the system. The number of clusters has been expressed by the cluster sizes, which in the case of a fractal structure of clusters should have the long-tailed distribution.

We have focused the attention on the cases described by the Cole-Cole and Cole-Davidson susceptibility functions. For these functions we have shown what should be assumed about the distribution of cluster sizes and relaxation rates of the clusters to obtain by formula (2) the corresponding effective relaxation rate $\tilde{\beta}$. We have used the obtained results to get numerically the distribution of $\tilde{\beta}$. Namely, having chosen the cumulated Pareto distribution for the cluster size, we have calculated the empirical distributions of number of clusters in the system. Then we have approximated the distributions of the effective relaxation rate and compared the results to the theoretically derived distributions. It has appeared that it is enough to take system consisting of $10^7$ particles to make the difference between the approximated and theoretically derived distributions negligible.

5. ACKNOWLEDGEMENTS

This work was supported by KBN Grant No. 2 P03B 100 13.

6. REFERENCES


